CHAPTER 1

# THE CATALYTIC, ENANTIOSELECTIVE MICHAEL REACTION

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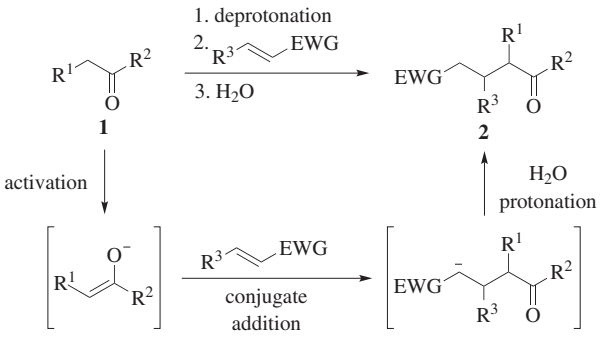
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## INTRODUCTION

The conjugate addition reaction is a fundamental transformation in synthetic organic chemistry for the construction of carbon–carbon and carbon–heteroatom bonds. This reaction consists of the addition of a nucleophile to the β-carbon of an electrophilic olefin, leading to the formation of a stabilized anion, which after protonation or subsequent treatment with another electrophile, furnishes the final addition product. The conjugate addition of resonance-stabilized carbanions (an enolate or related species), also known as the Michael reaction, has received great attention among synthetic chemists as a general tool for the preparation of 1,5-dicarbonyl compounds. Since the first example was reported in 1887 by Arthur Michael,[1] this transformation has demonstrated extraordinary generality. A wide range of compounds is able to participate in the reaction as nucleophiles

or electrophiles (also referred to as Michael donors and Michael acceptors, respectively), which has expanded the usefulness of this transformation to a high level of sophistication.

The overall process of the Michael reaction can be defined in terms of three different steps (Scheme 1): (1) the activation of the pronucleophile takes place, generating an enolate or a related nucleophilic species such as a silyl enol ether or an enamine; (2) the conjugate addition reaction itself occurs; and (3) the reaction ends with the addition of a second electrophile (a proton is the most commonly encountered terminating electrophile), which reacts with the stabilized anionic intermediate generated in the conjugate addition process. All of these steps can be achieved in a one-pot manner or by isolating the intermediates if these are stable compounds. For example, the latter scenario provides the Mukaiyama–Michael reaction in which the silyl enol ether nucleophile is prepared and purified in one operation and in a second one is allowed to react with the Michael acceptor in the presence of a Lewis acid catalyst. Alternatively, the activation of the pronucleophile can take place under the same reaction conditions employed in the conjugate addition step; therefore, all the participating reagents (the Michael donor, the Michael acceptor, and the catalyst) are combined in the reaction vessel leading to the direct formation of the final Michael adducts. This situation is known in the chemical literature as the "direct" Michael reaction and is feasible, for example, when a highly acidic carbon pronucleophile like a 1,3-dicarbonyl compound is employed as Michael donor since it can undergo an in situ deprotonation process.




**Scheme 1**

The Michael reaction can occur with the concomitant generation of one or more stereogenic centers, which means that highly functionalized, enantiomerically-enriched compounds can be easily constructed if the stereochemical outcome of the reaction is controlled. In this context, asymmetric catalysis has proven to be a highly efficient method for achieving stereocontrol. The benefits associated with the use of a substoichiometric amount of a chiral catalyst for promoting the reaction include cost, performance, and atom economy. In the case of the Michael reaction, the catalyst can influence the stereochemical outcome of the overall process in different ways depending on the mechanism of the reaction,

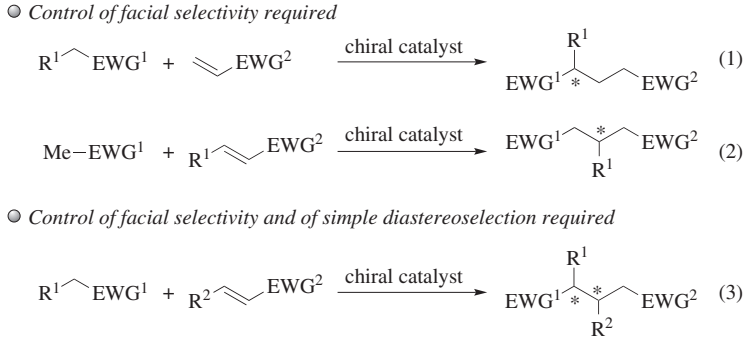
the nature of the substrate/catalyst interactions, and the way that the catalyst differentiates the prochiral faces of the Michael donor and/or the Michael acceptor. Catalytic, enantioselective Michael reactions can be classified into two main groups according to the nature of the catalytically active species, namely metal catalysis and organocatalysis. In the first group, the catalyst is a chiral metal complex that engages in the activation of the Michael donor by forming a chiral metal enolate, by activating the Michael acceptor through Lewis acid/Lewis base interactions, or by simultaneously activating both components. The second group is comprised of metal-free small organic molecules that promote the Michael reaction. The mechanism by which these organocatalysts participate in the activation of the Michael acceptor or the Michael donor is quite diverse, although most cases fall into two broad categories: those organocatalysts that activate the reagent or reagents participating in the reaction through reversible covalent bonding and those in which the substrate–catalyst interaction relies on weaker forces such as H-bonds or electrostatic effects.

This chapter covers the different catalytic systems and methods developed for achieving enantioselective Michael reactions through the end of 2012 (supplemental references are provided for articles published after that time through the first half of 2015) and it is limited exclusively to those examples in which the final Michael addition product is obtained after protonation of the conjugate addition intermediate. Therefore, tandem, domino, or cascade processes initiated by Michael reactions lie outside the scope of this work, albeit a number of reviews have been published.[2−13] In addition, several relevant reviews have appeared that provide a general view of the asymmetric conjugate addition reaction and in which the importance of the Michael reaction is specifically highlighted,[14−21] and organocatalytic conjugate reactions have also been reviewed recently.[22−24] With respect to treatises specifically covering this transformation, the book by Perlmutter,[25] and two reference chapters by Heathcock[26,27] have remained as the only reference works for a very long time; however, several books and book chapters of the Michael reaction have recently been published,[28,29] some of which focus exclusively on the organocatalytic versions.[30]

## MECHANISM AND STEREOCHEMISTRY

Three possibilities exist for the formation of a chiral molecule by means of a Michael reaction which involve: (1) a prochiral Michael donor, (2) a prochiral Michael acceptor, or (3) both a prochiral donor and prochiral acceptor (Scheme 2). This fact has important implications when trying to develop a catalytic enantioselective version of this transformation, as the catalyst must recognize the corresponding prochiral substrate in each case and exert the required facial stereodiscrimination. Moreover, in case (3) wherein both substrates participating in the Michael reaction are prochiral, the catalyst must control the facial selectivity as well as the relative arrangement among the substituents of the two substrates (simple diastereoselection). This aspect can also be dominated by the structure of the substrates and/or the mechanism itself. Under this scenario, the catalyst must establish the corresponding

interactions with the Michael donor, the Michael acceptor, or both, according to the various mechanisms operating in their activation.



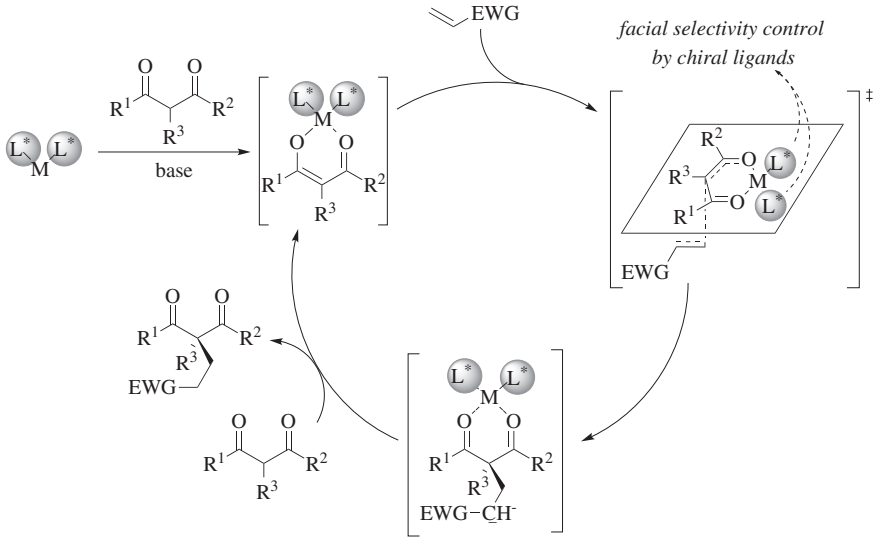

**Scheme 2**

## Metal-Catalyzed Reactions

Metal complexes incorporating chiral ligands have been used extensively for catalyzing Michael reactions. Two main mechanistic types are utilized to facilitate this transformation. Metal-based catalysts can be employed to enolize acidic carbonyl compounds or related reagents to form chiral metal enolate intermediates that subsequently react with the Michael acceptor (the so-called *direct Michael reaction*). Alternatively, a metal-based chiral complex can promote the *Mukaiyama–Michael reaction* in which an enoxysilane derivative participates as the Michael donor that reacts with the Michael acceptor after activation of the latter by complexation with the Lewis acidic metal catalyst.

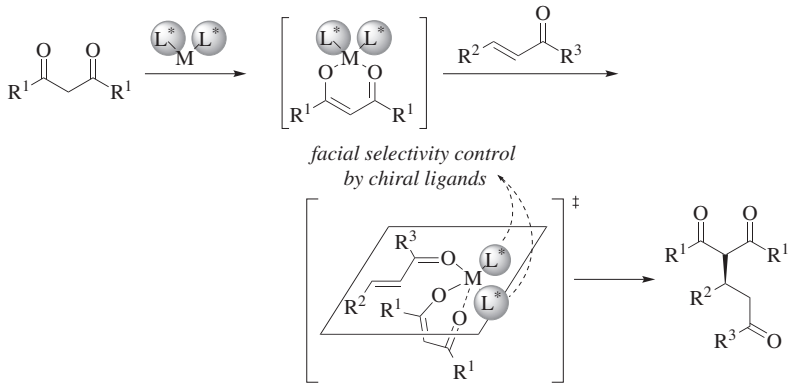
**Metal-Catalyzed Direct Michael Reaction.** One of the most common situations found in the catalytic, enantioselective variants of the direct Michael reaction using metal catalysis involves the use of highly acidic pronucleophiles such as 1,3-dicarbonyl compounds or related derivatives. In these cases, a sub-stoichiometric amount of a weak base is needed to promote deprotonation to generate the required enolate. In this way, malonates, β-keto esters, β-keto amides, nitroacetates and other related compounds are outstanding substrates that can be used as pronucleophiles in the Michael reaction with a wide variety of electron-poor olefins in the presence of an appropriately designed chiral metal catalyst. Other less acidic carbonyl compounds such as simple ketones, esters, nitriles, or amides as enolate sources typically do not participate in this reaction because these pronucleophiles have to be activated by a strong base and their corresponding conjugate acids are unable to protonate the conjugate addition product, which is required for the turnover of the reaction. Moreover, the enolate species that is formed in those cases is highly

reactive and has a pronounced tendency to undergo an uncatalyzed, background Michael reaction, leading to the formation of a racemic product. Deprotonation of a prochiral 1,3-dicarbonyl compound forms an enolate that can interact with the metal catalyst in a bidentate fashion and this activated chiral nucleophile undergoes a subsequent conjugate addition reaction with the electron-poor olefin, very often a β-unsubstituted Michael acceptor, allowing chirality transfer from the ligands present on the catalyst structure to the newly formed stereocenter (Scheme 3). In this sense, and taking into account the poor configurational stability associated with tertiary stereogenic centers containing two carbonyl-type substituents, dissymmetric α-substituted 1,3-dicarbonyl compounds ($R^3 \neq H$) can be employed as Michael donors, leading to the formation of a configurationally stable quaternary stereocenter after the conjugate addition process takes place.




**Scheme 3**

In many cases, the transition state associated with this configuration-determining step also implies a complexation between the electron-withdrawing group of the electrophile and the Lewis acidic metal center which, if possible, results in a more favorable and well-organized transition state that accounts for very high stereocontrol. Some important examples of metal-catalyzed direct Michael reactions involve a prochiral Michael acceptor (typically a β-substituted α,β-unsaturated carbonyl compound or a related derivative). An interaction between this substrate and the metal center is required to exert sufficient influence at the stereocenter generated at the β-position of the Michael acceptor reagent (Scheme 4).

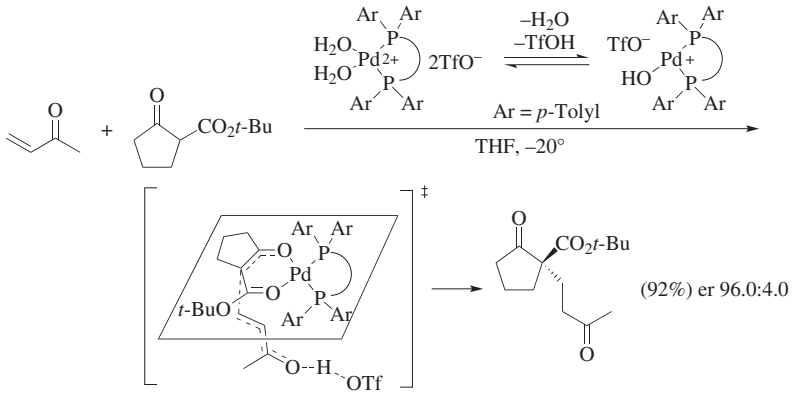



**Scheme 4**

Designing a highly effective metal catalyst to promote this type of transformation involves the consideration of two different features. On one hand, the metal ion used for the catalyst should be capable of activating the starting materials and providing the required rate-accelerating effect on the reaction with respect to the possible uncatalyzed background reaction. On the other hand, the activated catalyst–substrate complex must lead to the formation of a well-defined structural arrangement around its coordination sphere to favor the preferential participation of a single diastereomeric transition state in the reaction that results in high facial selectivity. For this reason, the typical chiral ligands employed often possess $C_2$ symmetry to reduce the number of possible diastereoisomeric transition states present at the stereodetermining step of the reaction.

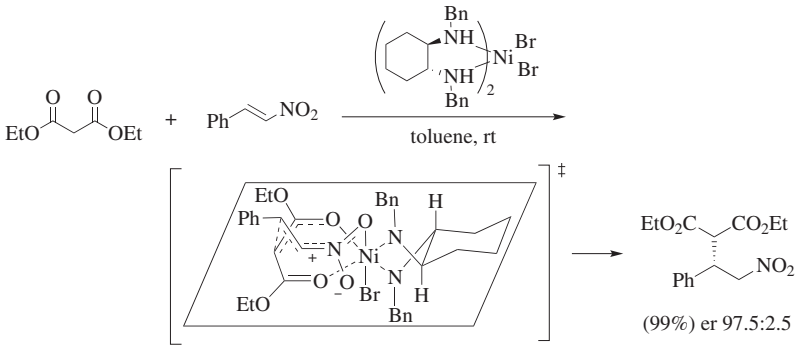
Several reactions that display this behavior are illustrated in the following examples. The enantioselective Michael reaction of several α-substituted β-keto esters with methyl vinyl ketone catalyzed by an (*R*)-Tol-BINAP/Pd(II) complex has been proposed to occur through the formation of an intermediate in which the metal catalyst is exclusively involved in the activation of the pronucleophile (Scheme 5).[31,32] The authors suggest that the initial cationic Pd(II)–$H_2O$ complex is in equilibrium with a monomeric Pd(II)-hydroxo complex that reacts with the starting β-keto ester to generate a chiral palladium enolate. Conjugate addition of this chiral enolate takes place at the less hindered face and without any participation of the catalyst in the activation of the Michael acceptor due to the preference of Pd(II) to remain in a square-planar $d^8$ configuration. The authors further propose that the activation of the enone occurs externally by protonation by the TfOH present in the reaction medium.

Other systems are based on the simultaneous activation of both substrates participating in the reaction. For the cases in which a prochiral Michael acceptor is involved in the active intermediate, the stereochemical influence of the catalyst is enhanced by its proximity to the newly forming stereocenter. This double activation occurs directly




**Scheme 5**

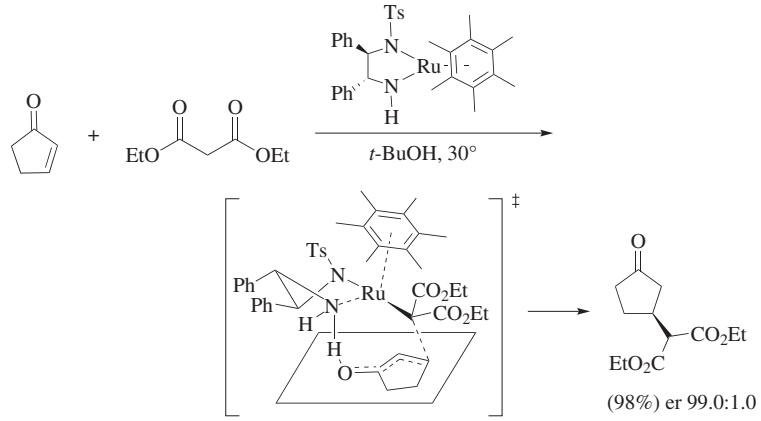
through the metal atom center (Scheme 6).[33] The chiral Ni(II)-diamine complex catalyzes the Michael reactions of 1,3-dicarbonyl compounds with nitroalkenes through the formation of an intermediate in which the enolate (linked to the metal complex in a bidentate fashion) and the nitroalkane (through the most basic oxygen atom of the nitro group) are bonded to the Ni(II) center, resulting in a highly ordered assembly that translates into excellent levels of enantiocontrol.[33] Kinetic studies show that the reaction is first order in both malonate and nitroalkene but that the reaction exhibits an induction period to reach a constant rate that is attributed to the need for one of the diamine ligands to dissociate in order to form the catalytically active species. The latter has available binding sites to complex with both the malonate enolate and the nitroalkene reagent. The diamine ligand released in this initial activation process is also proposed to participate as a Brønsted base that deprotonates the pronucleophile, generating the corresponding enolate.




**Scheme 6**

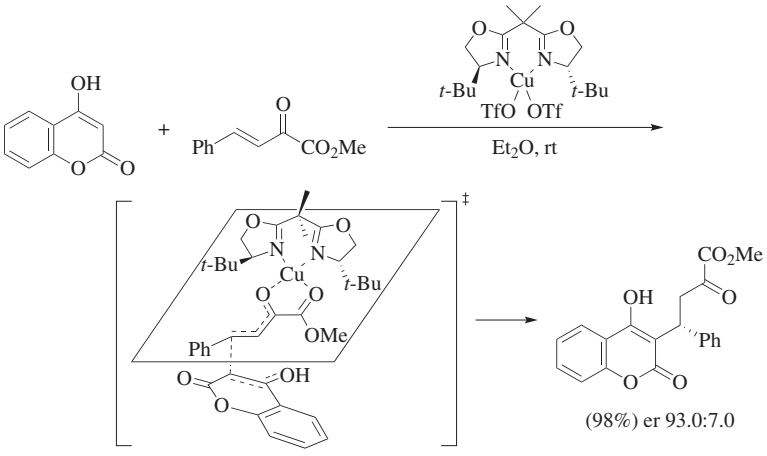
The activation of the Michael acceptor can also occur by interactions at the second coordination sphere of the metal center, as illustrated in the Ru(II)-diamine-catalyzed Michael reaction of malonates with cyclic enones (Scheme 7).[34] In this

case, the activation of the pronucleophile is achieved through the formation of a C-bonded ruthenium enolate, which subsequently reacts with the enone that is already interacting with the catalyst through the formation of an H-bond with one of the free NH groups of the diamine ligand. Thus, this situation recalls the model proposed for the closely related enantioselective transfer-hydrogenation in which the same type of catalyst is employed.[35–37]




**Scheme 7**

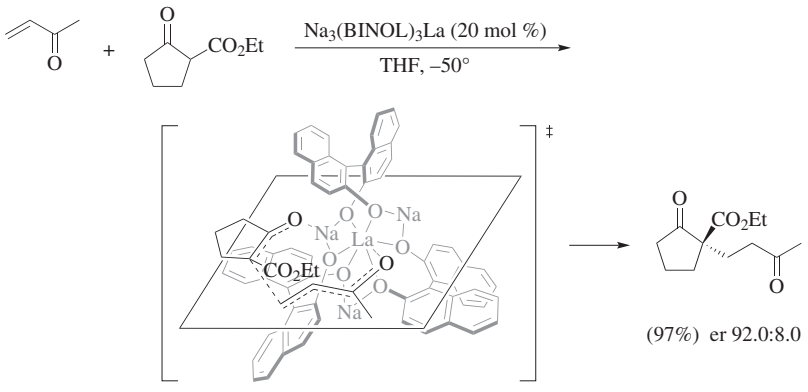
A third scenario involves those enantioselective Michael reactions in which exclusive activation of the Michael acceptor takes place through Lewis acid–Lewis base interactions between the metal center and the activating group of the Michael acceptor. In this sense, the tendency of the enolate component to coordinate to the metal center must be overcome by introducing additional ancillary coordination points at the electrophilic olefin. An illustrative example is shown in Scheme 8, in which




**Scheme 8**

a cyclic 1,3-dicarbonyl compound reacts with a β,γ-unsaturated α-keto ester in the presence of a chiral bis(oxazoline)-copper(II) complex to provide the corresponding Michael addition product with good to excellent enantiocontrol for a variety of different substrates.[38] The ability of the α-keto ester moiety to interact with the Lewis acidic copper center in a bidentate fashion, together with the inability of the enolate to chelate the same metal because of its cyclic nature, results in a transition state in which the nucleophile approaches the olefin through its less hindered face. The α,β-unsaturated ketone system remains in an *s-cis* reactive conformation as proposed for other related transformations involving Cu-Box complexes and β,γ-unsaturated α-keto esters.[39–42]

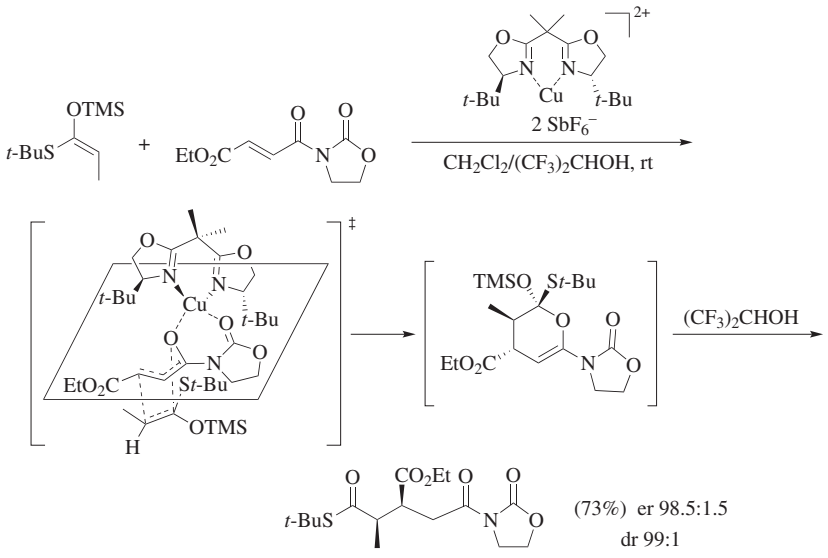
Catalysts that rely on a bimetallic architecture have also been identified as excellent promoters of a variety of direct Michael reactions.[43–47] These catalysts are composed of two metal atoms which play two different roles in the reaction: one participates as the counterion of a Brønsted base, which generates the enolate by deprotonation of the pronucleophile, whereas the other is a Lewis acidic center that activates the Michael acceptor through coordination. Although several examples of homobimetallic catalysts have been used in this reaction, mostly based on Zn(II),[48] the majority of the work carried out in this area has focused on the use of heterobimetallic derivatives for promoting several enantioselective Michael reactions using a variety of structurally diverse Michael acceptors and donors. One representative example catalyst is illustrated in Scheme 9.[49–51] It is comprised of a complex molecular architecture based on three BINOL ligands arranged around a central Lewis acidic rare earth element and contains three Brønsted basic alkali-metal centers about the lanthanide. This complex catalyzes the Michael reaction between β-keto esters and chalcone. Extensive mechanistic studies[51,52] demonstrate the involvement of this ternary 3:3:1 BINOL/alkaline metal/rare earth complex and reveal the lack of ligand exchange with solvent or with any of the reagents participating in the reaction, therefore confirming the bifunctional nature of the catalyst, even though some authors have suggested that the reaction can proceed through an intermediate in which one of the BINOL ligands has been replaced by the enolate.[53] The reaction is believed to proceed through a




**Scheme 9**

transition state in which the three species participating in the C–C bond forming event (the catalyst, the Michael acceptor, and the Michael donor) are arranged around the metal center in a well-defined orientation which leads to a highly enantioselective process. Moreover, the dual roles played by the catalyst allow the direct reaction between the pronucleophile and the electrophile without employing any external base for the formation of the enolate intermediate, a characteristic that translates into exceptionally mild reaction conditions.

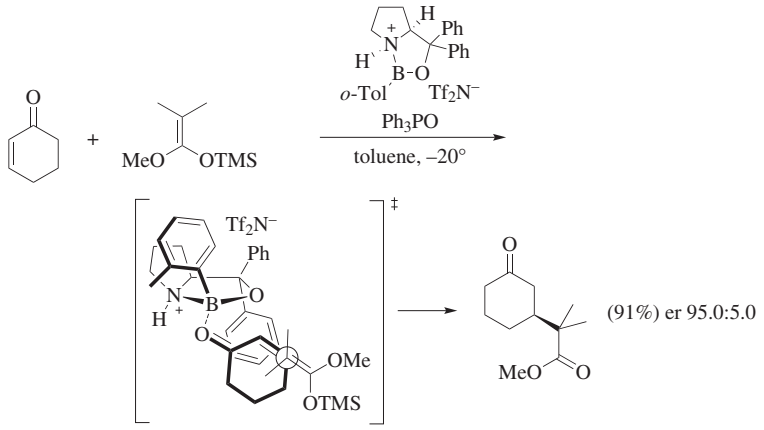
**Metal-Catalyzed Mukaiyama–Michael Reaction.** In this variant of the Michael reaction, an enoxysilane derivative is employed as the active carbon nucleophile, undergoing a 1,4-addition reaction with an α,β-unsaturated carbonyl compound or related derivative in the presence of a Lewis acid catalyst. In this process, the metal promoter accelerates the reaction by means of the LUMO-lowering effect associated with coordination to the Michael acceptor. For this reason, and with the aim of facilitating the formation of this complex, most systems make use of a modified Michael acceptor capable of forming a stable complex with the Lewis acid through chelation, also allowing a better control of the geometry and of the organization of the transition state in the C–C bond-forming event. An example is shown in Scheme 10, in which a copper(II)-*t*-Bu-Box complex serves as the catalyst for the enantioselective Mukaiyama–Michael reaction employing both α-unsubstituted and α-substituted silyl ketene acetals as donors, the latter also providing the final adducts with an excellent degree of diastereoselection.[54,55] Complexation of the bidentate Michael acceptor with the catalyst leads to a conformationally locked electrophile in which the copper center adopts a distorted square-planar arrangement




**Scheme 10**

that results in a very effective steric shielding of one of the enantiotopic faces of the α,β-unsaturated imide. A mechanistic study indicates that the reaction most likely proceeds through a hetero-Diels–Alder mechanism, leading to the formation of a dihydropyran intermediate that forms the final Michael adduct after a ring-opening reaction accelerated by the presence of a protic additive.[41] This mechanistic proposal also provides an explanation for the high diastereospecificity observed in the reaction due to the fact that (*Z*) silyl enol ethers provide the *syn* diastereoisomers as major products whereas the corresponding (*E*) isomers preferentially deliver the *anti*-configured Michael adducts.

Although this type of hetero-Diels–Alder mechanism has also been invoked to explain other examples of Lewis acid catalyzed Mukaiyama–Michael reactions, there are also many of these transformations that proceed through the conventional Mukaiyama-type mechanisms in which the nucleophile approaches the Michael acceptor in an open transition state. This latter scenario is illustrated in Scheme 11, in which a chiral oxazaborolidine catalyzes the Michael reaction between a silyl ketene acetal and 2-cyclohexenone. In this case, the hetero-Diels–Alder type mechanism is not possible because the enone cannot adopt the required *s-cis* conformation.[56]



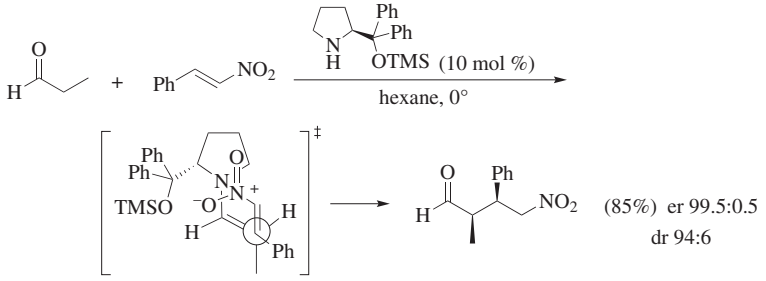

**Scheme 11**

## Organocatalyzed Reactions

Small organic molecules are highly effective catalysts for enantioselective Michael reactions. In many cases, these catalysts provide a complementary approach to the metal-catalyzed reactions by allowing the use of Michael donors and acceptors that are not compatible with the use of Lewis acid catalysts. These organocatalysts participate in the Michael reaction through different mechanisms, depending on the type of interaction by which the substrates are activated. Chiral primary and secondary amines are able to activate Michael donors (aldehydes or ketones) and acceptors (enals and enones) through the formation of active azomethine intermediates in which the catalyst is covalently bound to the substrates (via catalytic formation of enamines or α,β-unsaturated iminium ions). Alternatively, other organocatalysts make use of

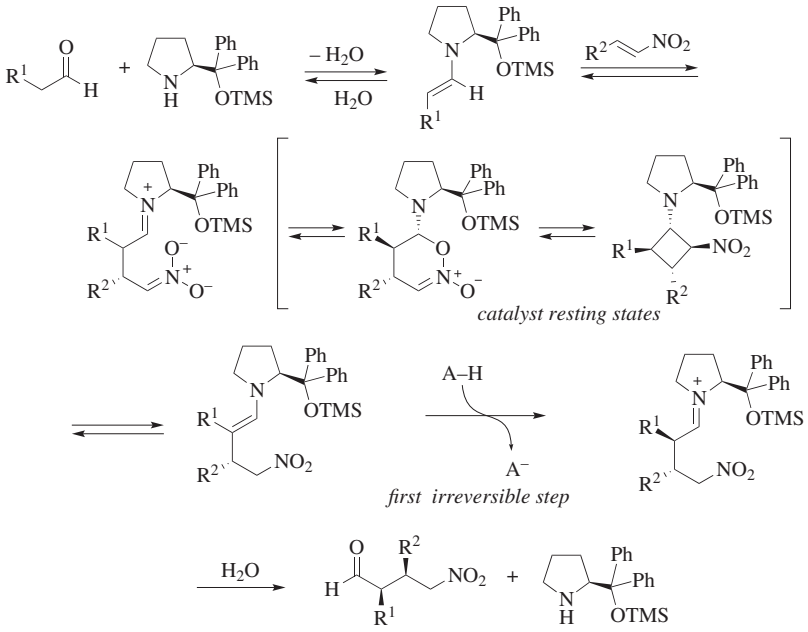
noncovalent interactions such as H-bonding or ion pairing to establish an interaction with the reagents participating in the Michael reaction.

**Enamine Activation.** Primary or secondary amines catalyze the Michael reaction via reversible formation of an enamine intermediate. This enamine undergoes conjugate addition with the Michael acceptor, generating an iminium ion that upon hydrolysis releases the product and regenerates the amine catalyst ready to participate in a subsequent catalytic cycle.[57−59] Pyrrolidine-based chiral amines are outstanding catalysts for several Michael reactions, especially when using aldehydes as Michael donors. The chiral pyrrolidine effects a diastereoselective conjugate addition in which the approach of the Michael acceptor takes place preferentially on one of the two diastereotopic faces of the enamine intermediate. Stereocontrol arises either by steric bias or by the incorporation of stereodirecting elements able to engage in secondary interactions with the Michael acceptor. In addition, controlling the enamine geometry is an important issue that has to be considered for achieving high stereocontrol because the key enamine intermediate can be present as two interconverting diastereoisomers that also possess a high degree of conformational flexibility. These geometrically isomeric intermediates lead to the formation of the new stereocenters with different configurations. For this reason, the structural elements incorporated in the catalyst must also guarantee a well-defined enamine geometry if a highly diastereo- and enantioselective process is to be achieved. The *O*-TMS protected α,α-phenylprolinol derivative shown in Scheme 12 is a good example of an outstanding catalyst for the Michael addition of aldehydes to nitroalkenes.[60] (There is a simultaneous report on the use of this catalyst in other reactions under enamine activation[61], and reviews about the use of diarylprolinols as organocatalysts[62−64]). The key for the success of this catalyst relies on the presence of the bulky substituent at the 2-position of the pyrrolidine ring, which provides effective geometric control of the enamine orientation, favoring the *anti* conformer of the (*E*) diastereoisomer. This arrangement also leads to a highly efficient steric shielding of one of the diastereotopic faces. With respect to simple diastereoselection, the reaction is typically proposed to occur via a synclinal acyclic transition state,[65] facilitated by electrostatic interactions between the positively charged nitrogen of the enamine and the negatively charged oxygen atoms at the electron-withdrawing group of the Michael acceptor that develop as the reaction proceeds.




**Scheme 12**

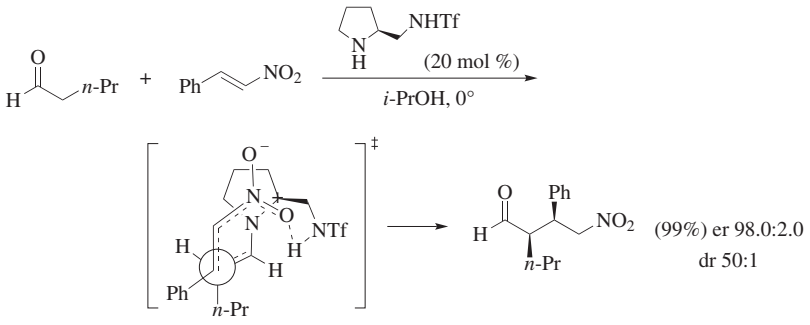
The covalent nature of the substrate-to-catalyst interaction implies the presence of many different intermediates in the reaction medium, which in most cases are rapidly interconverting. The large number of intermediates complicates the establishment of the stereodetermining step. The models developed to explain the stereochemical outcome and the mechanism of most of the reported examples are merely simplified versions of a very complex chemical system. The reaction shown in Scheme 12 has been the subject of a thoughtful mechanistic study that reveals several intermediates in the catalytic cycle which had not been previously considered (Scheme 13).[66–72] Specifically, it has been proposed that a stable cyclobutane intermediate is formed as a catalyst resting state after the initial reaction between the enamine and the nitroalkene. This cyclobutane species undergoes a subsequent ring-opening process delivering a 1,2-oxazine intermediate (also detected), which upon ring opening reveals a third stable enamine intermediate. Next, protonation to form the corresponding iminium ion followed by final hydrolysis of the latter releases the product and the free amine catalyst. Kinetic experiments demonstrate that the protonation/hydrolysis of the nitroenamine/1,2-oxazine equilibration mixture is the first irreversible step in the overall catalytic cycle. All of the previous intermediates are in equilibrium and the stable cyclobutane and 1,2-oxazine intermediates are the catalyst resting states, rather than parasitic species that sequester the catalyst, although in some cases, and depending on the nature of the substitution pattern of the aldehyde and/or the nitroalkene, some of these intermediates might become stable enough to become catalyst traps that prevent turnover. These results indicate that the




**Scheme 13**

stereodetermining step might not be the one in which C–C bond formation takes place, as had been suggested in initial models, but rather establish a more complex situation in which enantioselectivity depends on the combination of two independent factors: one kinetic component given by the relative rate constants for the first irreversible step and a second that is determined by the relative concentrations of all the equilibrating diastereoisomeric intermediates that are formed before this first irreversible step. This proposal is also consistent with the beneficial effect of incorporating a Brønsted acid co-catalyst into this type of reaction. The Brønsted acid protonates the nitro/enamine intermediate to form the corresponding iminium ion, the first irreversible step, prior to catalyst releasing.

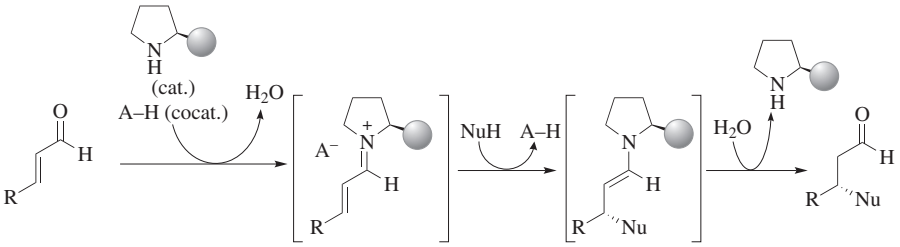
An alternative catalyst design contains a stereodirecting element that can establish secondary interactions with the Michael acceptor as represented by a sulfonyldiamine catalyst (Scheme 14).[73] In this case, the formation of a defined hydrogen-bonded transition state between the highly acidic NHTf moiety of the catalyst and the nitro group of the Michael acceptor determines one preferred reactive arrangement for the enamine intermediate and also the approach of the electrophile from one of the diastereotopic faces of the enamine.




**Scheme 14**

**Iminium Activation.** A primary or secondary amine can also catalyze the Michael reaction through the activation of the Michael acceptor (an α,β-unsaturated aldehyde or ketone) via the reversible formation of an iminium ion upon condensation.[74] When the iminium ion is formed, the Michael acceptor is activated for a conjugate addition reaction by the lowering of its LUMO; therefore, addition to the unsaturated iminium ion becomes faster than the background reaction. Once the conjugate addition takes place, an enamine intermediate is formed which, upon hydrolysis, delivers the Michael adduct and releases the catalyst to participate in a subsequent catalytic cycle (Scheme 15).[74] As with the enamine activation manifold, this mechanistic scenario is again a simplified picture of a more complex mechanistic manifold in which the position of each of the equilibria participating in the catalytic cycle and the rate of each step could vary depending on the structure of the reagents involved in the process. Nevertheless, this simplified representation still results in an useful working model to account for the stereoselectivity of the reaction, assuming

that C–C bond formation is the stereodetermining step. Under those conditions, the chiral amine catalyst is controlling the approach of the Michael donor at one of the two diastereotopic faces of the iminium ion intermediate. In this sense, controlling the geometry of the α,β-unsaturated iminium ion is also a key parameter to be considered if high stereocontrol is to be realized.




*The bulky group provides π-facial discrimination and favors (E) geometry.*

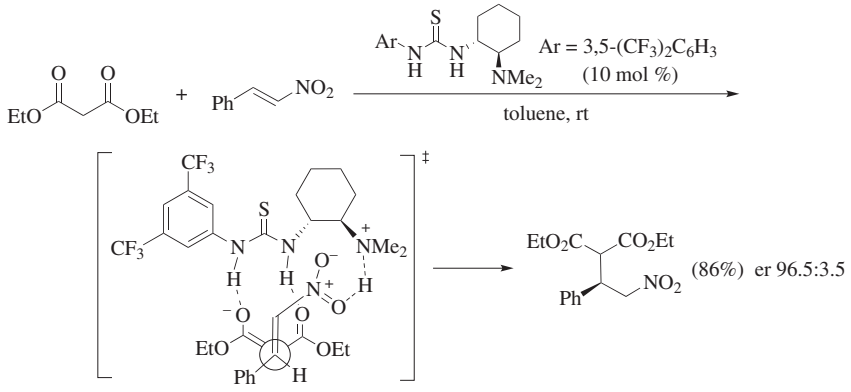
**Scheme 15**

As shown in Scheme 15, the typical conditions associated with Michael reactions under iminium activation involve the incorporation of a Brønsted acid cocatalyst, which is assumed to participate by facilitating the formation of the iminium ion intermediate. In addition, the conjugate base of this cocatalyst could also be involved in the activation of the Michael donor by deprotonating the pronucleophile, although in many cases it is proposed to remain as a simple spectator in the catalytic cycle.

**H-Bonding Activation.** Molecules that act as hydrogen-bond donors are able to activate α,β-unsaturated carbonyl compounds and nitro olefins by the formation of a hydrogen-bonded structure, removing electron density from the π-system with attendant activation toward the Michael reaction.[75–85] This mechanism of action closely resembles that operating in the activation of electrophiles by metal-centered Lewis acid catalysts, in which the same LUMO-lowering effect operates as a consequence of the formation of a dative bond between the metal and the Lewis basic site at the electrophile. Moreover, in a catalytic enantioselective version, the backbone structure of the catalyst should also provide the required steric bias that would allow stereochemical control of the reaction. This activation is typically achieved by designing catalysts that can engage in multiple H-bonding interactions, some of which also involve the presence of additional secondary interactions with the Michael donor. Bifunctional catalysis results and the reaction proceeds through a conformationally defined intermediate that enforces a specific orientation of the reagents in the transition state.

Chiral thioureas such as the one shown in Scheme 16 constitute a growing family of highly efficient catalysts that operate through this type of activation.[86] The design of these catalysts involves a modular structure in which one of the nitrogen atoms incorporates an electron-withdrawing substituent to increase the H-bonding ability of the thiourea moiety and the other nitrogen atom carries a

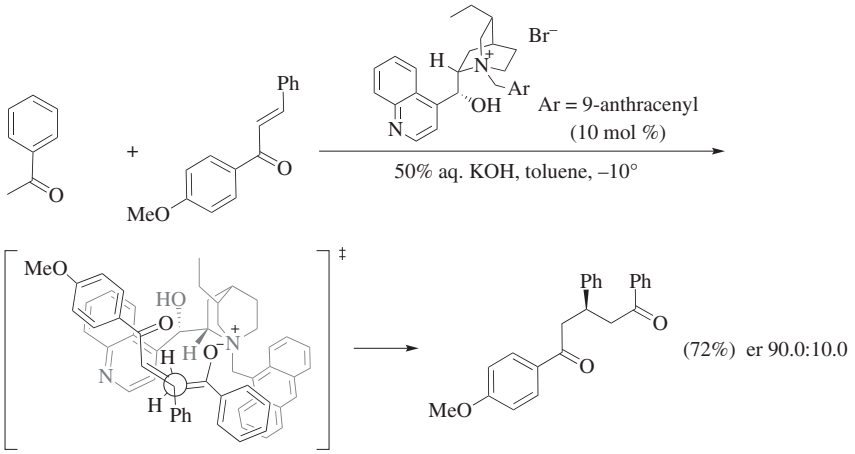
chiral substituent for stereocontrol. In addition, a second functional group which is able to activate the Michael donor through deprotonation is typically incorporated in the chiral substituent. The resulting conjugate acid is also able to participate as an additional H-bond donor unit. Several kinetic studies carried out for the reaction shown in Scheme 16 demonstrate that it is first order in the catalyst, the pronucleophile, and the Michael acceptor,[87] pointing toward the formation of a trimolecular complex in the transition state. Computational studies also support the cooperative contribution of the thiourea and dimethylamino moieties in the activation of both reagents, showing that the nitroalkene acceptor can be activated by the protonated dimethylammonium moiety through a single H-bonding interaction. The enolate derived from the 1,3-dicarbonyl compound binds the thiourea moiety by a double H-bonding network.[88]




**Scheme 16**

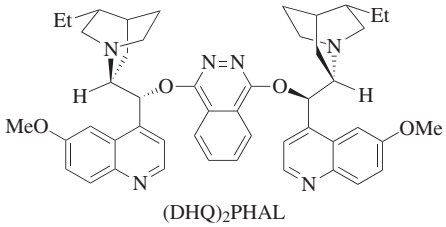
**Phase-Transfer Catalysis (PTC).** Quaternary ammonium or phosphonium salts and several crown ethers are known to accelerate the reaction between a nucleophile and an electrophile located in immiscible phases by the formation of ion-paired intermediates. Thus, the catalyst interacts with the charged nucleophile, generated by deprotonation at the interface, increasing the solubility of this species in the organic solvent and therefore facilitating the reaction with the electrophile, which is located in the organic phase.[89–93] The formation of a chiral ion-pair between the nucleophile and the catalyst is the key phenomenon operating in the stereocontrolled formation of the new stereogenic center. Quaternary ammonium salts derived from *Cinchona* alkaloids are good examples of effective catalysts for the Michael reaction under PTC conditions (Scheme 17).[94] In this particular case the quaternary quinuclidinium moiety provides the basis for the interaction with the anionic Michael donor, and the organic scaffold around the tetrasubstituted nitrogen atom furnishes the required lipophilicity for the complex to be soluble in organic solvents. The stereochemical control of the reaction is achieved by the combination of many interactions with the

various substituents on the quinuclidinium moiety, which are often dominated by π-stacking interactions.




**Scheme 17**

**Chiral Brønsted Base Catalysis.** A chiral base can also be used to activate the pronucleophile. The resulting enolate ion pair can remain tightly associated, thus allowing stereochemical control of the reaction. This activation mode is the same as that operating in chiral PTC, although in this case the reaction proceeds in a homogeneous environment. The dimeric *Cinchona* alkaloid based compound $(DHQ)_2PHAL$ illustrates this type of organocatalyst, in which the chiral Brønsted basic quinuclidine sites serve to activate the Michael donor (Figure 1). The use of pseudoenantiomeric quinine- or quinidine-based substructures typically leads to catalysts with opposite stereoinducing effects.




$(DHQ)_2PHAL$

**Figure 1**. Structure of $(DHQ)_2PHAL$

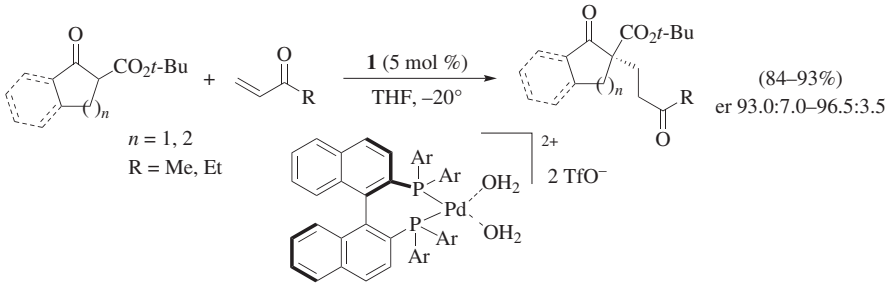
It should also be pointed out that participation of chiral bases in enantioselective Michael reactions is very often a part of a bifunctional catalyst system, especially catalysts operating by H-bonding interactions, as mentioned before.

SCOPE AND LIMITATIONS

## Metal-Catalyzed Michael Reactions

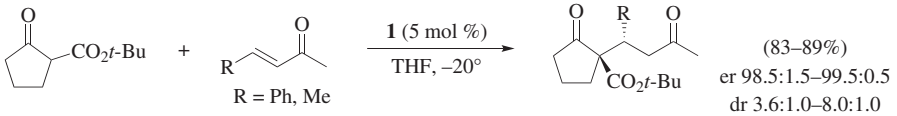
**Metal-Catalyzed Direct Michael Reaction.** Many different chiral metal complexes have been employed for promoting the Michael reaction between 1,3-dicarbonyl compounds (active methylene compounds) and a variety of Michael acceptors. As mentioned before, the reaction typically involves the formation of an active metal enolate species through deprotonation by the catalyst of the highly acidic pronucleophile. A variety of transition-metal or lanthanide complexes incorporating chiral ligands have been employed as catalysts for this reaction. In general, most of the methods reported in this context involve the use of monometallic complexes as catalysts, although several homobimetallic and heterobimetallic compounds are also outstanding promoters of the Michael reaction.

*Monometallic Complexes.* BINAP-based palladium complex **1** is an efficient catalyst for the asymmetric Michael reaction. This particular complex is used to carry out the reaction of α-substituted β-keto esters with vinyl ketones[31] to provide good yields and high enantioselectivities in the formation of Michael adducts containing a quaternary stereocenter. (An immobilized version of this catalyst has also been described.[95]) The complex performs especially well when cyclic β-keto esters are used (Scheme 18).[31] When less reactive β-alkyl or β-aryl substituted enones are employed, the reaction also proceeds equally well; leading to the corresponding Michael adducts containing two adjacent stereocenters with acceptable levels of diastereoselection and very high enantiocontrol (Scheme 19).[31]



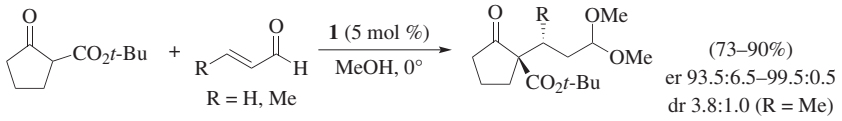

**1**

**Scheme 18**



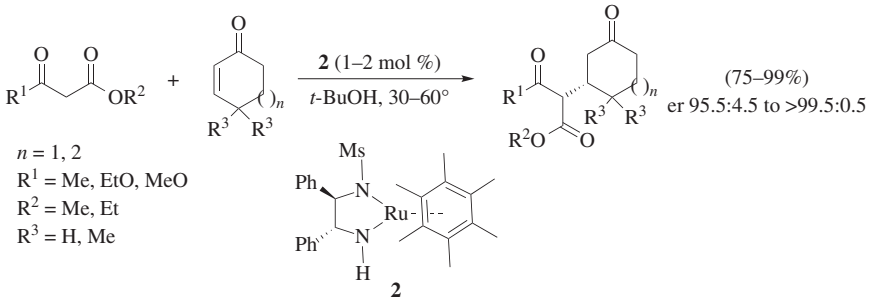

**Scheme 19**

The catalyst also performs satisfactorily with 1,3-diketones as Michael donors.[32] These substrates are often challenging to use because of their instability under basic conditions. When an α,β−unsaturated aldehyde is the Michael acceptor, the use of methanol as solvent contributes to the stabilization of the Michael adduct as the corresponding dimethyl acetal (Scheme 20).[32]




**Scheme 20**

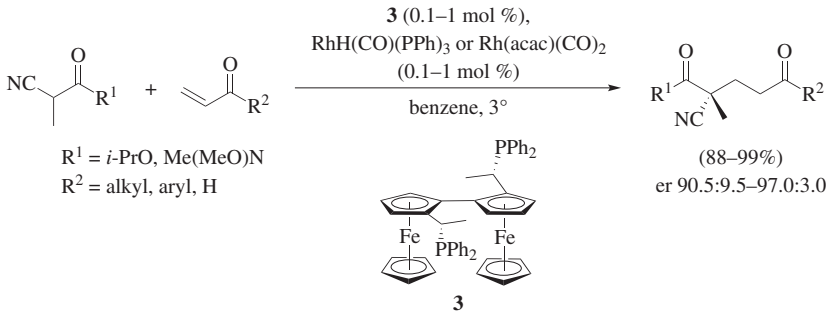
The well-defined chiral ruthenium amido complex **2** is also an outstanding catalyst for the direct, catalytic, enantioselective Michael reaction of ethyl acetoacetate or malonates with cyclic enones (Scheme 21).[34] The reaction requires only 1–2 mol % of the catalyst and furnishes the conjugate addition products in yields higher than 75% and enantioselectivities over 95.0:5.0 er. A remarkable feature of this catalyst is the fact that the reaction proceeds with similar levels of efficiency regardless of the ring size of the electrophilic cyclic enone. This situation is not common; cyclopentenone and cycloheptenone usually lead to poor yields and/or enantiocontrol compared to cyclohexanones. A closely related catalyst has also performed well in the Michael reaction of β-keto esters or 1,3-diketones with nitroalkenes.[96]




**Scheme 21**

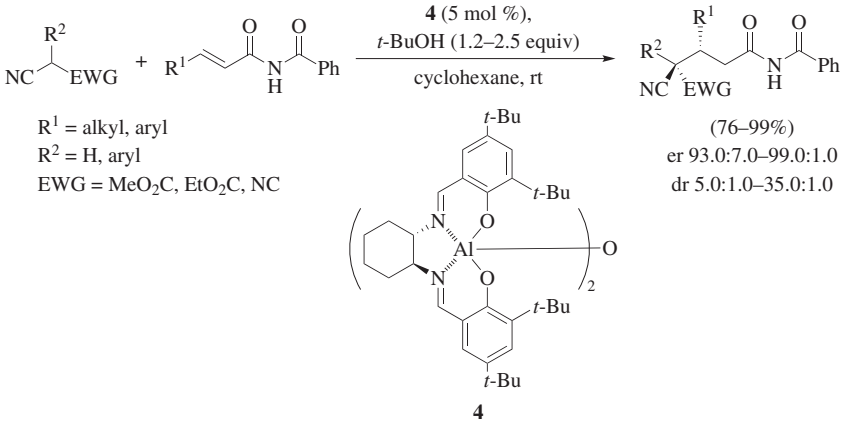
Rhodium complexes have also been used effectively for catalyzing Michael reactions. A complex derived from 0.1–1 mol % of $RhH(CO)(PPh_3)_3$ and chiral diphosphine **3** catalyzes the Michael reaction of α-cyanopropanoates with vinyl ketones or acrolein to provide selectivities around 92.5:7.5 er (Scheme 22).[97] The nature of the alkoxide substituent at the ester moiety exerts an important influence on the stereocontrol, requiring the use of the rather bulky isopropyl propanoates as the Michael donors to provide optimal results. Further work has also demonstrated that Weinreb-type derivatives of these α-cyanopropanoates are also very effective Michael donors in this reaction, furnishing enantiomeric ratios in the range of 94.5:5.5–97.0:3.0 er

and therefore increasing the synthetic potential of the method in view of the many possibilities of further functionalization of the Weinreb amides.[98]



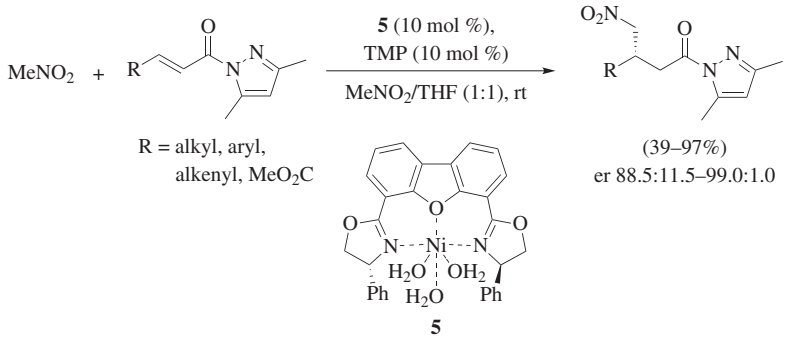

**Scheme 22**

The same type of Michael donors undergoes conjugate addition to α,β-unsaturated imides using Al(III) salen-based catalyst **4** (Scheme 23).[99] In this case, the reaction proceeds in high yields and enantioselectivities and also furnishes very high diastereoselectivities when β-substituted α,β-unsaturated imides react with disubstituted cyanoacetate derivatives, generating two vicinal stereocenters, one of them being quaternary. In addition, the simpler methyl cyanoacetate and malononitrile also react with the same type of Michael acceptors, providing the corresponding adducts in very high yield and enantioselectivities greater than 93.0:7.0 er.[99] Other types of Michael donors, such as malonates or β-keto esters, were also tested but the nitrile-based pronucleophiles are unique in terms of stereocontrol. These findings imply that the catalyst acts as a Lewis acid with the bis-chelating imide moiety of the Michael acceptor and does not compete for the cyanoacetate or malononitrile for which bidentate chelation with the metal center of the catalyst is disfavored because of geometric constraints.



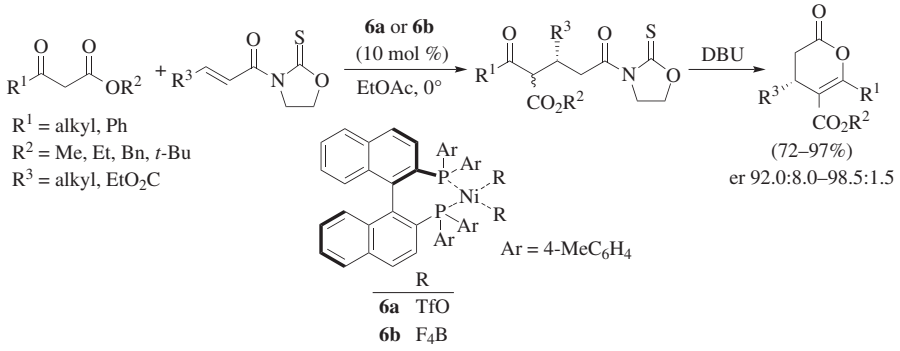

**Scheme 23**

Chiral Ni(II)-complexes also promote enantioselective Michael reactions. For example, complex **5** catalyzes the asymmetric conjugate addition of nitromethane to *N*-enoylpyrazoles (Scheme 24).[100] The reaction is carried out with an excess of the Michael donor (in a 1:1 mixture of $MeNO_2$/THF as solvent) and requires a secondary amine such as 2,2,6,6-tetramethylpiperidine (TMP) as a Brønsted base cocatalyst engaged in the activation of the Michael donor through formation of the corresponding nitronate. The use of the α,β−unsaturated acyl pyrazole as the Michael acceptor is also crucial for attaining high enantioselectivity, presumably due to the need for a bidentate coordination of the substrate to the Lewis acidic nickel center to ensure proper alignment during the conjugate addition step. Under optimized conditions the reaction provides the Michael adducts with moderate to high yields and enantiomeric ratios of >95.0–5.0 er in almost all cases. The reaction also has broad scope with respect to the β-substituent of the Michael acceptor, allowing the use of both β-alkyl and β-aryl substituents, although the greater the steric bulk at this position, the lower the yield or the longer reaction time. Nitroalkanes other than nitromethane were not tested in the reaction.



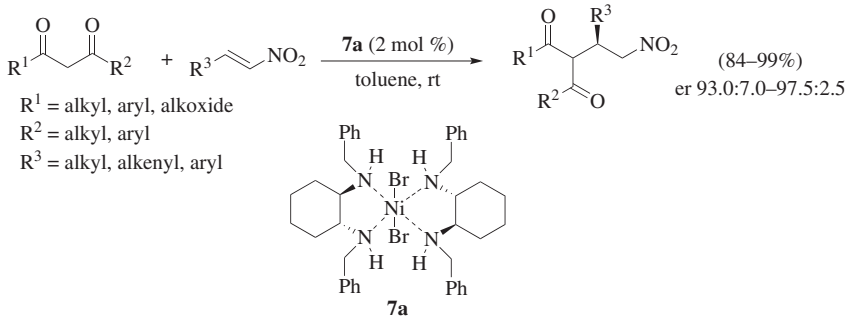

**Scheme 24**

Ni(II)-Tol-BINAP-based complexes **6a** and **6b** also catalyze the conjugate addition of β-keto esters to α,β-unsaturated *N*-acylthiazolidinethiones with high catalytic activity and enantiocontrol (Scheme 25).[101] This reaction does not require the incorporation of a Brønsted base cocatalyst, and the desired adducts are formed as mixtures of diastereoisomers because the stereogenic center between both carbonyl moieties is configurationally labile. This problem is circumvented by treating the Michael adduct in situ with DBU, which forms a dihydropyrone as a result of enolization/lactonization. This enantioselective Michael reaction/lactonization sequence was successfully applied to the reaction of β-keto esters with a wide range of β-substituted-α,β-unsaturated *N*-acylthiazolidinethiones. The final products are highly enantioenriched, although the steric bulk at the β-position of the Michael acceptor has a pronounced influence on the reaction rate. The same rate-decreasing effect is also observed when a cinnamate-derived Michael acceptor is used.




**Scheme 25**

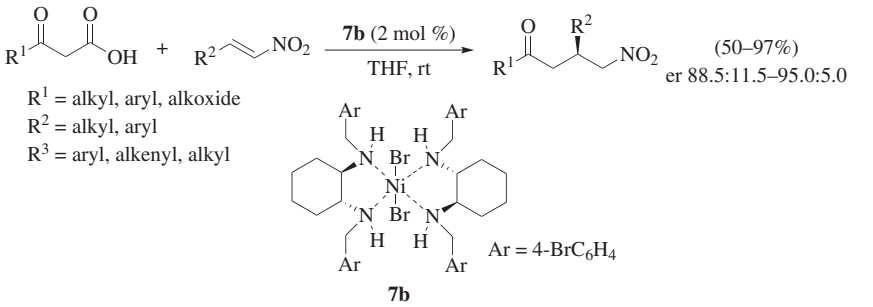
Chiral diamine-based Ni(II) complex **7a** is a good catalyst for the Michael reaction of malonates, 1,3-diketones, and β-keto esters with nitroalkenes (Scheme 26).[33] The reaction is wide in scope, not only allowing the nitrostyrene derivatives typically used as Michael acceptors, but also performing well with β-alkyl-substituted nitroalkenes such as 1-nitrohept-1-ene. 1,3-Diketones provide slightly inferior enantiocontrol (around 93.5:6.5–93.0:7.0 er) but the Michael adducts are formed almost quantitatively and with >95.0:5.0 er when using malonates and β-keto esters. The latter afford mixtures of diastereoisomers because of the configurational lability of the stereocenter between the two carbonyl moieties. α-Alkyl-substituted malonates that can lead to the formation of two contiguous stereocenters also react with high selectivity, although somewhat more slowly.




**Scheme 26**

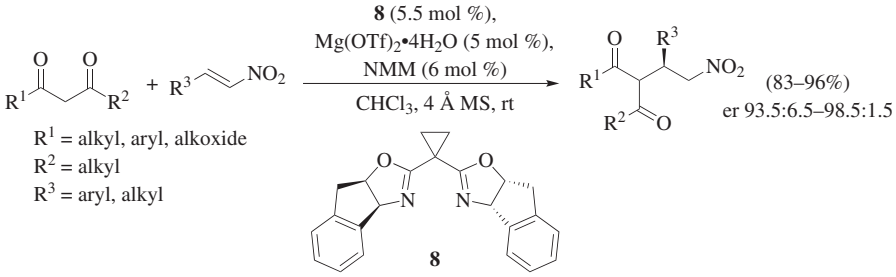
Mechanistic studies suggest the participation of an active catalytic species comprised of a Ni(II)(diamine) complex; the other diamine ligand released from the precatalyst serves to activate the Michael donor as a Brønsted base. In fact, the existence of an uncatalyzed, background reaction between the enolate and the highly electrophilic nitroalkene is proposed to be the reason for the decrease in enantioselectivity observed with several substrates. This observation has led to the preparation and

evaluation of modified catalysts with benzyl substituents at the diamine ligand with different electronic properties. This type of substitution influences the reaction rate and improves the results for those especially challenging substrates. For example, modified catalyst **7b** effects the Michael addition of β-keto acids to nitroalkenes, which, following decarboxylation, afford the γ-nitro ketones in moderate to excellent yields and enantioselectivities for a variety of substrates (Scheme 27).[33]




**Scheme 27**

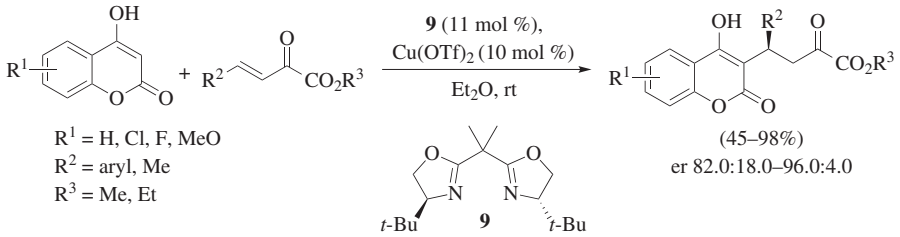
The Mg(II) with the chiral bisoxazoline ligand **8**, can facilitate the same type of Michael reaction, furnishing the adducts in excellent yields and enantioselectivities (Scheme 28).[102] β-Keto esters and malonates effectively combine with nitroalkenes, including both nitrostyrene and the more challenging β-alkyl-substituted nitroalkenes.[102,103] On the other hand, α-alkyl-substituted β-keto esters that lead to the formation of a quaternary stereocenter after the Michael reaction furnish rather poor levels of stereoselection. Interestingly, the reaction conditions require the use of hydrated $Mg(OTf)_2$ to generate the catalyst, although the incorporation of molecular sieves as water scavengers is also necessary for obtaining high conversions. The authors do not clearly state the role of water in the reaction, suggesting that it could be necessary for the initial formation of the catalytically active species by preventing aggregation, whereas at the same time the water also acts as an inhibitor of the catalyst during the Michael reaction. In addition, and as is also the case with



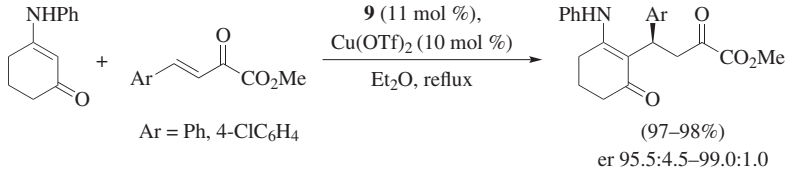

**Scheme 28**

the reaction shown in Scheme 24, the presence of a Brønsted base cocatalyst such as *N*-methylmorpholine (NMM) is needed for the generation of the nucleophile by deprotonation of the Michael donor.

Cu(II)-bisoxazoline complexes, such as that derived from $Cu(OTf)_2$ and bisoxazoline **9**, also catalyze the Michael reaction of cyclic 1,3-dicarbonyl compounds or enamines with β,γ-unsaturated α-keto esters.[38] Once again, the particular structure of the Michael acceptor is crucial for the success of the reaction by enabling the formation of a rigid chelate with the Lewis acid catalyst. In this case, the cyclic 1,3-dicarbonyl compound is also unique as it incorporates a fused aromatic ring that stabilizes the corresponding enol tautomer that is believed to act as the active nucleophile (Scheme 29).[38] Remarkably, the reaction also proceeds with good results using enamines derived from cyclic 1,3-diketones (Scheme 30).[38] These reactions require higher temperatures and longer reaction times.

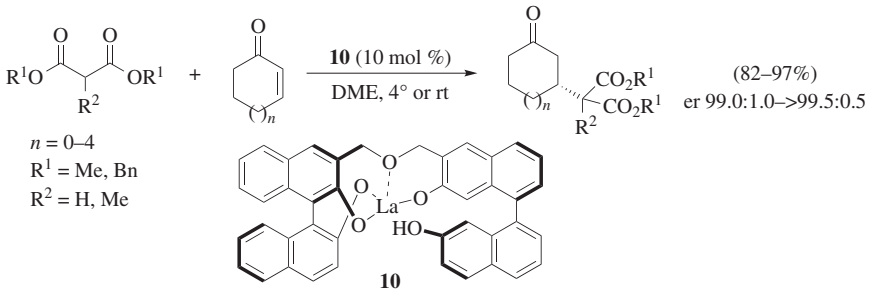



**Scheme 29**



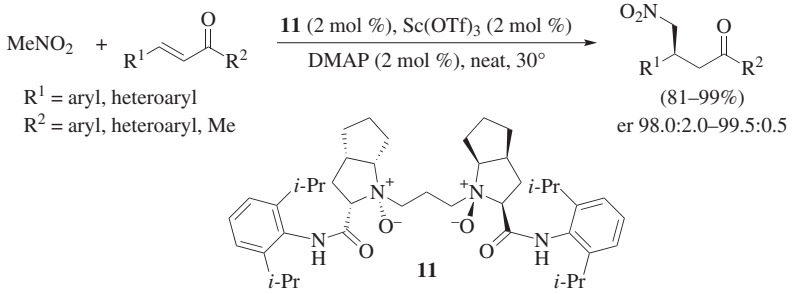

**Scheme 30**

Finally, rare earth elements have also been used in monometallic complexes to catalyze the Michael reaction. The La(III)-BINOL complex **10** promotes the Michael reaction of malonates with enones in excellent yields and enantioselectivities (Scheme 31).[104] The most remarkable feature of this catalyst system is the fact that the metal complex is a stable, easily handled solid that may be prepared in advance and stored for a prolonged time without loss of catalytic potential. Moreover, the catalyst can also be recovered after the reaction by precipitation and recycled up to four times without loss of catalytic activity. This catalyst is particularly effective for cyclic enones but provides somewhat lower enantioselectivities when acyclic enones are employed.

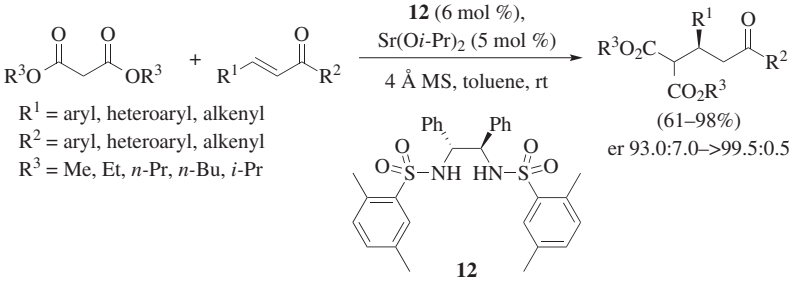



**Scheme 31**

The *N*,*N*′-diamine-dioxide-Sc(III) complex derived from ligand **11** is another example of a rare earth-based catalyst for the Michael reaction, especially for the conjugate addition of nitromethane to β-aryl-substituted enones (Scheme 32).[105] This reaction is very efficient with a rather broad substrate scope that includes chalcones and other β-aryl-substituted enones bearing substituents of varying electronic properties. The same catalyst also performs very well in the reaction of malonates with chalcone[106] and in the conjugate addition of pyrazolin-5-ones to 4-oxo-4-arylbutenoates.[107] In a different approach, a chiral Sr(II) complex incorporating chiral disulfonamide ligand **12** has been identified as another excellent catalyst for the Michael reaction of malonates with chalcones (Scheme 33).[108]



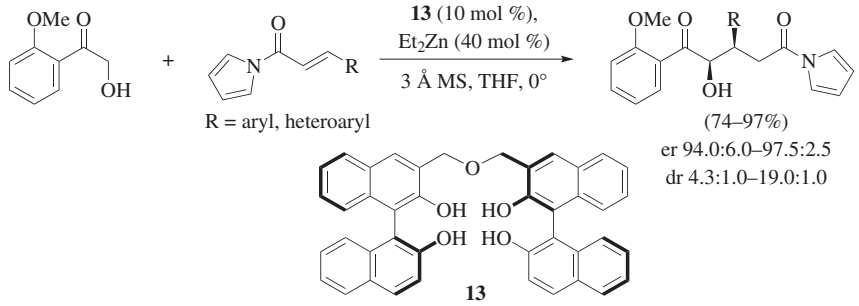

**Scheme 32**



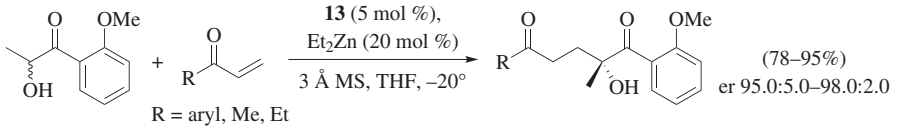

**Scheme 33**

*Polymetallic Complexes.* Chiral metal complexes incorporating two or more metal atoms within their structures have been used as bifunctional catalysts for promoting enantioselective Michael reactions. The design of this type of catalyst relies on the participation of one metal center as the Lewis acid to activate the electrophilic partner. A Brønsted base (that binds to the other metal) activates the Michael donor by deprotonation.

One of the first examples of this type of multimetallic complex for catalyzing the direct Michael reaction is the use of a Zn(II) complex and BINOL-based ligand **13**. This homobimetallic, multinuclear catalyst promotes the conjugate addition of 2-methoxy-α-hydroxyacetophenone to α,β-unsaturated *N*-acylpyrroles with excellent results in terms of both yield and stereoselectivity, even though the best results are obtained for β-aryl-substituted Michael acceptors (Scheme 34).[109,110] The 2-methoxy substituent of the hydroxyacetophenone donor is crucial for the reaction to proceed with efficiency, leading to the proposal that a chelated bidentate Zn(II) enolate is formed during the reaction and that the 2-methoxy substituent is engaged in a secondary interaction with the catalyst. Accordingly, the better performance of a multimetallic catalyst with a 1:4 ligand/Zn(II) ratio can be rationalized. The reaction provides excellent results when vinyl ketones are used as Michael acceptors in combination with racemic 2-hydroxy-1-(2-methoxyphenyl)propanone, providing the desired chiral tertiary alcohols with excellent enantioselectivities for a variety of enones (Scheme 35).[48]



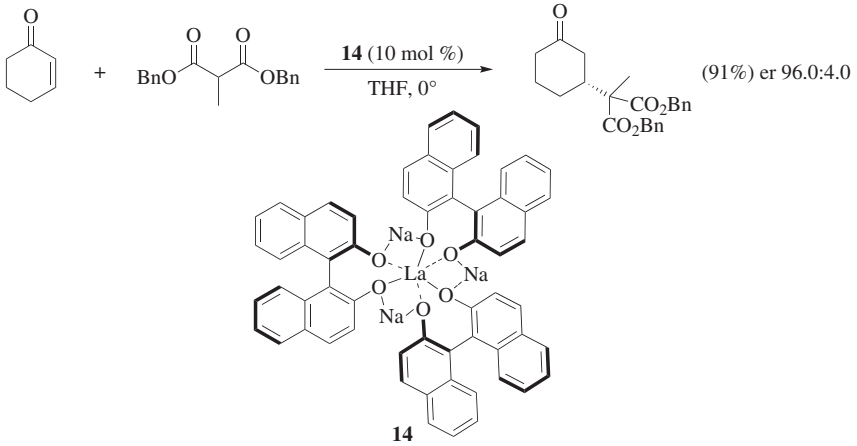

**Scheme 34**




**Scheme 35**

Heterobimetallic complexes are effective bifunctional catalysts for the direct Michael reaction. Particularly useful examples incorporate the architecture represented in structure **14** (Scheme 36),[50] in which one rare earth-based Lewis

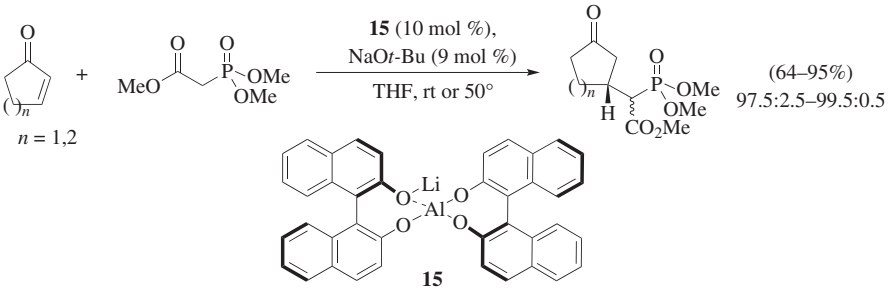
acidic center is surrounded by three alkali metal cations assembled around three BINOL-based binaphthoxide units (participating as the Brønsted base entities). These complexes are outstanding catalysts for the Michael reaction of nitromethane with chalcones,[111] for the conjugate addition of β-keto esters to methyl vinyl ketone and alkyl acrylates (Scheme 9),[51] and for the Michael reaction of malonates with cyclic enones (Scheme 36).[50]




**14**

**Scheme 36**

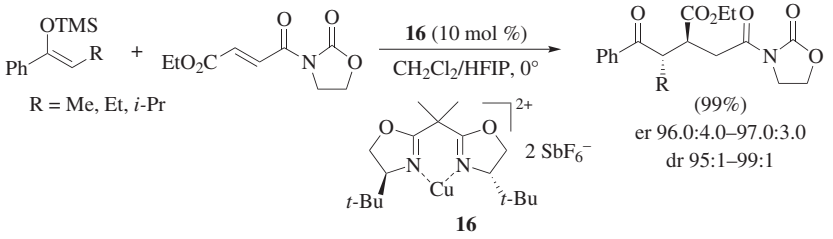
In a related approach, heterobimetallic complex **15** that incorporates Al(III) as the Lewis acidic central atom and $Li^+$ phenoxide as the Brønsted basic alkoxide moiety is an excellent catalyst for the same reaction (the Michael reaction of malonates with cyclic enones)[112] and also performs very well in the conjugate addition of phosphonoacetates to cyclic enones (Scheme 37).[113] However, in the latter case, an external Brønsted base (NaO*t*-Bu) is needed for more efficient activation of the Michael donor.



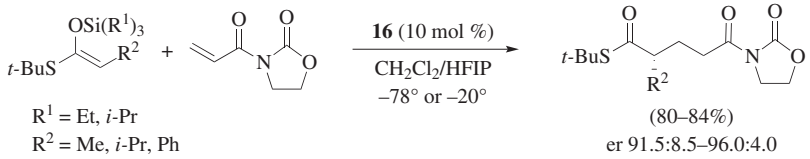

**15**

**Scheme 37**

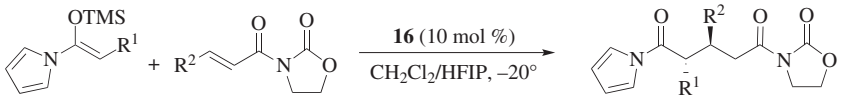
**Metal-Catalyzed Mukaiyama–Michael Reaction.** Only a few catalysts are effective for the conjugate addition of silyl enol ethers to electron-poor olefins in a catalytic and enantioselective fashion. Perhaps one of the most efficient and widest in scope is the Cu(II)-bisoxazoline family of complexes, an example of which is catalyst **16** (Scheme 38).[55] This catalyst system relies on the use of *N*-enoyloxazolidinones as α,β-unsaturated carboxylic acid derivatives. The Michael acceptor structure allows bidentate binding of the metal catalyst during the conjugate addition step. With respect to the Michael donor, the wide applicability of the reaction allows the use of silyl enol ethers derived from ketones,[55] thio esters (Scheme 39),[55] and pyrrole amides (Scheme 40).[55] Importantly, both unsubstituted or substituted enol ethers can be employed as Michael donors and lead to the formation of one or two stereocenters, respectively, after reaction with the corresponding β-substituted α,β-unsaturated *N*-enoyloxazolidinone. In the latter case, the reaction also proceeds with good diastereoselectivity favoring the formation of the *anti*-configured Michael adducts when (*E*) enol silanes are used, whereas the *syn* diastereoisomers are obtained starting from diastereoisomeric (*Z*) enol silanes. (Note that this is valid for silyl enol ethers derived from ketones and amides, whereas the change in priority rules when thioester-based enol silanes are used dictates that *anti*-configured Michael adducts are obtained from (*Z*) silyl ketene thio acetals.) Both alkyl and aryl groups at the β-position of the Michael acceptor can be accomodated, in most cases performing well in both yields and stereoselection, although increasing the steric bulk at this position has a deleterious effect on the yield of the reaction. Finally, the use of substituted enol silanes as Michael donors in combination with β-substituted *N*-acryloyloxazolidinones furnishes good results (Scheme 40).[55]




**Scheme 38**




**Scheme 39**

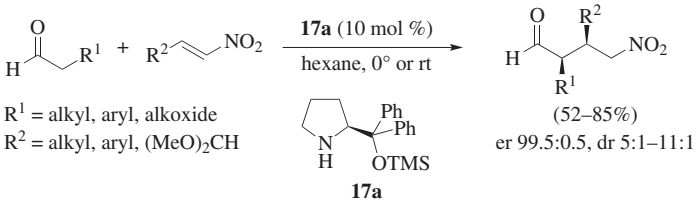



**Scheme 40**

The oxazaborolidine catalyst developed by Corey is an effective chiral Lewis acid catalyst[114,115] for the Mukaiyama–Michael reaction.[56] The reaction of silyl ketene acetals and thio acetals with several cyclic and acyclic enones takes place smoothly in the presence of this type of catalyst, leading to the formation of Michael adducts in good yields and high enantioselectivities (Scheme 11).[56] Importantly, this process is complementary to the one presented above because it performs very well with simple enones as Michael acceptors. On the other hand, the reaction has not been examined with substituted silyl enol ethers that would lead to the formation of two stereocenters.

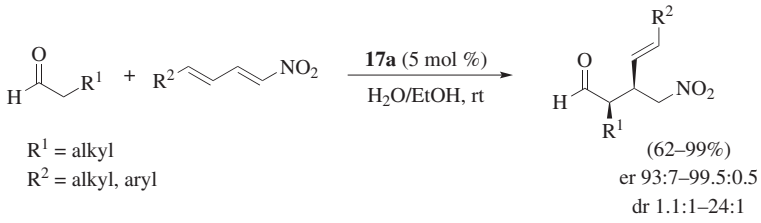
## Organocatalyzed Michael Reactions

**Enamine Activation.** A wide variety of chiral primary and secondary amines catalyze the enantioselective Michael reaction of enolizable aldehydes or ketones with electron-deficient olefins via formation of an enamine intermediate. However, the poor reactivity of enamines in Michael reactions limits this approach to highly electrophilic acceptors. Accordingly, most of the catalytic systems operating through this mechanism have been tested with nitroalkenes. *O*-Trialkylsilyl α,α-diarylprolinols such as **17a** are one of the most effective families of catalysts for the conjugate addition of aldehydes to nitroalkenes in terms of yields, stereoselectivities, and scope (Scheme 41).[60,116–120] This catalytic system leads to the formation of predominantly *syn* diastereoisomers of the Michael adducts with a wide variety of substitution patterns on both the aldehyde and the nitroalkene reagents. Nitrostyrenes as well as β-alkyl-substituted nitroalkenes react efficiently under very mild reaction conditions. α,β,γ,δ-Nitrodienes are also suitable substrates that undergo the Michael reaction with aldehydes in the presence of **17a** to provide single 1,4-addition products in high yields and with excellent stereocontrol (Scheme 42).[121] In addition, this method allows the use of acetaldehyde as the Michael donor. This aldehyde is difficult to handle because of its tendency for self-condensation. Despite this, in the presence of **17a** and under carefully controlled conditions, acetaldehyde reacts with a variety of nitroalkenes, allowing the preparation of β-substituted-γ-nitroaldehydes in acceptable yields and enantioselectivities (Scheme 43).[122,123] This catalyst also promotes reactions between aldehydes and nitroethylene with excellent results.[124] An important benefit of this method is the operational simplicity of the experimental protocol because of the compatibility of the intermediates in the catalytic cycle with moisture and oxygen.

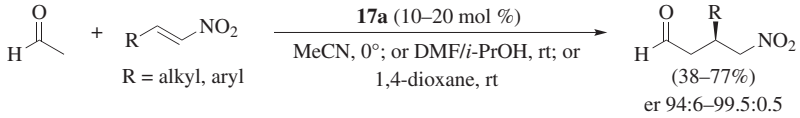



**17a**

**Scheme 41**

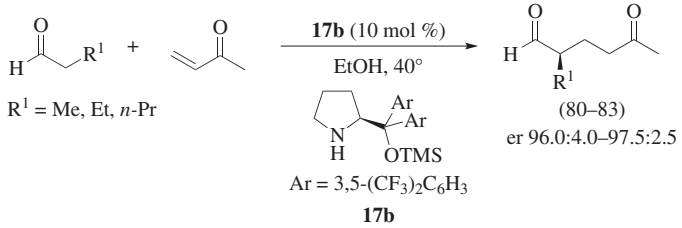



**Scheme 42**



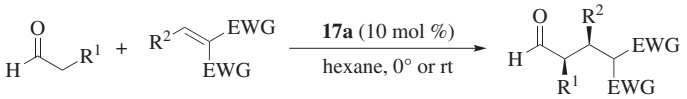

**Scheme 43**

Moreover, modified *O*-TMS diarylprolinol **17b** catalyzes the Michael reaction of aldehydes with other types of electron-poor olefins as acceptors, such as methyl vinyl ketone (Scheme 44),[61] although β-substituted enones are unreactive or react very slowly. Highly electrophilic olefins incorporating two electron-withdrawing groups such as vinyl bis(sulfones),[125] alkylidenemalonates,[126,127] or vinyl bis(phosphonates)[128,129] can also be used in combination with aldehydes as Michael donors providing, in the presence of **17a**, the corresponding Michael adducts in good yields and stereoselectivities (Scheme 45).[125,126,128]




**17b**

**Scheme 44**

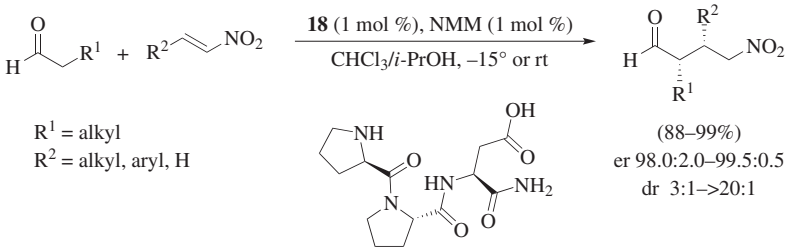



$R^1$ = alkyl, H
$R^2$ = alkyl, aryl, H
EWG = $EtO_2C$, $(EtO)_2P(O)$, $PhO_2S$

(60–96%)
er 73.0:27.0–99.5:0.5
dr 4:1–14:1

**Scheme 45**

Catalysts incorporating stereodirecting elements within their structures that can engage in secondary interactions with the Michael acceptor are also good alternatives for this type of reaction. A good example of a highly effective catalyst, which performs well with differently substituted substrates, for the Michael reaction of aldehydes with nitroalkenes is shown in Scheme 12.[73] Tripeptide **18** is a prime example of this type of catalyst, performing excellently in this type of reaction with a low catalyst loading (typically 1 mol %) compared to other catalysts that are typically used in the range of 10–30 mol % (Scheme 46).[130] In this case, the terminal carboxy group of the asparagine unit is believed to activate the Michael acceptor through H-bonding with the nitro moiety, whereas the terminal proline residue activates the nucleophile for enamine formation. Moreover, this catalyst also performs exceptionally well in the challenging Michael reaction of aldehydes with nitroethene.[131] A similar design has been followed in the development of 4-hydroxyproline-based catalyst **19**, which affords excellent results in the reaction between aldehydes and nitroalkenes (Scheme 47).[132] In this procedure, equimolar amounts of aldehyde donor and nitroalkene acceptor can be employed and therefore this protocol overcomes an important drawback associated with many of the other methods that require a large (between 3- and 10-fold) excess of the Michael donor to achieve high conversions. Using this system, excellent yields and stereoselectivities are obtained for a variety of both β-aryl- and β-alkyl-substituted nitroalkenes while employing acceptable catalyst loadings (5–10 %).

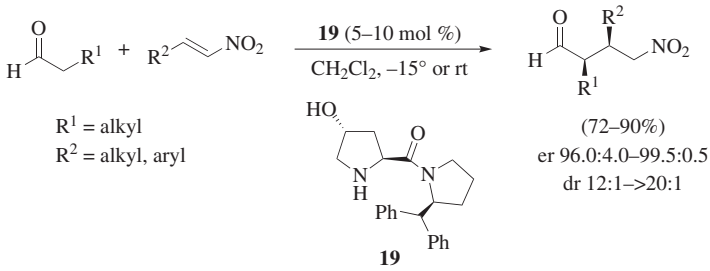



$R^1$ = alkyl
$R^2$ = alkyl, aryl, H

(88–99%)
er 98.0:2.0–99.5:0.5
dr 3:1–>20:1

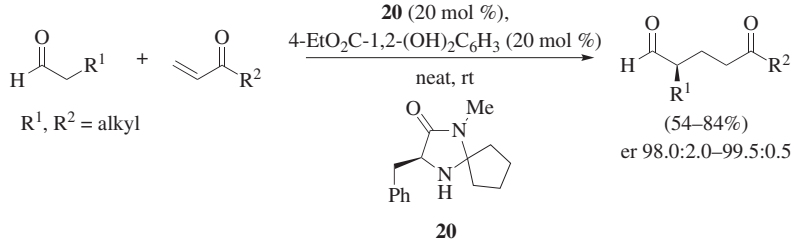
**18**

**Scheme 46**

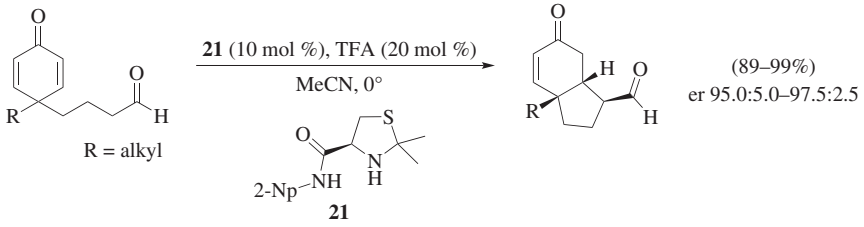



**Scheme 47**

Chiral imidazolidinones such as **20** represent another privileged architecture for active catalysts operating in the enamine manifold. In particular, this imidazolidinone efficiently catalyzes the Michael reaction between aldehydes and vinyl ketones (Scheme 48).[133] A related derivative, thiazolidine **21**, promotes intramolecular Michael reactions of substrates that contain an enolizable aldehyde as the Michael donor and an enone moiety as the internal electrophile (Scheme 49).[134,135] In both cases, incorporating a Brønsted acid co-catalyst is critical for the reaction, which is interpreted in terms of the need to activate the enone through H-bonding interactions with this co-catalyst.

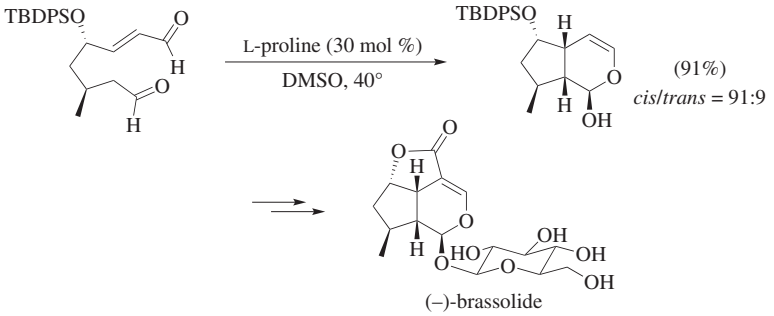



**Scheme 48**




**Scheme 49**

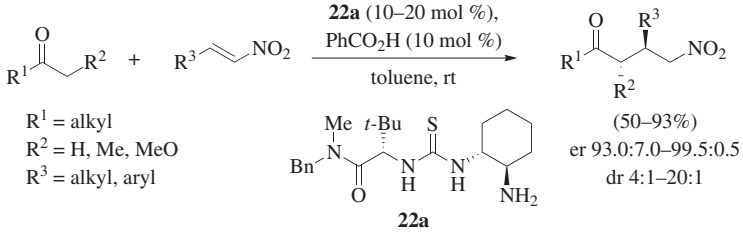
L-Proline, the archetypical chiral secondary amine catalyst, has also been used in this type of reaction, but affords very poor levels of enantioselection in intermolecular Michael reactions between aldehydes and ketones with a variety of nitroalkenes.[136−139] Despite these limitations, proline has been successfully used in an intramolecular version of this reaction (Scheme 50).[140] This variant employs a chiral starting material and is the key step in the total synthesis of (−)-brassolide. The dialdehyde undergoes a proline-catalyzed intramolecular Michael reaction under exclusive catalyst control to form the thermodynamically less stable *cis* diastereoisomer that is required to access to the target compound.



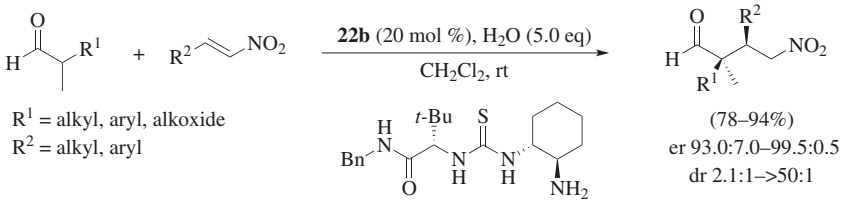

**Scheme 50**

Unfortunately, the chiral secondary amine catalysts that perform well with aldehydes as Michael donors usually provide poor results with ketones. On the one hand, the lower catalytic activity arises from the inherent difficulty in the formation of the enamine intermediate. In addition, controlling the geometry and conformation of these much more sterically congested enamine intermediates is a challenging task, the success of which depends on the relative size of all substituents. This latter aspect is not a problem when symmetrically substituted ketones such as cyclohexanone or acetone are employed; however, the use of unsymmetrically substituted ketones as Michael donors makes this issue of enormous relevance in the design of useful chiral amine catalysts. A solution to this problem is provided by the use of primary amines as catalysts,[141−143] because the condensation of a ketone and a primary amine is sterically more feasible and also provides better geometric control of the enamine intermediate due to the greater difference in bulk between the coplanar enamine substituents. In particular, primary amino thiourea **22a** performs extremely well in the Michael reaction of ketones with nitroalkenes, providing excellent results in terms of stereoselectivity and substrate scope. A wide variety of differently substituted ketones and nitroalkenes can be used, including the more challenging β-alkyl-substituted nitroalkenes (Scheme 51).[144] For these reactions, a crucial element for the catalyst design is the incorporation of the secondary thiourea functionality, which interacts with the nitro group by formation of two hydrogen bonds between the NH groups and the nitro moiety. This type of catalyst (for example catalyst **22b**) is also able to activate α,α-disubstituted aldehydes as Michael donors (Scheme 52),[72] another class

of substrates that does not perform effectively with secondary amines as catalysts. Importantly, this reaction also requires the use of five equivalents of water to facilitate catalyst turnover by hydrolysis of intermediate species, namely, the cyclobutane and 1,2-oxazine intermediates shown in Scheme 13.

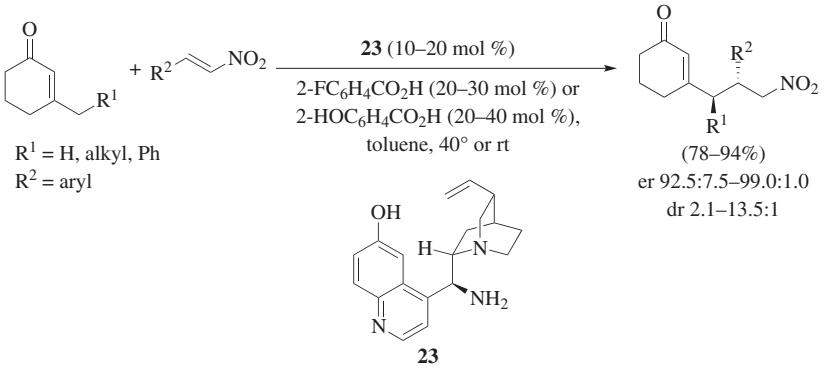



**Scheme 51**




**Scheme 52**

Enolizable α,β-unsaturated ketones undergo γ-addition with nitroalkenes in the presence of *Cinchona* alkaloid-based primary amine catalyst **23** (Scheme 53).[145] The activation of the enone takes place through formation of a dienamine intermediate

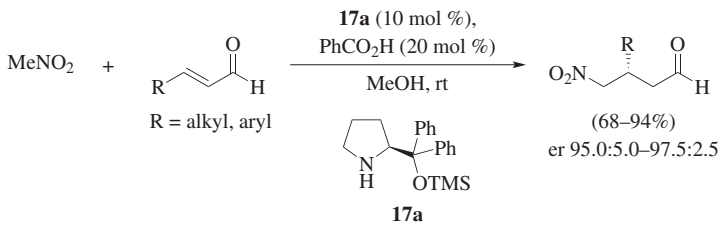



**Scheme 53**

after condensation with the catalyst in the first step of the catalytic cycle. This dienamine undergoes selective γ-addition to deliver the conjugate addition products in good yields and high diastereo- and enantioselectivities. This type of vinylogous reactivity has also been studied with α,β-unsaturated aldehydes, but these substrates tend to react with highly activated Michael acceptors, such as nitroalkenes or alkylidenemalonates through Diels–Alder cycloadditions. The dienamine intermediate participates as an electron-rich diene[146–151] and in those cases in which the Michael reaction occurs, α-addition is usually the observed pathway.[120]

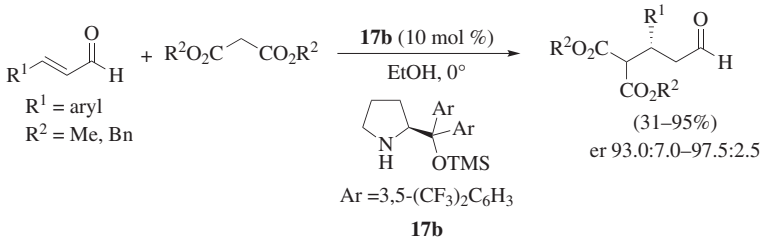
**Iminium Ion Activation.** Primary and secondary amines can also catalyze the conjugate addition reaction by forming iminium ions with α,β-unsaturated aldehydes or ketones. As with reactions proceeding by enamine activation, this strategy is highly atom-efficient and also operationally simple. In addition, the use of α,β-unsaturated aldehydes as Michael acceptors is an important feature because these substrates cannot be easily used with Lewis acidic metals. On the other hand, the covalent interaction between the catalyst and the substrate and the need for reversible reactions for the attachment and the removal of the catalyst lead to low catalyst TOF (turnover frequency) values. Moreover, this mechanism of organocatalytic activation requires the use of a pro-nucleophile incorporating a rather acidic C–H group that is able to be deprotonated under the neutral or slightly acidic reaction conditions associated with iminium ion catalysis. Accordingly, this type of activation works well with 1,3-dicarbonyl compounds and nitroalkanes as the Michael donors. This limitation places an upper limit on the p$K_a$ of the pronucleophile used in iminium ion activation to approximately 16–17.[152]

Among the many different catalysts developed for activation via iminium ion formation, *O*-trialkylsilyl-α,α-diarylprolinol derivatives such as **17a** or **17b** constitute a privileged family of catalysts that provide outstanding results in this context. The concept behind the catalyst design is based on the presence of a very bulky diaryltrimethylsilyloxy substituent, which allows excellent control of the intermediate iminium ion geometry after condensation with the enal. This catalyst also exerts a very effective steric bias on the heterotopic faces of the Michael acceptor. In general, these catalysts are effective in the Michael reaction of nitroalkanes (Scheme 54)[153] and malonates (Scheme 55).[154] This type of catalyst is also able to promote the reaction using other 1,3-dicarbonyl compounds such as 1,3-diketones[155] or β-keto esters[156] and other active methylene compounds such as β-keto sulfones,[157,158]

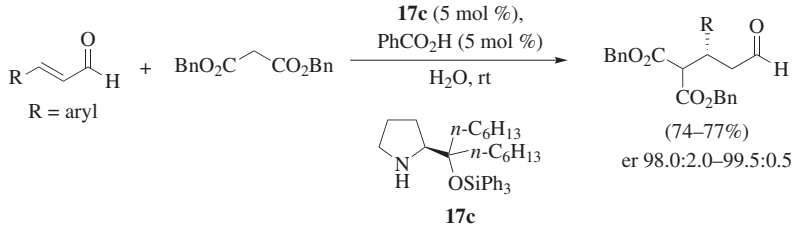



**Scheme 54**

β-keto sulfoxides,[159] bis-sulfonylmethanes,[160–165] and azlactones[166]. A useful variant of this family of catalysts specifically designed for carrying out this reaction in water (for example prolinol derivative **17c**) incorporates hydrophobic alkyl side chains into the prolinol scaffold that presumably form a hydrophobic pocket that conscripts the organic substrates into the catalytic site (Scheme 56).[167]

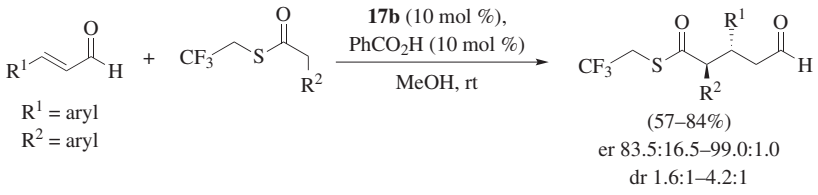



**Scheme 55**



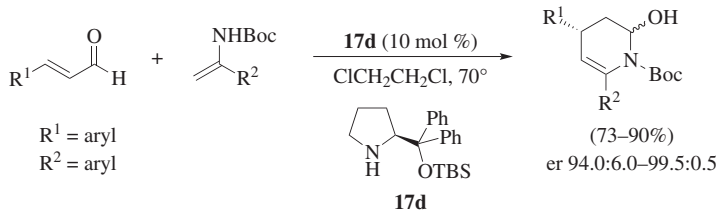

**Scheme 56**

The use of less acidic pronucleophiles under iminium ion activation is limited to a few modified reagents. In one case, the formal conjugate addition of simple esters to α,β-unsaturated aldehydes has been addressed by using trifluoroethyl thioesters as the Michael donors (Scheme 57).[152] The higher acidity of thioesters compared to the corresponding esters and the incorporation of a highly electron-withdrawing fluorine-containing thiolate substituent makes them active in the Michael reaction with enals using **17b** as catalyst, but the reaction is restricted to α-aryl-substituted thioacetates. An alternative approach involves the use of preformed enamides as activated pronucleophiles. With diarylprolinol **17d** as the catalyst, several




**Scheme 57**

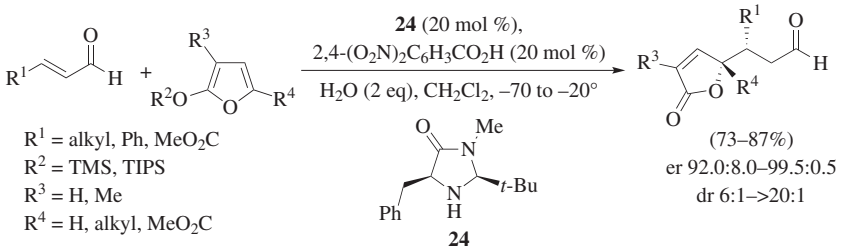
α-unsubstituted enamides react with a variety of α,β-unsaturated aldehydes leading to the Michael adducts as the corresponding hemiaminal isomers in high yields and stereoselectivities (Scheme 58).[168]




**17d**

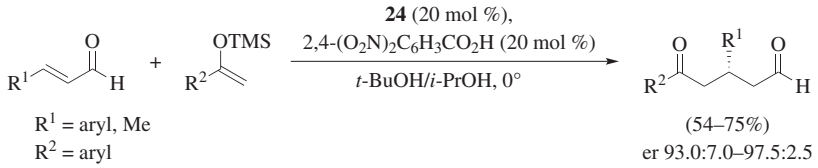
**Scheme 58**

Silyloxyfurans react under iminium ion activation with α,β-unsaturated aldehydes using imidazolidinone **24** as the catalyst to provide a direct and efficient route to γ−butenolides (Scheme 59).[169] A Brønsted acid co-catalyst (2,4-dinitrobenzoic acid) assists in the formation of the activated iminium ion and two equivalents of water are added to overcome the loss of water from the catalytic cycle by the formation of hexamethyldisiloxane. The same catalyst also catalyzes the Mukaiyama−Michael reaction of acyclic silyl enol ethers with enals (Scheme 60).[170] In this case, a *t*-BuOH/*i*-PrOH solvent mixture scavenges the trimethylsilyl cation.




**24**

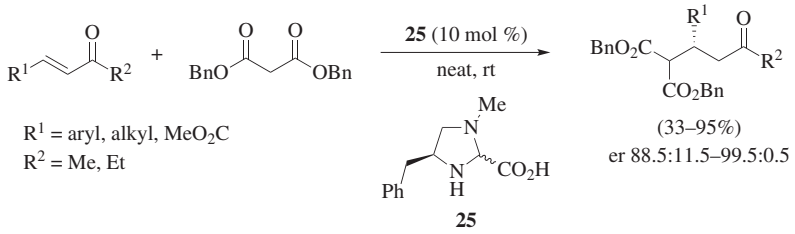
**Scheme 59**



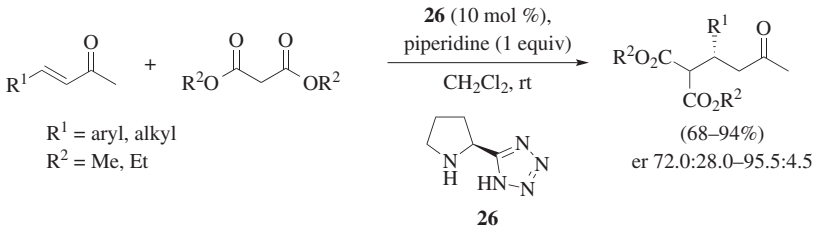

**Scheme 60**

The application of iminium activation to enones as Michael acceptors is much less developed. Despite many reports of the use of a variety of chiral secondary amines as

catalysts (most derived from proline), the reactions generally lead to variable yields and stereoselectivities. Among the catalysts reported, imidazolidine **25** is the most general for the conjugate addition of malonates to acyclic enones (Scheme 61).[171] The reaction proceeds well for a wide range of substituted arylideneacetophenones as well as for cyclohexenone, but yields tend to decrease when the carbonyl moiety is substituted with bulkier groups. In addition, the nature of the malonate reagent has a significant impact on enantioselectivity such that dibenzyl malonate and diethyl malonate produce the best results: the model reaction between dimethyl malonate and benzylideneacetone gives a 66% yield and 85.0:15.0 er compared to a 73% yield and 95.5:4.5 er using diethyl malonate and 93% yield and >99.5:0.5 er using dibenzyl malonate. The major drawbacks of this reaction are the need for a large excess of the malonate donor (it is used as the reaction solvent) and for long reaction times (typically 7–10 days) to reach good conversions. This type of imidazolidine catalyst is also effective in the Michael reaction with acyclic enones using cyclic 1,3-diketones[172] and nitroalkanes[173] as the Michael donors. Alternatively, catalyst **26** allows the use of the more accessible and economical diethyl and dimethyl malonates as the Michael donors and also avoids the use of such large amounts of the pronucleophile. However, the reaction is rather limited in scope, affording excellent yields and enantioselectivities for cyclohexenone and alkenyl methyl ketones, but poorer results with aryl alkenyl ketones (Scheme 62).[174] This method also requires the incorporation of one equivalent of piperidine to activate the nucleophile. This catalyst is also active in the Michael reaction of nitroalkanes with cyclic enones.[175]

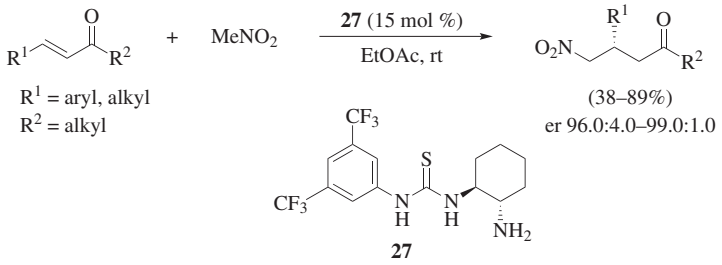



**Scheme 61**




**Scheme 62**

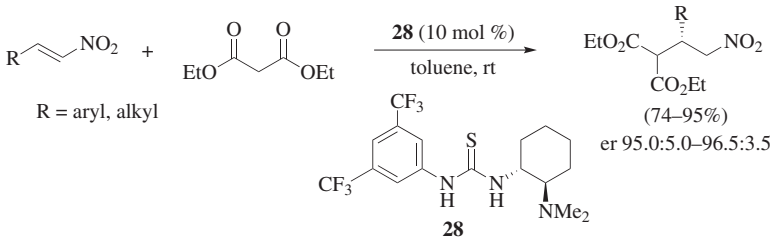
Interestingly, further mechanistic studies of the reaction shown in Scheme 61 point toward the participation of a primary amine as the catalytically active species,[176] which could be generated by in situ hydrolysis of imidazoline **25**. This observation comports with the better performance of primary amines when are activated enones through iminium ion formation. In line with these findings, other primary amines have been used with success in this reaction, mostly in the form of bifunctional catalysts. Primary amine-thiourea catalyst **27** derived from cyclohexanediamine is a representative example of this type of catalyst, which has been used in the Michael reaction of nitromethane with acyclic and cyclic enones (Scheme 63) with good yields and enantioselectivities.[177] The reaction with nitroethane proceeds well with respect to yield and enantioselectivity but affords a 1:1 mixture of diastereoisomers.



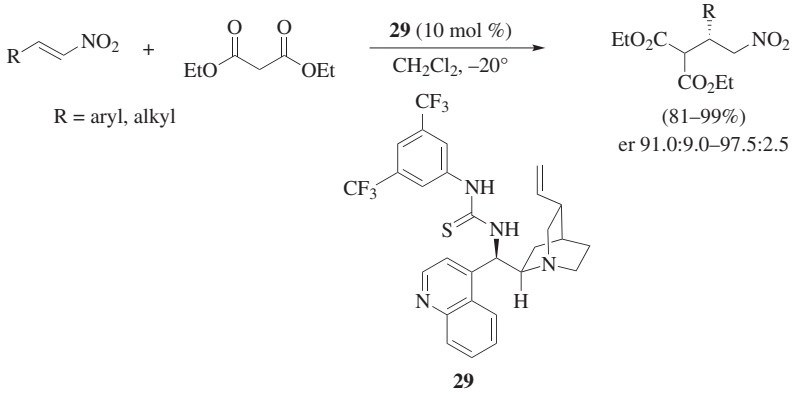

**Scheme 63**

**Hydrogen-Bonding Catalysis.** Organic molecules capable of establishing interactions with the activating group of the Michael acceptor through H-bonding can catalyze the Michael reaction by removing electronic density from the electrophile (i.e. LUMO lowering). A synergistic situation arises when chiral thioureas are used to catalyze the conjugate addition reaction to nitroalkenes because of the ability of this functional group to engage in selective H-bonding interactions with the nitro group through the formation of two hydrogen bonds between the NH's and the oxygen atoms of the nitro group. This thiourea-nitroalkene interaction is rather strong, occurring even in the presence of water, and it also provides a highly chemoselective reaction if other basic groups or potential Michael acceptors are present in the substrate. Bifunctional thioureas **28**[86,87] and **29**[178–180] are some of the most effective catalysts for this particular class of Michael reaction (Schemes 64[86] and 65[178,180]). These catalysts were initially examined in the Michael reaction between malonates and nitroalkenes, but are also outstanding catalysts that permit the use of other types of Michael donors. An advantage common to the use of the *Cinchona* alkaloid-based family of catalysts like thioureas **29** and **30** is the availability of the pseudoenantiomeric quinine- or quinidine-based thioureas, which lead to the formation of both enantiomers with essentially the same level of stereoselectivity (Schemes 65[178,180] and 66[178]). However, this catalyst type is restricted to the use of highly acidic pronucleophiles such as 1,3-dicarbonyl compounds or nitroalkanes and therefore other less

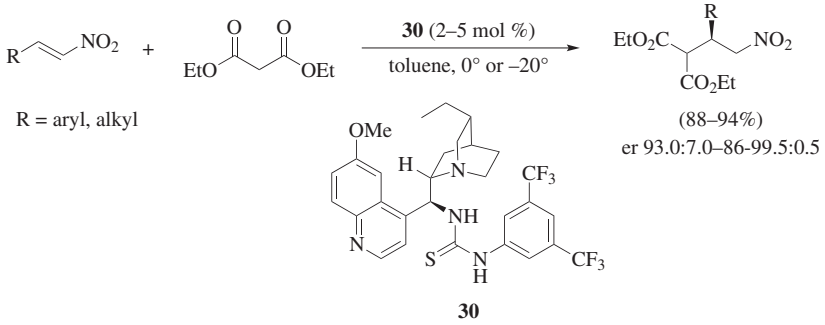
active Michael donors such as simple ketones, esters, or amides are not susceptible to this organocatalytic activation manifold.




**Scheme 64**

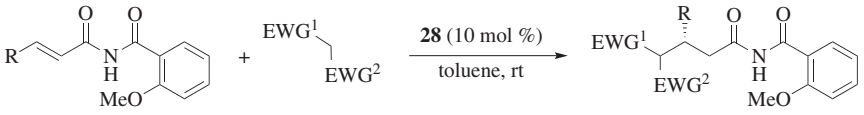



**Scheme 65**




**Scheme 66**

Other electron-deficient olefins capable of engaging in similar H-bonding interactions can also be activated by this type of thiourea catalyst, thereby expanding the scope of the method. For example, the imide moiety can efficiently play this role with a variety of active methylene compounds in a reaction that takes place with excellent yields and enantioselectivities in the presence of thiourea **28** (Scheme 67).[181,182]



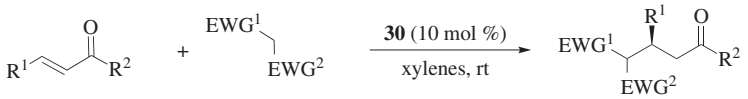

R = alkyl, aryl
$EWG^1$, $EWG^2$ = NC, $MeO_2C$, $O_2N$

(92–99%)
er 90.0:10.0–96.5:3.5

**Scheme 67**

The structure of the imide acceptor is crucial for achieving good results. α,β-Unsaturated 2-methoxybenzimides are highly reactive electrophiles, an observation rationalized by the stability of one conformer of the acceptor by the presence of an intramolecular H-bonding between the NH group of the imide and the methoxy substituent. This interaction would lead to a decrease of the electron density at the nitrogen atom and also favor a suitable orientation of the substrate for complexation of the thiourea catalyst.

In addition to the highly effective H-bonding interactions achieved for nitroalkenes with α,β-unsaturated imides, simple enones can also be used in the Michael reaction with these types of thiourea catalysts. Nevertheless, these substrates are more challenging because of the lower Lewis basicity of the carbonyl group and due to the fact that enones can participate in H-bonding interactions with the catalyst using only a single oxygen atom. For example, bifunctional thiourea/tertiary amine catalyst **30** is successfully employed in the Michael reaction of a variety of 1,3-dicarbonyl compounds and related derivatives such as malonates, malononitriles, β-keto esters, 2,4-pentanedione, and ethyl nitroacetate with chalcones (Scheme 68),[183] in the Michael reaction of nitromethane with acyclic enones (Scheme 69),[180] in the conjugate addition of α-cyano esters and α-cyano ketones to acrylonitriles,[184] and in one example of an intramolecular Michael reaction involving a nitroalkane as the Michael donor and a monoactivated α,β-unsaturated ester as internal electrophile.[185] In the same manner, cyclohexanediamine-based thiourea catalyst **28** has been employed in the

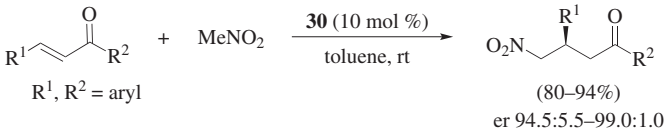



$R^1$ = aryl
$R^2$ = aryl, Me
$EWG^1$, $EWG^2$ = NC, $RO_2C$, $O_2N$

(61–99%)
er 92.5:7.5–99.0:1.0

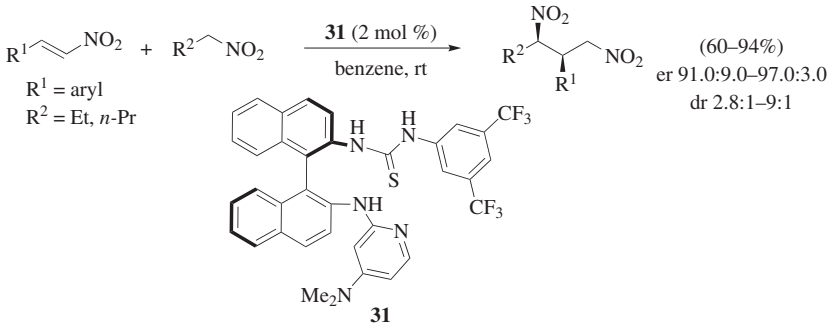
**Scheme 68**

Michael reactions between enones and different types of Michael donors with good results.[186–188] Moreover, the same catalyst is able to activate acrylates in the Michael reaction with α-aryl-α-cyanoacetates.[189]




**Scheme 69**

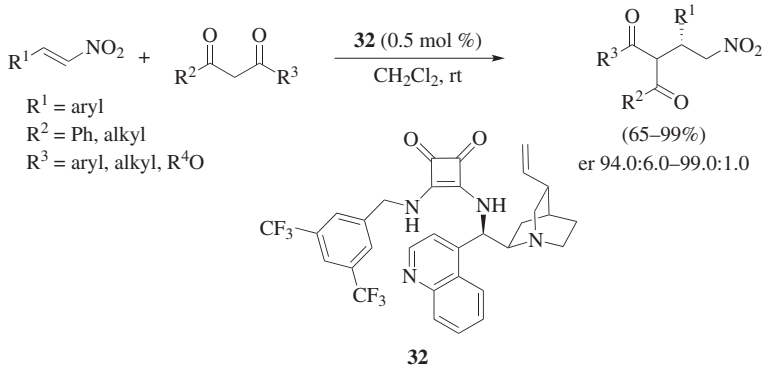
The axially chiral binaphthylamine scaffold has also been used as the central motif for designing other related bifunctional tertiary amine/thiourea catalysts active in Michael reactions. In particular, catalyst **31** has been used in the conjugate addition of nitroalkanes to nitroalkenes, a particularly challenging situation because of the chemoselectivity issues arising due to the presence of two nitro compounds in the reaction scheme. In this case, the catalyst incorporates an aminopyridine moiety that participates selectively in the activation of the nitroalkane donor by assisting its deprotonation and by stabilizing the resulting nitronate via double H-bonding interactions. This catalyst also contains a thiourea moiety, which activates the nitroalkene as in the previous examples. Under the optimized reaction conditions, the Michael reaction of nitropropane and nitrobutane with nitrostyrenes leads to the generation of adducts with two contiguous stereogenic centers in good yields and diastereo- and enantioselectivities (Scheme 70).[190]




**Scheme 70**

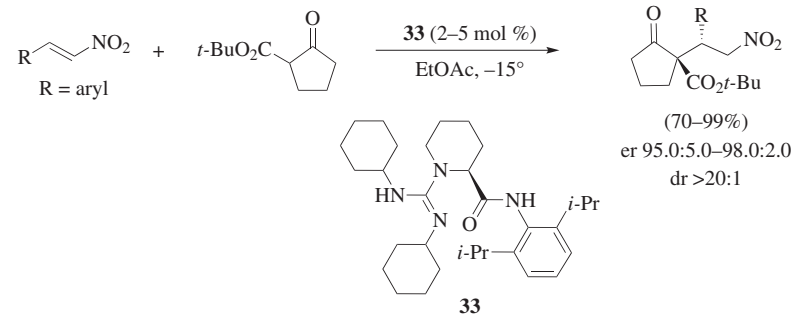
The squaramide moiety is another privileged platform for the activation of nitro olefins and other related Michael acceptors by H-bonding interactions. The aromatic character of the squaramide unit leads to a planar and very structurally rigid motif that facilitates the formation of the H-bonded network and also leads to the generation of

a conformationally rigid intermediate during the conjugate addition step.[191] Furthermore, the distances between the two donating hydrogens and the C–N–H bond angles in the squaramide moiety allow the NH groups to lie in a more optimal orientation towards the H-bonding acceptor basic site of the activated olefin, which leads to improved binding. In particular, bifunctional squaramides containing an additional Brønsted basic site that are related to the thioureas described earlier are outstanding catalysts for different enantioselective Michael reactions.[192] Squaramide **32** catalyzes the Michael reaction of 1,3-diketones with nitroalkenes in relatively short reaction times (about 7 hours) and with only 0.5 mol % of catalyst, thus demonstrating the high efficiency and stereocontrol using this type of chiral catalyst (Scheme 71).[192]

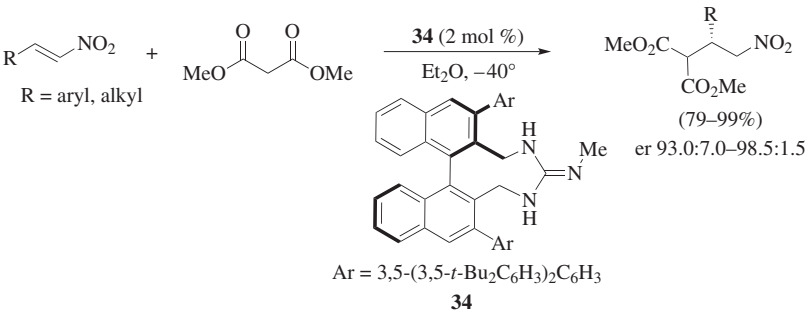



**Scheme 71**

Guanidines represent another class of organic compounds that can activate Michael acceptors through H-bonding interactions. Bifunctional guanidine **33** is excellent in the Michael addition of cyclic β-keto esters to nitrostyrenes (Scheme 72).[193] This bifunctional catalyst is proposed to activate the pronucleophile by deprotonation through the highly basic guanidine moiety and simultaneously the guanidine group engages in multiple H-bonding interactions with both the nitroalkene and the enolate nucleophile, the latter also establishing an additional H-bond with the lateral secondary arylamide moiety. This multiple array of H-bonding interactions leads to a well-ordered arrangement of the reagents in the transition state and accounts for the excellent diastereo- and enantioselectivities. The strongly basic character of the guanidine moiety enables a very effective deprotonation of the pronucleophile, and as such results in a highly active catalyst that requires low loadings. Another active guanidine-type catalyst containing an axially chiral backbone is also reported to be very effective in promoting the reaction of dimethyl malonate with nitroalkenes (Scheme 73).[194] Guanidine **34** does not incorporate any other secondary functionality for establishing multiple interactions with both the Michael donor and the acceptor. The approach of the electrophile is controlled by the axial chirality of the catalyst and in particular by the presence of the very bulky 3,5-bis(3,5-di-*tert*-butylphenyl)phenyl groups placed at the 3- and 3′- positions of the binaphthyl backbone.



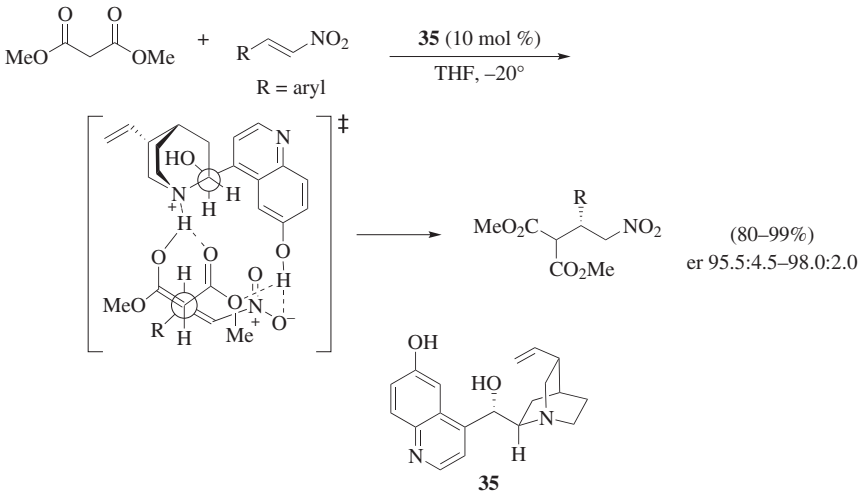

**Scheme 72**



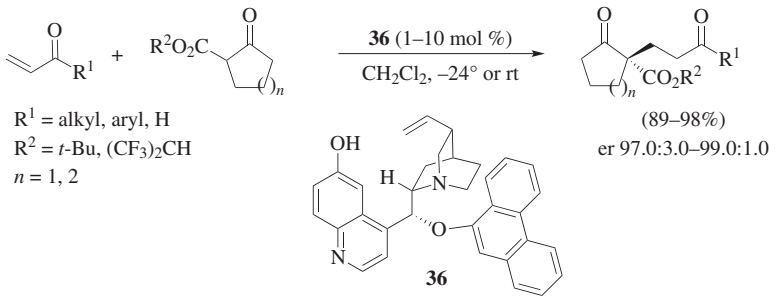

**Scheme 73**

Alternatively, molecules that participate in the activation of the electrophile by the formation of a single hydrogen bond with the electron-withdrawing group of the Michael acceptor are also efficient catalysts for this reaction. In particular, a simple *Cinchona* alkaloid derivative such as cupreidine (**35**) is an excellent catalyst for the Michael reaction of dimethyl malonate (Scheme 74)[195] and other 1,3-dicarbonyl compounds[196,197] with nitrostyrenes. The catalyst is proposed to activate the electrophile through H-bonding interaction with the phenolic OH group, and the quinuclidine basic moiety is responsible for the activation of the 1,3-dicarbonyl pronucleophile. The secondary OH group is only involved in the stabilization of a reactive conformation of the substrate-catalyst complex in which the two substrates that participate in the Michael reaction can approach each other. This is demonstrated by the fact that the same catalyst in which the phenolic group is modified as the corresponding methyl ether provides poor enantioselectivity and also by the fact that related *Cinchona* alkaloids that contain the phenolic OH group and in which the secondary alcohol is modified as the corresponding allyl or phenanthryl ether are also active in other Michael reactions, such as in the conjugate addition (facilitated by alkaloid **36**) of β-keto esters to vinyl ketones and acrolein, providing comparable

stereoselectivities (Scheme 75).[198,199] Other examples of the utility of these phenolic *Cinchona* alkaloid-based catalysts include the Michael reaction of β-keto esters with *N*-acylpyrroles,[200] the conjugate addition of different active methylene compounds to 2-chloroacrylonitrile,[201] and the Michael reaction of α-cyano esters with vinyl sulfones.[202]



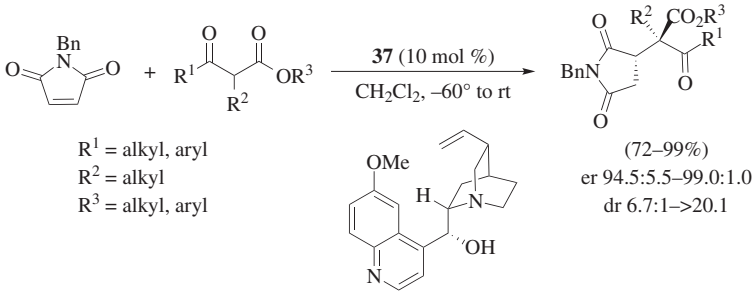

**Scheme 74**




**Scheme 75**

Naturally occurring *Cinchona* alkaloids such as quinine (**37**) or the pseudoenantiomeric quinidine, in which the phenolic position is present as the corresponding methyl ether, are also good catalysts, although with a narrower substrate scope. In particular, quinine catalyzes the Michael reaction of β-keto esters and 1,3-diketones with maleimides, to afford a family of products containing two stereogenic centers in excellent yields and diastereo- and enantioselectivities (Scheme 76).[203] As in the previous cases, the use of the pseudoenantiomeric natural quinidine leads to the formation of the enantiomer of the product obtained in the reaction with quinine and

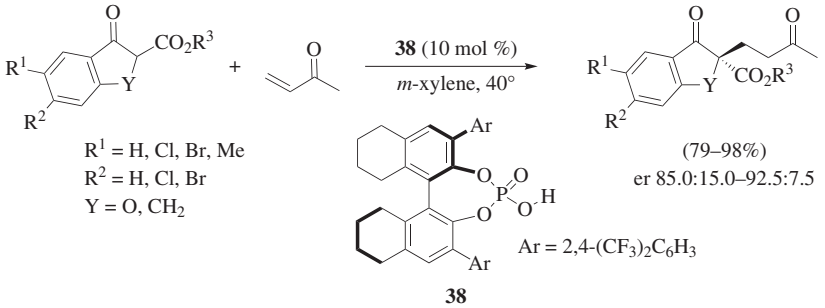
with comparable levels of stereocontrol.[203] Control experiments clearly demonstrate that the presence of the free hydroxy group on the catalyst is also essential for reactivity and stereoselectivity, which suggests the participation of quinine as an acid–base bifunctional catalyst in which the Brønsted basic quinuclidine moiety engages in activation of the Michael donor whereas the secondary alcohol activates the maleimide by H-bonding interactions.




**37**

**Scheme 76**

Finally, chiral Brønsted acids such as phosphoric acid **38**, prepared from BINOL, have also been utilized in this transformation. The composition of this type of catalyst involves a strongly acidic phosphoric acid moiety that is involved in the activation of the Michael acceptor through the formation of an H-bond and the presence of an axially chiral backbone that also incorporates bulky substituents at the 3,3′-positions of the BINOL scaffold, which are the main features responsible for distinguishing the enantiotopic faces of the Michael acceptor. Scheme 77 illustrates the result of this type of catalyst in the Michael reaction of cyclic β-keto esters with methyl vinyl ketone.[204] This acidic catalyst can also participate in the reaction through a slightly different mechanism of activation that involves electrophile protonation leading to a tight ion-pair intermediate. Mechanistic studies in other reactions indicate that there is a thin line between H-bond formation and protonation in reactions using chiral



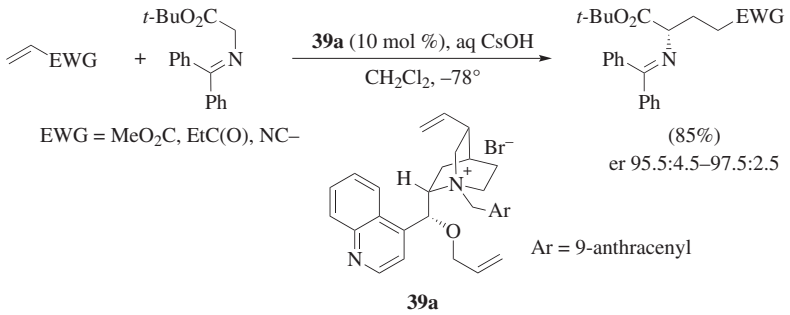

**38**

**Scheme 77**

phosphoric acids as catalysts and that subtle changes in the structure strongly influences the ratio between the H-bonded complex and ion-pairing.[205] However, no conclusive data has been provided for the particular Michael reaction presented in Scheme 77.

**Phase-Transfer Catalysis (PTC).** The formation of a chiral ion pair between an anionic nucleophile and a chiral cation (typically an ammonium or phosphonium salt) has been applied in catalytic, enantioselective Michael reactions under phase-transfer catalysis (PTC) conditions. PTC conditions are very convenient for this transformation because a wider range of Michael donors can be activated through deprotonation of the pronucleophile by an external base. Nevertheless, this mode of activation is not very general because the base employed for this purpose has to be strong enough to deprotonate the Michael donor but it must also be compatible with water. Thus, Michael donors that typically require strong bases such as metal amides for the generation of the corresponding enolates cannot be employed. For this reason, most of the reported examples focus on the use of *N*-protected α-amino esters (usually glycinate-benzophenone imines) as Michael donors, which feature an α-proton that is acidic enough to undergo deprotonation using bases such as aqueous metal hydroxides or carbonates. In addition, other active methylene compounds and nitroalkanes have been employed.

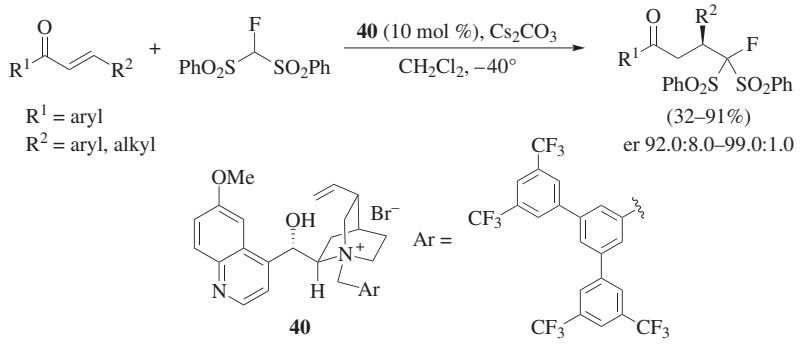
Quaternary ammonium salts based on *Cinchona* alkaloids, such as ammonium salt **39a**, are a common family of PTC catalysts useful for promoting Michael reactions. The quaternary quinuclidinium nitrogen engages in electrostatic interactions with the anionic nucleophile, and the organic scaffold around the nitrogen cation ensures the required lipophilicity to be soluble in organic solvents. These catalysts have been used in the conjugate addition of *tert*-butyl glycinate benzophenone imine to several Michael acceptors such as ethyl vinyl ketone, methyl acrylate, and acrylonitrile (Scheme 78).[94,206] *Cinchona*-based quaternary ammonium salts, for example catalyst **40**, also catalyze Michael reactions with enones using other acidic carbon pronucleophiles, as exemplified by fluorobis(phenylsulfonyl)methane (Scheme 79),[207] nitroalkanes,[208] or malonates,[209] among others. Moreover, the PTC



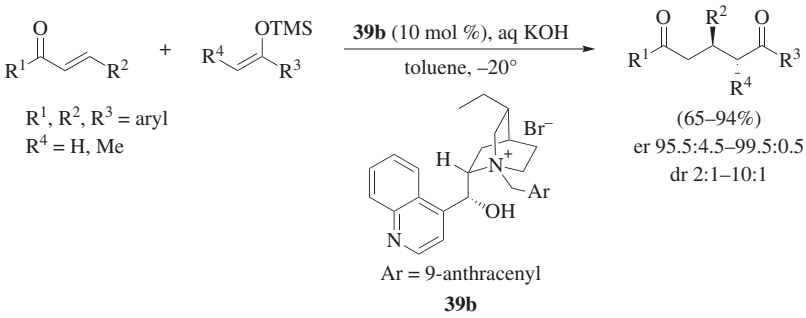

**39a**

**Scheme 78**

approach has also been used for promoting Mukaiyama–Michael-type reactions, which allow the use of carbonyl compounds of lower acidity as Michael donors. For example, ammonium salt **39b** catalyzes the conjugate addition of silyl enol ethers to chalcones leading to the Michael adducts in good to excellent yields and with very high enantioselectivities (Scheme 80).[210] Importantly, α-substituted silyl enol ethers are also reactive under the conditions employed, leading to the diastereoselective formation of conjugate addition products containing two contiguous stereocenters, which favor the formation of the *anti* adducts while maintaining the excellent efficiency observed in analogous reactions with α-unsubstituted silyl enol ethers.



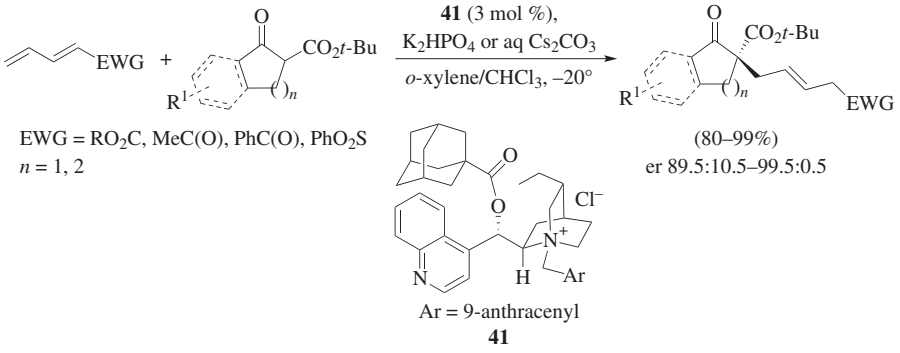

**Scheme 79**



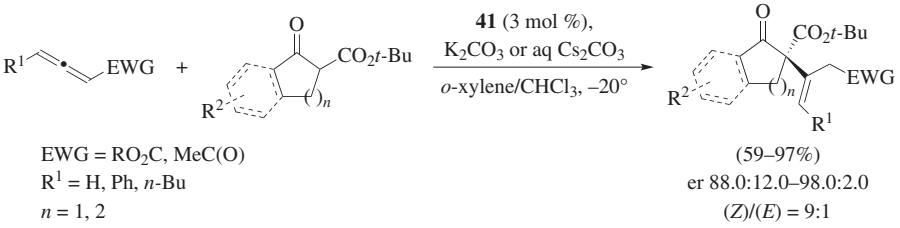

**Scheme 80**

These catalysts (for example ammonium salt **41**) have also been employed in the Michael reactions of β-keto esters and of *tert*-butyl glycinate benzophenone imine with α,β,γ,δ-unsaturated enones, esters, and sulfones, which lead to exclusive 1,6-addition rather than the usual 1,4-chemoselectivity (Scheme 81).[211] The reaction leads to the formation of β,γ-unsaturated products, which in

exceptional cases undergo isomerization to the more stable conjugated adducts. The reaction of allenic ketones and esters as Michael acceptors takes place at the β-position, also furnishing β,γ-unsaturated adducts and generating a quaternary stereocenter (Scheme 82).[212] Moreover, when γ-substituted allenes are employed, excellent diastereoselectivity is achieved with respect to the C=C double bond in the product, which favors the formation of the sterically less hindered (*E*) diastereoisomer.

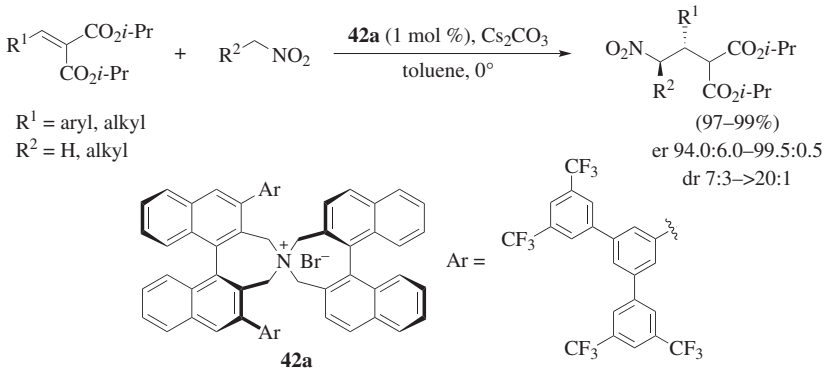



**Scheme 81**



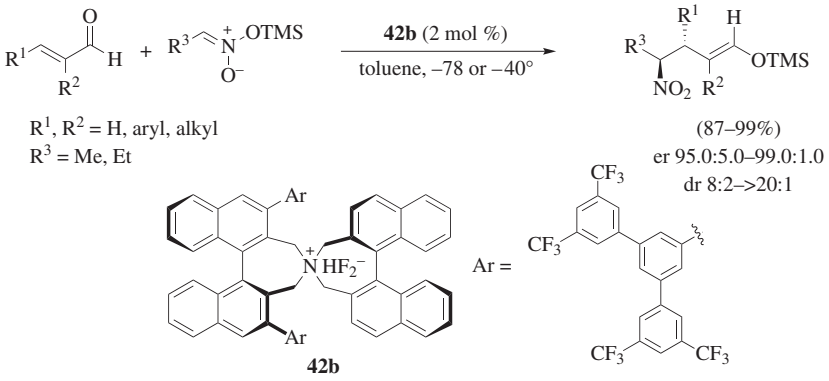

**Scheme 82**

Other chiral ammonium salts based on different architectures have also been developed and among them, quaternary ammonium salts derived from BINOL are particularly effective for catalyzing many Michael reactions using a variety of donor and acceptor substrates. For example, *N*-spiro ammonium bromide **42a** is an outstanding catalyst for the conjugate addition of nitroalkanes to alkylidenemalonates (Scheme 83),[213] and of cyclic β-keto esters to methyl vinyl ketone and acrolein.[214] In addition, this catalyst and other structurally related ones are employed for promoting the Michael reaction of β-keto esters with vinyl ketones,[214] of nitroalkanes with cyclohexenone,[215] and for the conjugate addition of malonates to chalcones,[216] in addition to other similar examples.



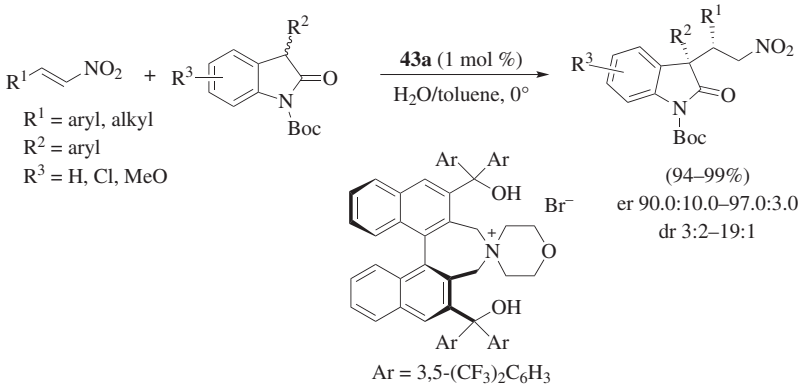

**Scheme 83**

These spiroammonium salts are also active in one remarkable case of a Mukaiyama–Michael reaction in which enals are used as Michael acceptors in the reaction with silyl nitronates in the presence of fluoride ammonium salt **42b** (Scheme 84).[217] In this reaction, the bifluoride $HF_2^-$ counterion is required for the in situ activation of the silyl nitronate. Under optimized reaction conditions, a variety of substituted nitronates and enals react with each other in a highly efficient manner and with excellent diastereoselectivities, therefore overcoming the limitations typically associated with the enantioselective nitro-Michael reaction under Lewis acid catalysis. Moreover, α,β-disubstituted enals also react successfully, forming products containing three contiguous stereocenters after acid hydrolysis, and typically providing excellent yields and stereoselectivities.



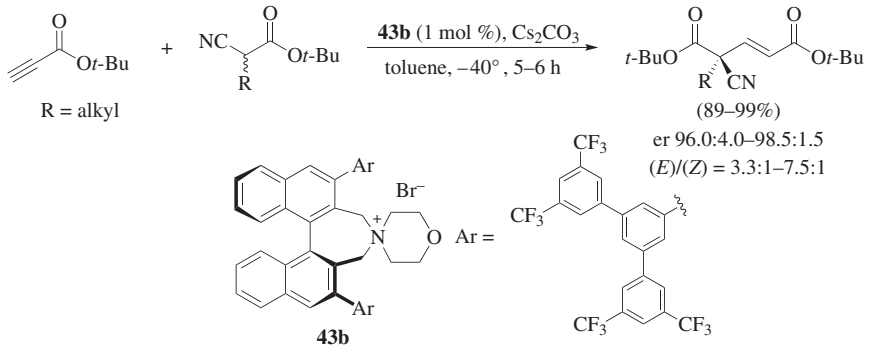

**Scheme 84**

Other related BINOL-based catalysts incorporating only a single binaphthylamine core have also been used in enantioselective Michael reactions. For example, ammonium salt **43a** is an excellent promoter for the Michael reaction of oxindoles with nitroalkenes (Scheme 85),[218] since the latter are a very challenging class of Michael acceptors to be used under PTC conditions owing to their high electrophilicity, which makes the uncatalyzed background reaction highly competitive. In this particular case, deuterium labeling experiments indicate that oxindoles undergo fast deprotonation in neutral aqueous media only in the presence of the catalyst, and in contrast they remain essentially unchanged when this catalyst is not present or when other quaternary ammonium salts are added. Under these conditions, the reaction of a variety of α-substituted oxindoles with a series of nitroolefins occurs smoothly in the presence of **43a**, furnishing the expected conjugate addition products in excellent yields and enantioselectivities. The diastereoselectivity of the reaction is highly dependent on the nature of the α-substituent of the oxindole donor and on the β-substituent of the nitroalkene acceptor. The reaction also tolerates substitution in the nitroalkene, allowing the use of both aromatic and aliphatic nitroalkenes with similar results. On the other hand, only α-aryl-substituted oxindoles can be used as Michael donors. Poor results are obtained with α-alkyl-substituted oxindoles, probably due to the lower acidity of these compounds. The related *N*-spiro ammonium salt **43b** catalyzes the Michael reaction of α-substituted cyanoacetates with acetylenic esters to provide the final adducts in almost quantitative yields and with excellent enantioselectivities (Scheme 86).[219] However, control of the alkene geometry is moderate, with (*E*)/(*Z*) ratios ranging from 3.3:1 to 7.5:1.



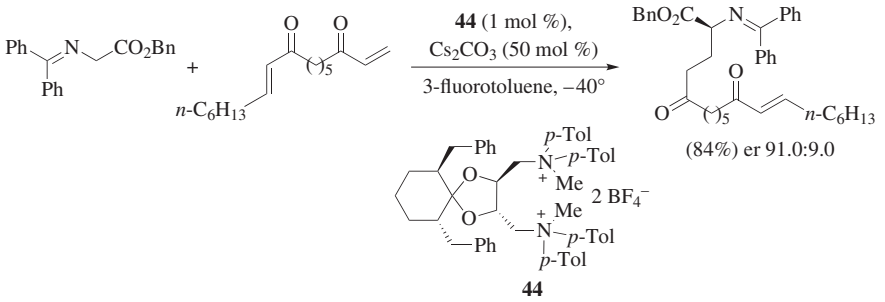

**43a**

**Scheme 85**



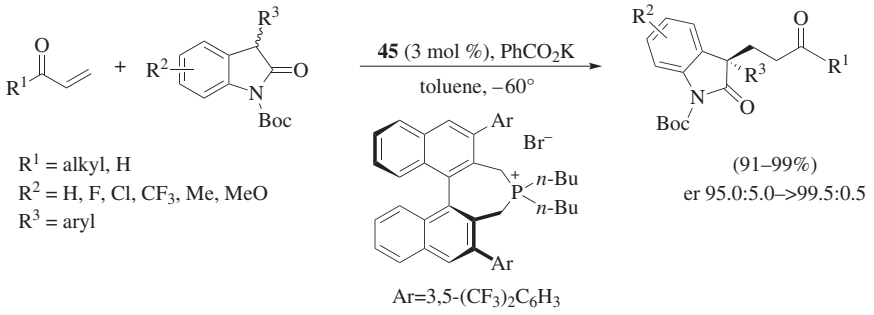

**Scheme 86**

Bis-ammonium salt **44** derived from TADDOL is another outstanding phase-transfer catalyst for Michael reactions. This compound is a good promoter of the Michael reaction of benzyl glycinate benzophenone imine with acrylates, and has also been applied to the total synthesis of the natural product, (+)-cylindrizine A, using a simple vinyl ketone as the Michael acceptor (Scheme 87).[220]



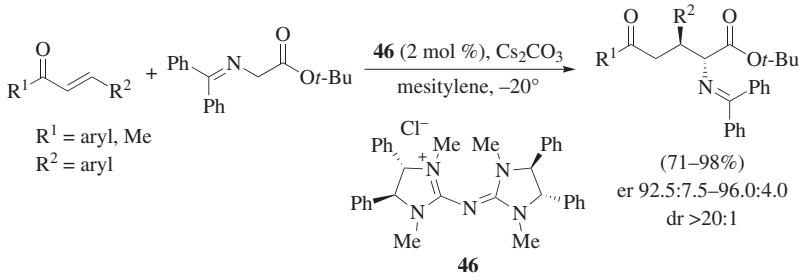

**Scheme 87**

Enantioselective Michael reactions under PTC conditions do not exclusively rely on the use of chiral ammonium salts as catalysts, since chiral phosphonium salts have also been employed successfully in this context. Binaphthyl-containing phosphonium salt **45** is an excellent catalyst for the Michael addition of oxindoles to enones (Scheme 88).[221] The high acidity of the 3-aryloxindoles as Michael donors permits the use of a very mild base such as potassium benzoate for the activation of the nucleophile. Moreover, chiral pentanidinium cation **46** is a novel architecture for building PTC catalysts, and is excellent in the Michael reaction between glycinate imines and acyclic enones (Scheme 89).[222] A novel feature of this type of catalyst is the fact that it contains a planar ammonium salt entity, in contrast to all previous examples in which a tetrahedral quaternary ammonium or phosphonium salt typically forms the basis of the catalyst structure.




**45**

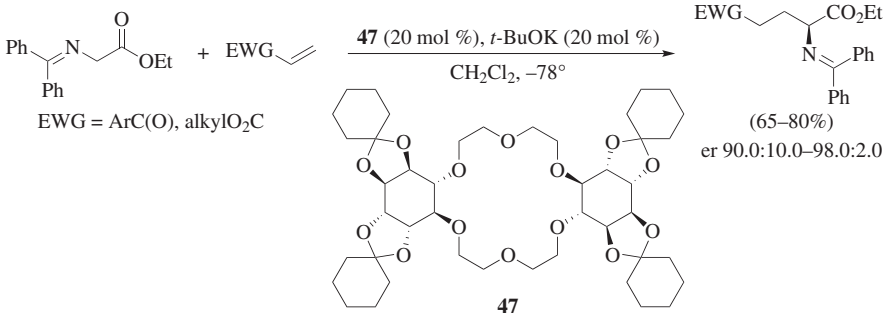
**Scheme 88**




**46**

**Scheme 89**

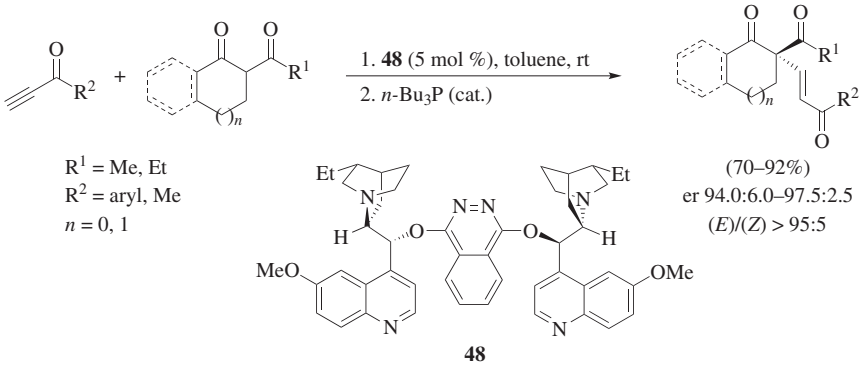
Chiral crown ethers are another class of compounds that have been employed to catalyze the Michael reaction under PTC conditions. Crown ethers can transfer cations between the organic/aqueous interface through complexation/decomplexation by the heteroatoms of the macrocycle. A representative example is shown in Scheme 90, in which crown ether **47** is used to catalyze the Michael reaction of glycine imines with vinyl ketones and alkyl acrylates in good yields and enantioselectivities.[223]




**47**

**Scheme 90**

**Brønsted Base Catalysis.** The use of chiral tertiary amines as Brønsted bases to catalyze the Michael reaction has not received as much attention as other organocatalytic methods. However, it should be pointed out that chiral Brønsted basic sites present in the structure of bifunctional catalysts have been extensively used as illustrated previously. Nevertheless, several examples exist in which simple tertiary amine bases are employed as monofunctional catalysts without the presence of other functionalities that engage in secondary interactions with the substrates. For example, dimeric *Cinchona* alkaloid based catalyst **48** is able to catalyze the Michael reaction of 2-alkyl-substituted 1,3-diketones with alkynones (Scheme 91).[224] This catalyst incorporates multiple Brønsted basic sites in its structure that can create a binding site for the substrate. The reaction proceeds with good enantioselectivity but provides the products as a mixture of (*E*) and (*Z*) isomers which have to be treated with a catalytic amount of *n*-$Bu_3P$ to promote in situ isomerization leading to the exclusive formation of the (*E*) diastereoisomer.




**Scheme 91**

## General Overview

From the examples presented in the preceding sections it can be concluded that the performance of each catalytic system developed to date for carrying out catalytic, enantioselective Michael reactions is strongly dependent on the structure of the substrates (Michael donor and acceptor). This outcome is a logical consequence of the wide structural variability of the reaction. Nevertheless, and for a given donor/acceptor combination, it is also true that the results are variable when the substitution pattern changes. For this reason, the first overall conclusion is that there is not yet a general catalytic system that allows the execution of this reaction in satisfactory yield and stereoselectivity, and that a careful selection of the catalyst has to be carried out depending on the substrates that are going to be employed in the Michael reaction.

Despite this, some general trends can be identified to guide the choice of the most efficient catalytic system: (1) in general, metal catalysis may be the method of choice for the Michael reaction between active methylene compounds (especially

malonates, 1,3-diketones, and β-keto esters) with α,β-unsaturated ketones, esters, and amides, (2) the general behavior of metal catalysts is that substitution at the β-position of the Michael acceptor does not appear to have a very profound influence on the reaction outcome, (3) organocatalytic methods are powerful and efficient for many of the cases where metal catalysis is difficult or impossible to apply; in particular, the iminium-activation approach is the best option for reactions involving the use of enals as Michael acceptors, and H-bonding catalysis is useful for the reactions involving nitroalkenes, α,β-unsaturated imides, and even enones, and (4) PTC is also particularly effective for reactions with enones and acrylic acid derivatives.

Regarding the Michael donor, the majority of the protocols, that is, organocatalytic or metal-mediated methods, involve the use of a C–H acidic pronucleophile such as an active methylene compound or a nitroalkane. For this reason, the use of other Michael donors that do not fulfill this requirement is a more challenging situation. Ketones and aldehydes can be employed efficiently as Michael donors by means of enamine activation but other Michael donors that contain a single activating group such as simple esters or amides require the Mukaiyama–Michael approach in which, with a few exceptions, metal catalysts are superior to organocatalysts.

Finally, and in terms of practical application and/or operational simplicity, it is clear that organocatalytic methods are generally easier to implement on the laboratory scale because of the compatibility of the catalysts and the reactive intermediates with air and/or moisture. Thus, solvents do not need to be dried before use and the reactions can also be carried out in open air and ambient atmosphere. On the other hand, organocatalytic reactions typically require longer reaction times and higher catalyst loadings than those usually found in the corresponding metal-catalyzed versions.

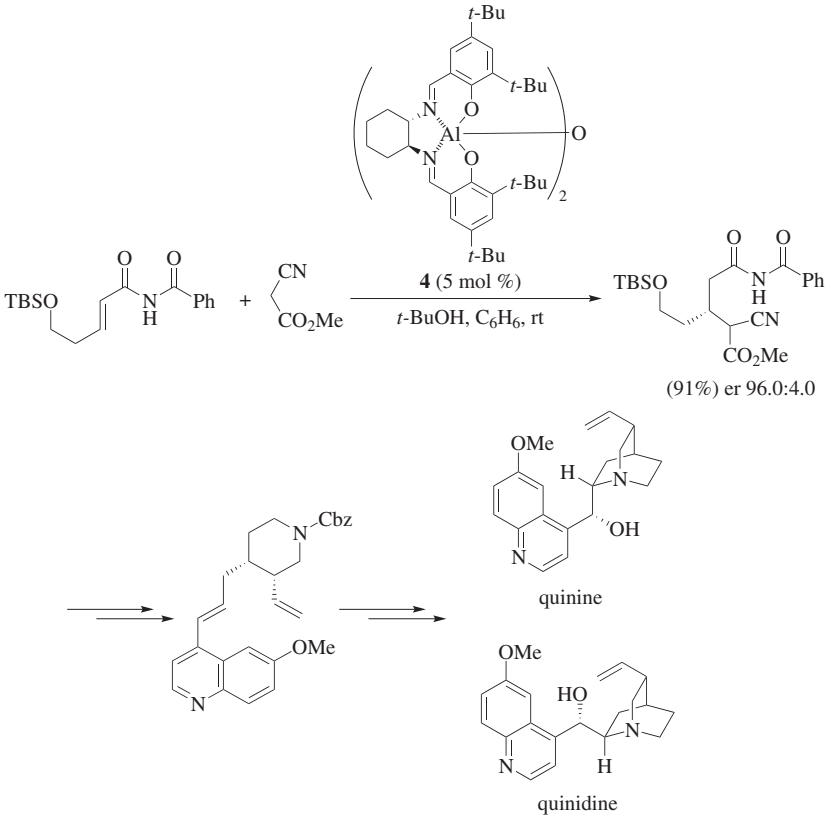
## APPLICATIONS TO SYNTHESIS

The following section contains selected examples in which catalytic, enantioselective Michael reactions are used as crucial steps in the stereoselective total synthesis of a natural product or an active pharmaceutical ingredient. Examples illustrating the behavior of the different catalysts have been selected according to their activation mode (metal catalysis or organocatalysis) and their mechanism of action.

### Quinine and Quinidine (Al/Salen Metal Catalysis)[225]

The catalytic, asymmetric total synthesis of quinine and quinidine using the Michael reaction as the key step is accomplished using salen-Al complex **4** as the chiral catalyst. Thus, the Michael addition of methyl cyanoacetate to an α,β-unsaturated acyclic imide that contains the required functionalization for the subsequent steps proceeds smoothly at room temperature to generate the Michael adduct in 91% yield in an excellent enantiocontrol (96.0:4.0 er). The subsequent steps include reduction of the cyanide group by hydrogenation, which proceeds together with cyclization to the δ-lactam, *trans* to *cis* isomerization, vinyl-substituent generation, and finally

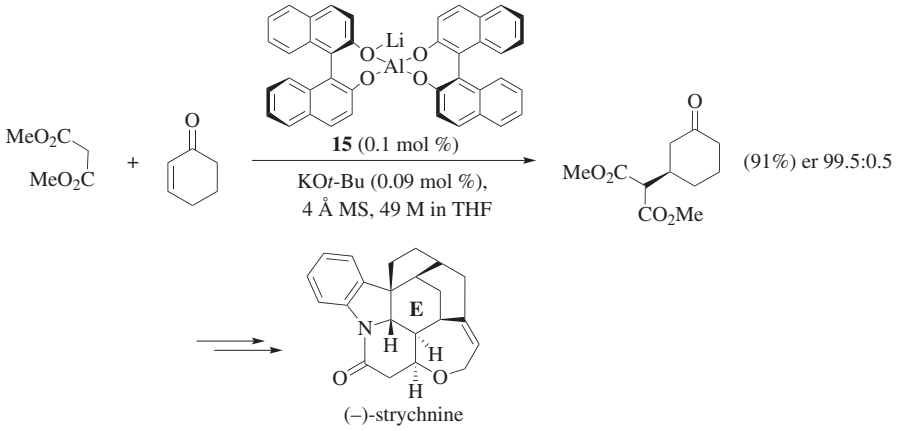
Suzuki cross-coupling to generate a common intermediate for the synthesis of both quinine and quinidine (Scheme 92). For the synthesis of both natural products, an indirect epoxidation is effected through Sharpless dihydroxylation/epoxide ring formation, and final cyclization in a diastereodivergent manner is accomplished using AD-mix-α and AD-mix-β, respectively, during the *syn* diol synthesis.




**Scheme 92**

## Strychnine (La/Al Binuclear Metal Catalysis)[226]

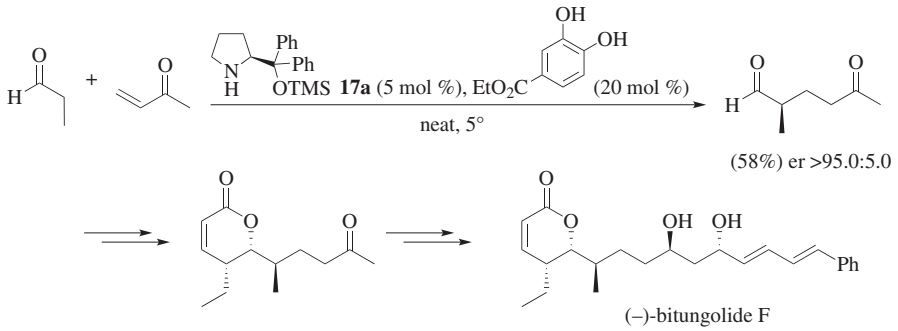
The catalytic asymmetric Michael reaction using a heterobimetallic catalyst provides access to a key synthetic intermediate in kilogram quantities for the synthesis of strychnine. The synthesis begins with the catalytic Michael reaction of dimethyl malonate with cyclohexenone and uses only 0.1 mol % of (*R*)-AlLibis(binaphthoxide) (**15**) under almost neat conditions (Scheme 93). In this step the first stereocenter at C15 in the **E** ring is created, which is able to control the stereochemical course of all the subsequent steps. Nevertheless, the synthesis of this alkaloid still needed more than 30 chemical steps to complete.




**Scheme 93**

## (–)-Bitungolide F (Enamine Catalysis)[227]

Bitungolides, polyketides isolated from the Indonesian sponge *Theonella cf. swinhoei* that incorporate a dihydropyranone, an *anti* 1,3-diol, and a diene, are natural products that exhibit cytotoxic effects, therefore making them attractive targets for both synthetic and medicinal chemists. The synthesis of (–)-bitungolide F is achieved using an approach in which a catalytic enantioselective Michael reaction is used as the key step (Scheme 94). The Michael reaction between propanal and methyl vinyl ketone using enamine catalysis allows the construction of an enantiomerically enriched keto aldehyde, which represents a key synthetic intermediate. The reaction is carried out under neat conditions at 5° in the presence of 5 mol % of diphenylprolinol derivative **17a** with a catechol derivative as co-catalyst, and results in the formation of (*R*)-5-keto-2-methylhexanal in moderate yield but >95.0:5.0 er. This compound is then elaborated through organoboron-mediated addition to the aldehyde, reduction,

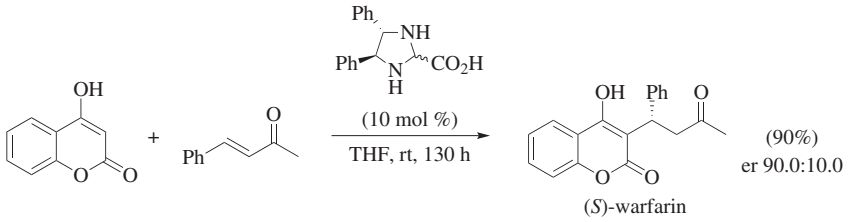



**Scheme 94**

esterification, and ring-closing metathesis to complete the key dihydropyranone intermediate. The synthesis of (–)-bitungolide F is accomplished after a final boron-mediated aldol reaction and reduction in 11.4% overall yield.

## Warfarin (Iminium Catalysis)[172]

Warfarin (also known as coumadin) is one of the most widely used anticoagulants. For more than 40 years it has been prescribed as a racemate although nowadays it is well known that the anticoagulant activity of the (*S*)-enantiomer is about 5–8 times higher than that of the (*R*) enantiomer. The synthesis of (*S*)-warfarin is accomplished using iminium ion activation of benzylideneacetone with 10 mol % of an imidazolidine catalyst (Scheme 95). The reaction takes place in THF at room temperature in 130 hours and affords (*S*)-warfarin directly (er 90.0:10.0). Alternatively, the synthesis of (*R*)-warfarin is realized simply by changing the absolute configuration of the catalyst. Importantly, both enantiomers can be enriched up to >99.95:0.05 er by simple recrystallization from acetone/water. The method succeeds on a kilogram scale without any decrease in yield or enantioselectivity. Recycling of the catalyst is also possible, thereby making this an attractive protocol.

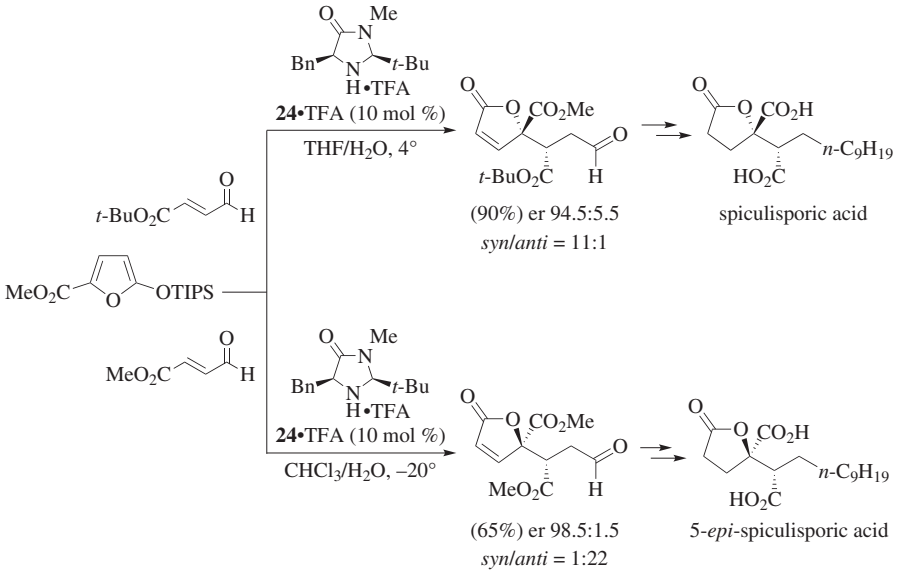



**Scheme 95**

## Spiculisporic Acid (Mukaiyama–Michael Reaction under Iminium Catalysis)[169]

The naturally occurring spiculisporic acid, a product obtained by fermentation from *Penicillium spiculisporum*, is a dicarboxylic acid that has found commercial application as a biosurfactant in several industrial processes. The enantioselective conjugate addition of a silyloxyfuran derivative to an α,β-unsaturated aldehyde under iminium ion activation is carried out using imidazolidinone catalyst **24** with TFA as cocatalyst to give the desired butenolide as a single constitutional isomer in 90% yield and with high levels of diastereo- and enantioselectivity (Scheme 96). Elaboration of the butenolide to the desired spiculisporic acid is accomplished in 54% yield using a three-step procedure which includes a $CrCl_2$•DMF mediated olefination, Pd/C catalyzed hydrogenation, and hydrolysis under basic conditions. The method also

allows the preparation of the 5-*epi*-spiculisporic acid following the same synthetic route but using a less congested aldehyde for carrying out the Mukaiyama–Michael addition (Scheme 96). In this case, the *anti* diastereoisomer is the major product. This butenolide is not readily available via fermentation or derivatization of the naturally occurring metabolite, thereby making its synthesis an important accomplishment.

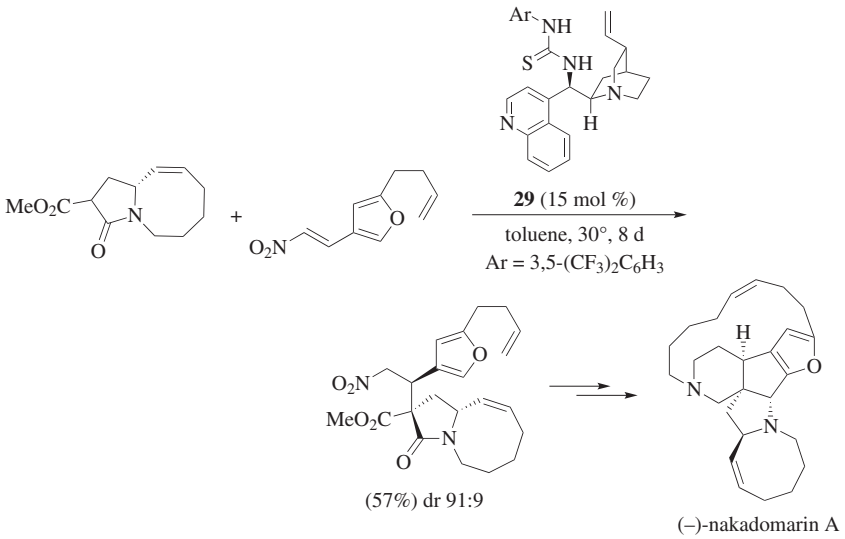



**Scheme 96**

## (–)-Nakadomarin A (H-Bonding Catalysis)[228,229]

The marine alkaloid of the manzamine family (–)-nakadomarin A, which exhibits cytotoxic and antimicrobial activity, is a natural product isolated from the sponge *Amphimedon sp.* in the waters off Kerama Island. Extraction from nature or total synthesis by previous methods only delivers milligram quantities. This synthesis requires the preparation of both the Michael donor (an amido ester) and acceptor (a nitroalkene) which are obtained in six and four steps, respectively, starting from readily available materials. The subsequent Michael reaction using 15 mol % of bifunctional thiourea **29** proceeds smoothly in 57% yield and with a very good stereocontrol (Scheme 97). The synthesis is then completed using a five-step sequence that includes: (1) a highly diastereoselective three-component nitro-Mannich/lactamization cascade reaction, (2) nitro group elimination, (3) a challenging highly chemoselective reduction of the carbonyl group of the γ-lactam,

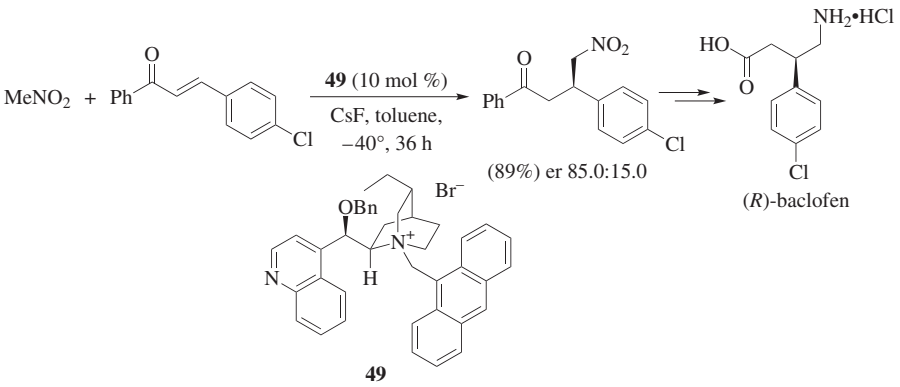
(4) partial reduction of the δ-lactam, and (5) a (*Z*)-selective olefin metathesis reaction.




**Scheme 97**

## Baclofen (Phase-Transfer Catalysis)[208]

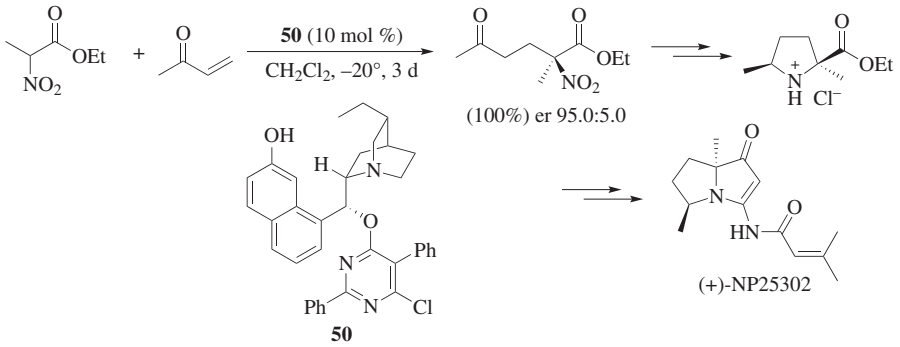
Racemic baclofen, a therapeutically useful GABA receptor agonist, is commonly employed to treat spasms caused by spinal-cord injury or disease, although it has been demonstrated that the (*R*) enantiomer is the active isomer. As a consequence, many studies directed to the asymmetric synthesis of (*R*)-baclofen have been reported. Described below is a catalytic route to form the desired γ-amino acid via the corresponding γ-lactam using an enantioselective Michael addition of nitromethane to 4-chlorobenzylidineacetophenone under PTC conditions. The cinchoninium salt **49** (10 mol %) was employed as the catalyst and cesium fluoride as the base in toluene at –40° for 36 hours to furnish the γ-nitro ketone in 89% yield with 85.0:15.0 er (Scheme 98). The (*R*) enantiomer can be easily enantioenriched up to 97.5:2.5 er by a simple recrystallization from EtOAc/hexane with good recovery. The remainder of the synthesis is achieved by a well-known reaction sequence involving a Baeyer–Villiger oxidation, reduction, and hydrolysis, to obtain the target compound as the hydrochloride. The enantiomer, (*S*)-baclofen, is easily obtained by simply using the related cinchonidium-based catalyst.




**Scheme 98**

## NP25302 (Brønsted Base Catalysis)[230]

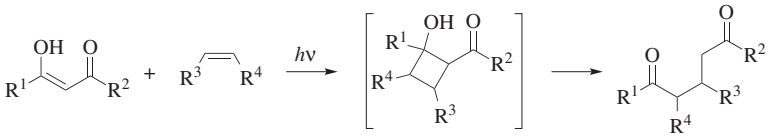
NP25302 is a natural product that contains a vinylogous urea functionality and exhibits several interesting pharmaceutical activities. The catalytic asymmetric synthesis of this natural product is accomplished using the Brønsted basic catalyst **50**, which allows the preparation of the enantioenriched Michael adduct containing all the necessary functional groups and substituents. Addition of ethyl nitropropionate to methyl vinyl ketone in the presence of 10 mol % of catalyst **50** using $CH_2Cl_2$ as solvent at –20° affords the Michael adduct in quantitative yield and with 95.0:5.0 er (Scheme 99). This acyclic intermediate is then converted into a *trans*-2,5-dimethylproline ethyl ester through a sequence of standard transformations. The completion of the synthesis involves a 5-step sequence that includes cyanamide formation, Claisen reaction, cyclization, and amide formation followed by hydrolysis/decarboxylation.



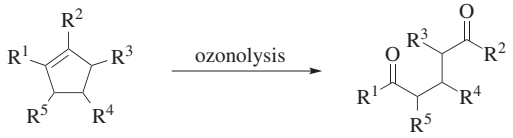

**Scheme 99**

## COMPARISON WITH OTHER METHODS

The possible approaches to the 1,5-dicarbonyl scaffold through methods other than the Michael reaction are scarce and very limited in scope, especially if the target compound is to be obtained as an enantioenriched material. The de Mayo reaction, which comprises the [2 + 2] photocycloaddition of alkenes with enols derived from 1,3-dicarbonyl compounds, followed by ring-opening of the resulting cyclobutanol through retro-aldol reaction may be a possibility (Scheme 100).[231–234] However, to date no catalytic enantioselective version of this transformation is known. Another possibility to accessing 1,5-dicarbonyls is by ozonolysis of cyclopentenes (Scheme 101)[232] but, in this case, the starting material must already be enantiopure and therefore the transformation itself does not involve the stereocontrolled generation of new stereogenic centers.

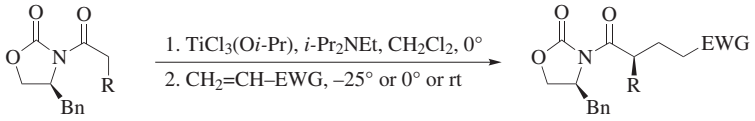


**Scheme 100**



**Scheme 101**

An alternative approach to catalytic, enantioselective Michael reaction relies on the use of chiral auxiliaries for stereocontrol. In this sense, most common methods typically incorporate the chiral auxiliary bound to the Michael donor rather than to the acceptor, perhaps because in this way the stereodirecting element is located closer to the point in which the new stereogenic center is formed. Among the different reports, the privileged Evans oxazolidinones are excellent in the conjugate addition of amide enolates to a variety of Michael acceptors, such as acrylonitrile, acrylates, and vinyl ketones (Scheme 102)[235], although the use of β-substituted electrophiles leads to poor diastereoselection.

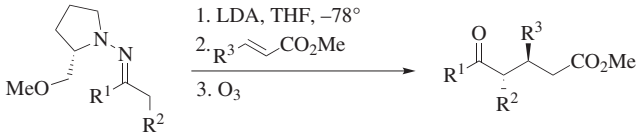


R = alkyl
EWG = EtC(O), NC–, $MeO_2C$

(70–93%)
dr 19:1–>20:1

**Scheme 102**

The Evans auxiliary tends to be most applicable to carboxylic acid derivatives as Michael donors. In contrast, SAMP/RAMP hydrazines have been employed for ketones and aldehydes. The reactions of hydrazones derived from enolizable aldehydes or ketones with α,β-unsaturated esters proceed with moderate yields but high diastereo- and enantioselectivities after cleavage of the auxiliary by ozonolysis (Scheme 103).[236,237] These hydrazones have also been used with other Michael acceptors such as alkenylsulfones[238] or vinylphosphonates.[239]

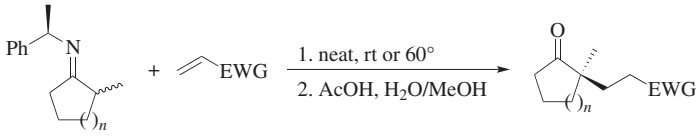



$R^1$ = H, alkyl
$R^2$ = H, alkyl
$R^3$ = alkyl, aryl

(38–62%)
er 96.0:4.0–>99.5:0.5
dr 95:5–>95:5

**Scheme 103**

As an alternative approach, ketones may be used as Michael donors through their conversion to the corresponding imines derived from α-methylbenzylamine, which undergo Michael reaction with a variety of acrylates and related Michael acceptors. These procedures take place with satisfactory results and in all these processes the chiral auxiliary is much more easily cleaved by simple hydrolysis (Scheme 104).[21,240] The imine pronucleophile does not need to be deprotonated by metalation as it is able to react with the electrophile directly at room temperature or upon heating via the corresponding enamine tautomer. Remarkably, this reaction allows the formation of quaternary stereocenters if an α,α-disubstituted ketone is employed as Michael donor, which is used directly as a racemic starting material and is particularly effective for 2-substituted cyclic ketones.

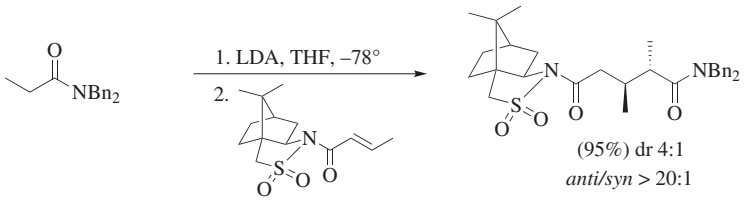



*n* = 1, 2
EWG = COMe, $CO_2Me$

(79–88%)
er 95.0:5.0–95.5:4.5

**Scheme 104**

Strategies involving the incorporation of the chiral auxiliary in the Michael acceptor are much less developed due to the fact that these processes are generally less efficient, making this strategy far less general. One example showing the use of a chiral Michael acceptor incorporating the Oppolzer sultam is shown in Scheme 105.[241] Examples illustrating the use of other chiral auxiliaries have also been described.[242–246]




**Scheme 105**

In general, covalently linked chiral auxiliaries used in stoichiometric amounts provide high stereoselectivities in a reliable way and with a broad substrate tolerance. However, the methods based on the use of catalytic amounts of the chiral agent are clearly preferable, especially in the case of large-scale preparations. Chiral auxiliary controlled asymmetric reactions can generally be scaled up more easily and are not as sensitive as catalytic asymmetric processes to minor perturbations such as impurities present in starting materials, solvents, and reagents. Moreover, if the reaction is not highly stereoselective, the diastereoisomeric byproducts are more easily separated from the product mixture. Nevertheless, the chiral auxiliary-based approach possesses important drawbacks compared to catalytic processes. First, it requires two additional steps for attaching the chiral auxiliary to the starting material and for its removal from the final product. Second, the requirement for stoichiometric amounts of the chiral agent cannot compete with the low amount of chiral agent required in the catalytic asymmetric transformations, although in some cases this problem can be circumvented by developing effective protocols for recovering and recycling the chiral auxiliary. The cost and availability of a given catalyst or chiral auxiliary that might mediate a similar reaction must also be evaluated on a case-by-case basis.

## EXPERIMENTAL CONDITIONS

In general, enantioselective Michael reactions carried out under metal catalysis require the use of an inert atmosphere and dry solvents. On the contrary, organocatalytic reactions are generally performed using reagent grade solvents that do not need to be previously dried, and the transformation is carried out under an open air atmosphere. In the following sections, arranged by the mechanism of catalytic activation, key representative methodologies are described including general comments on the preferred catalysts, solvents, and reaction conditions involved in each case.

**Metal-Catalyzed Direct Michael Reaction.** Typical conditions involve stirring the Michael acceptor with a slight excess of the Michael donor (normally an active methylene compound) in the presence of 0.1–5 mol % of the catalyst for the time required to reach completion. Usually the metal complex used as catalyst has been prepared previously and is directly incorporated into the reaction mixture, but in some cases it is formed in situ by mixing the metal salt precursor with the chiral ligand and stirring for a short period of time before adding the rest of the reagents. When the reaction is complete, isolation of the final adduct is normally achieved simply by removal of the volatiles followed by flash column chromatography.

**Metal-Catalyzed Mukaiyama–Michael Reaction.** The preferred conditions involve stirring the Michael acceptor with a slight excess of the silyl enol ether in the presence of the catalyst between 0° and –20°. The metal catalyst is used either as a pure isolated complex[56] or generated in situ, as with copper-bisoxazoline complex **16**, which is formed from the corresponding chloride by treatment with silver hexafluoroantimonate.[55] In addition, triphenylphosphine oxide or hexafluoroisopropanol, respectively, are required as silyl cation scavengers. Upon completion, the reaction mixture is subjected to standard aqueous work-up, and the isolation and purification of the Michael adducts is carried out by flash column chromatography.

**Michael Reaction under Enamine Activation.** Secondary amines derived from proline (*O*-TMS diarylprolinols like **17a** or **17b** are privileged structures) are the catalysts of choice for reactions using α-unbranched aldehydes as Michael donors, and chiral primary amines (typically derived from *trans*-cyclohexanediamine or from *Cinchona* alkaloids) are used as catalysts when ketones or α-branched aldehydes are employed. The usual catalyst loading is in the range of 10–20 mol %, although there are exceptions in which catalysts that are active under 0.1–1 mol % loading have been employed.[130] Typically, for those cases in which high catalyst loadings are required, a large excess of the aldehyde or ketone donor is also used in order to accelerate the reaction and/or improve conversion. The solvent employed varies largely with the nature of the Michael acceptor and usually reactions are carried out at room temperature. However, when prostereogenic Michael donors and acceptors are used concomitantly, slightly lower temperatures (–20° or 0°) must be used in order to optimize diastereoselection in the formation of the two consecutive stereogenic centers. The usual work-up typically involves removal of the volatiles, and purification of the final compound is carried out by flash column chromatography.

**Michael Reaction under Iminium Activation.** The same type of secondary amine catalysts that activates aldehydes and ketones under the enamine manifold are also particularly effective in promoting reactions between active methylene compounds or nitroalkanes with α,β-unsaturated aldehydes or ketones. Alternatively, imidazolidinone **24** is the catalyst of choice for the Mukaiyama–Michael reaction between silyl enol ethers and enals.[169,170] All of these reactions typically require rather large catalyst loadings (10–20 mol %) and the presence of a Brønsted acid co-catalyst. The most common reaction conditions also involve a slight excess of the Michael donor in order to improve conversion. The choice of solvent depends on the nature of the Michael donor.

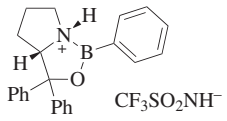
**Michael Reaction under H-bonding Activation.** For the conjugate addition of active methylene compounds to almost all kinds of α,β-unsaturated carboxylic acid derivatives or other related electron-poor olefins, bifunctional catalysts incorporating both a tertiary amine as the Brønsted basic site, and a thiourea or squaramide as the H-donor moiety are employed. Catalysts are normally synthesized from *trans*-cyclohexanediamine, from a *Cinchona* alkaloid, or from a BINOL-based scaffold.

Catalyst loadings are typically between 1–10 mol %, and solvents that do not interfere with the required formation of an H-bonded network between catalyst and substrates have to be employed, typically $CH_2Cl_2$ or aromatic hydrocarbons. Reactions usually involve the direct mixing of equimolar amounts of the Michael donor and the acceptor with the catalyst in the corresponding solvent at a variable temperature, this latter parameter being dependent upon the structure of the reagents. Work-up is usually carried out by simple evaporation of the solvents, followed by flash column chromatography to isolate and purify the Michael adduct.

**Michael Reaction under Phase-Transfer Catalysis.** The experimental setup typically involves stirring of the Michael acceptor and the Michael donor in the presence of 1–3 mol % of the catalyst in a biphasic mixture formed by an aromatic hydrocarbon or a halogenated solvent and an aqueous solution of the required inorganic base (typically a carbonate or KOH). The reaction can also be carried out in a solid/liquid biphasic mixture formed by the organic solvent and the solid inorganic base. Catalysts are usually quaternary ammonium salts, very often quaternized derivatives of *Cinchona* alkaloids or more complex scaffolds based on BINOL, although phosphonium salts such as **45** have also performed well.[221] The temperature of the reaction is very often kept below 0°. Work-up is usually carried out by dilution with water followed by extraction, removal of the solvent, and flash column chromatography purification.

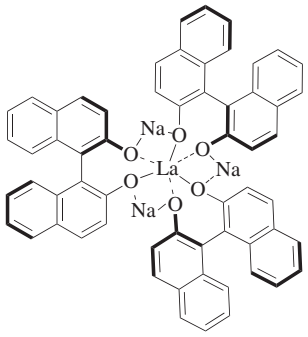
## EXPERIMENTAL PROCEDURES

### Preparation of Selected Ligands and Catalysts

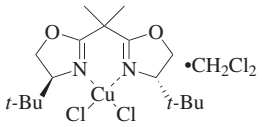



**(3a*S*,7*S*)-3,3-Diphenyl-1-(*p*-tolyl)hexahydro-1*H*-pyrrolo[1,2-*c*][1,3,2]oxazaborol-7-ium Triflamide [Preparation of Corey's Oxazaborolidine Catalyst].[56]** A 100-mL, two-necked, round-bottomed flask equipped with a stir bar, a glass stopper, and a 50-mL pressure-equalizing addition funnel (containing a cotton plug and ∼10 g of 4 Å molecular sieves, functioning as a Soxhlet extractor), and fitted on top with a reflux condenser and a nitrogen inlet adaptor, was charged with (*S*)-(−)-α,α-diphenyl-2-pyrrolidinemethanol (10.25 mmol, 2.59 g, 3.0 equiv), tri-2-tolylboroxine (3.42 mmol, 1.21 g, 1.0 equiv), and 40 mL of toluene. The resulting solution was heated to reflux (bath temperature ∼145°). After 3 h, the reaction mixture was cooled to ∼60°, and the addition funnel and condenser were quickly replaced with a short-path distillation head. The mixture was concentrated

by distillation (air-cooling) to a volume of ~15 mL. This distillation protocol was repeated three times by recharging with 3 x 35 mL of toluene. The solution was then allowed to cool to rt, and the distillation head was quickly replaced with a vacuum adaptor. Concentration under vacuum (~0.1 mm Hg, 1 h) afforded the oxazaborolidine as a clear oil. To an aliquot of the oxazaborolidine (0.286 mmol, theoretical) in toluene (2.0 mL) at –25° was added dropwise 2.0 mL of a freshly prepared 0.10 M solution of trifluoromethanesulfonamide in toluene (0.20 mmol). After 20 min at –20°, a colorless homogeneous solution of the title compound was obtained.

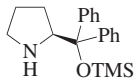



**LSB Complex [Preparation of Shibasaki's Binuclear Lanthanide/Alkaline Metal/BINOL Catalyst].[50]** To a stirred solution of (*R*)-BINOL (3.0 mmol, 859 mg, 3.0 equiv) in THF (11.3 mL) was added a solution of La(O*i*-Pr)$_3$ (1.0 mmol, 316 mg, 1.0 equiv) in THF (5 mL) at 0°. After stirring for 0.5 h at rt, a solution of NaO*t*-Bu (3.0 mmol, 288 mg, 3 equiv) in THF (3.8 mL) was added at 0°. The clear colorless solution thus obtained was directly used as a catalyst (0.05 M).

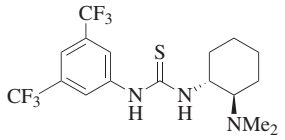



**(4*S*,4′*S*)-2,2′-(Propane-2,2-diyl)-bis(4-*tert*-butyl-4,5-dihydrooxazole)copper (II) Chloride • $CH_2Cl_2$ [Preparation of the Cu(II)/(*S*,*S*)-*t*-Bu-box Complex].[55]** A round-bottomed flask equipped with a magnetic stirrer was charged with 2,2-bis-(2-[4(*S*)-*tert*-butyl-1,3-oxazolinyl])propane ((*S*,*S*)-*t*-Bu-box, 5.0 mmol, 1.472 g, 1.0 equiv) and $CuCl_2$ (5.0 mmol, 0.672 g, 1.0 equiv). Methylene chloride (20 mL) was added via syringe, and the reaction mixture was stirred for 3.5 h, until the $CuCl_2$ had solubilized. The green solution was transfered under nitrogen into a Schlenk flask via cannula through a syringe fitted with a 0.45 μ filter. The solvent was removed under vacuum to deliver the title compound (4.6 mmol, 2.52 g, 99%) as a light-green

powder: mp >180°; $[\alpha]_D$ – 251 (*c* 1.06, $CH_2Cl_2$); IR (film) 2968, 1655, 1484, 1371, 1239, 1135, 947 $cm^{-1}$. Anal. Calcd for $C_{18}H_{32}Cl_4CuN_2O_2$: C, 42.08; H, 6.28; N, 5.45. Found: C, 42.21; H, 6.24; N, 5.51.

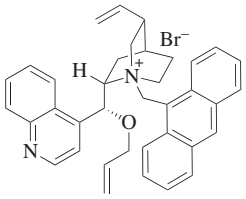



**(*S*)-2-[Diphenyl(trimethylsilyloxy)methyl]pyrrolidine (*O*-TMS Diphenylprolinol) [Preparation of the Jørgensen-Hayashi Catalyst].[247]** Trimethylsilyl trifluoromethanesulfonate (TMSOTf) (10 mmol, 1.81 mL, 1.3 equiv) was added at 0° to a solution of (*S*)-diphenyl(pyrrolidin-2-yl)methanol (7.6 mmol, 1.92 g, 1.0 equiv) and $NEt_3$ (10 mmol, 1.39 mL, 1.3 equiv) in $CH_2Cl_2$ (50 mL). The mixture was then allowed to reach ambient temperature and was stirred for 1 h until full conversion of the starting material was confirmed by TLC analysis. The reaction was quenched with water (50 mL). The product was extracted with $CH_2Cl_2$ (3 x 30 mL) and was dried over $Na_2SO_4$. After evaporation of the solvent the catalyst was isolated by flash column chromatography on silica gel (hexanes/EtOAc) to give the title compound (2.47 g, 7.6 mmol, >99%) as a white solid: $[\alpha]_D$ – 30.0 (*c* 1.0, $CH_2Cl_2$); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 7.36–7.30 (m, 10H), 4.86 (br s, 1H), 4.50 (t, *J* = 7.2 Hz, 1H), 3.10 (dt, *J* = 10.7, 6.7 Hz, 1H), 2.84 (dt, *J* = 10.7, 7.0 Hz, 1H), 2.05–1.99 (m, 1H), 1.96–1.82 (m, 2H), 1.58–1.51 (m, 1H), –0.01 (s, 9H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ 143.7, 143.7, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 82.4, 66.4, 47.1, 27.3, 24.6, 1.8.




**1-[3,5-bis(Trifluoromethyl)phenyl]-3-[(1*R*,2*R*)-2-(dimethylamino)cyclohexyl]thiourea [Preparation of Takemoto's Thiourea].[86]** Under an argon atmosphere, to a solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (2.23 mmol, 605 mg, 1.0 equiv) in dry THF (1.0 mL) was added (*R*,*R*)-*N*′,*N*′-dimethylcyclohexane-1,2-diamine (317 mg, 2.23 mmol, 1.0 equiv). The reaction mixture was stirred for 3 h, and was then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH/$NEt_3$, 100:5:1) to give the title compound (1.44 mmol, 597 mg, 65%) as a white amorphous solid: $[\alpha]_D$ – 32.7 (*c* 0.99, $CHCl_3$); IR ($CHCl_3$) 3402, 3200, 2942, 2865, 1528, 1469, 1383, 1278 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ 10.0 (s, 1H), 8.21 (s, 1H), 8.17 (s, 2H), 7.66 (s, 1H), 4.09 (br s, 1H), 2.54 (br s, 1H), 2.21 (s, 7H), 1.82 (br s, 1H), 1.74 (br s, 1H), 1.63 (br d, *J* = 11.0 Hz, 1H), 1.31–1.01 (m, 4H); $^{13}C$ NMR

(DMSO-$d_6$, 126 MHz) δ 178.6, 142.0, 130.8, 130.5, 130.3, 130.0, 126.5, 124.3, 122.2, 120.9, 120.0, 115.3, 65.0, 55.3, 45.7, 31.6, 24.6, 24.5, 21.0; MS–FAB$^+$ (*m*/*z*): $[M + H]^+$ 414 (100). Anal. Calcd for $C_{17}H_{21}F_6N_3S$: C, 49.39; H, 5.12; N, 10.16; F, 27.57. Found: C, 49.36; H, 5.28; N, 10.11; F, 27.71.

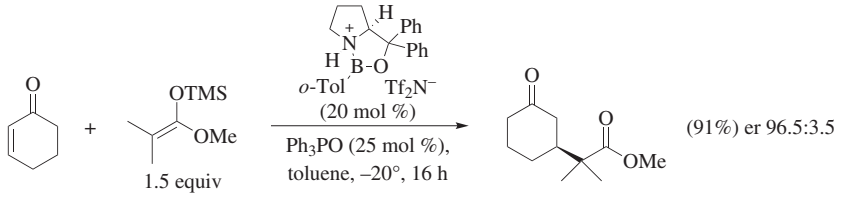



***O*-Allyl-*N*-(9-anthracenylmethyl)cinchonidium Bromide [Preparation of Corey's *Cinchona*-Based Ammonium Salt].[248]** To a suspension of cinchonidine (13.3 mmol, 3.91 g, 1.0 equiv) in toluene (40 mL) was added 9-(chloromethyl)anthracene (13.9 mmol, 3.15 g, 1.04 equiv), and the mixture was stirred at reflux for 2 h. The mixture was cooled to rt, poured into 200 mL of $Et_2O$, and filtered. The solids were collected to afford *N*-(9-anthracenylmethyl) cinchonidinium chloride (10.75 mmol, 5.59 g) as a light-yellow solid. Concentration of the mother liquor and crystallization from $CH_2Cl_2/Et_2O$ solvent mixture at –20° afforded additional product (2.13 mmol, 1.11 g) as a light-yellow solid (12.88 mmol, 6.70 g, 97% combined yield): mp 168° (dec.); $[\alpha]_D$ – 363 (*c* 0.81, $CHCl_3$); FTIR (film): 3500–2500, 1625, 1589, 1571, 1509, 1478, 1462, 1451, 1422, 1265, 1062 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 9.06 (d, *J* = 9.0 Hz, 1H), 8.85 (m, 2H), 8.71 (d, *J* = 9.0 Hz, 1H), 8.21 (d, *J* = 5.2 Hz, 1H), 8.02 (d, *J* = 4.4 Hz, 1H), 7.96 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 2.60 (m, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.38 (m, 1H), 7.24 (m, 4H), 7.20 (m, 2H), 6.83 (d, *J* = 13.5 Hz, 1H), 6.67 (d, *J* = 13.6 Hz, 1H), 5.42 (m, 1H), 5.25 (dd, *J* = 17.3, 1.0 Hz, 1H), 4.89 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.71 (m, 2H), 4.07 (br d, *J* = 12.9 Hz, 1H), 2.56 (dd, *J* = 12.8, 10.7 Hz, 1H), 2.40 (app. t, *J* = 11.1 Hz, 1H), 2.12 (br s, 1H), 1.80 (m, 2H), 1.68 (br s, 1H), 1.09 (m, 1H), 0.99 (m, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 149.4, 147.1, 145.7, 136.4, 133.2, 132.7, 131.1, 130.4, 130.2, 129.2, 128.6, 128.5, 128.3, 127.6, 127.4, 126.9, 126.3, 125.6, 124.9, 124.7, 124.2, 124.1, 120.1, 118.3, 117.7, 67.3, 67.0, 61.3, 54.8, 50.4, 38.5, 25.9, 168, 25.7; MS–FAB$^+$ (*m*/*z*): 485; HRMS–FAB$^+$ (*m*/*z*): $M^+$ calcd for $C_{34}H_{33}N_2O$, 485.2593; found, 485.2575.

To a suspension of *N*-(9-anthracenylmethyl)cinchonidinium chloride (9.50 mmol, 4.94 g, 1 equiv) in 40 mL of $CH_2Cl_2$ was added allyl bromide (28.9 mmol, 2.50 mL, 3.0 equiv) and 50% aqueous KOH (5 mL, 47 mmol, 4.9 equiv). The resulting mixture was stirred vigorously at rt for 4 h, during which time all of the solids dissolved. The mixture was diluted with 50 mL of water and was extracted with $CH_2Cl_2$ (3 x 50 mL). The combined organic extracts were dried over $Na_2SO_4$, filtered, and concentrated under vacuum. The product was dissolved in methanol, and $Et_2O$ was added dropwise at rt until the solution turned cloudy. Cooling to –20° precipitated the title compound (9.21 mmol, 5.56 g, 97%) as a light-orange solid: mp 194–196°; $[\alpha]_D$ – 320 (*c* 0.45,

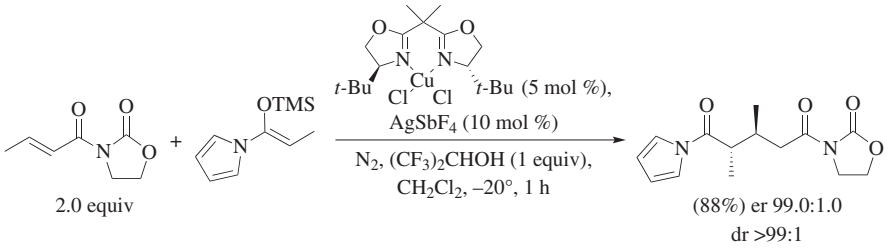
$CHCl_3$); FTIR (film) 3504, 3082, 2950, 2907, 2884, 1646, 1643, 1625, 1588, 1509, 1450, 1067, 996 $cm^{-1}$; $^1H$ NMR ($CD_3OD$, 400 MHz) δ 9.02 (d, $J = 4.6$ Hz, 1H), 8.89 (s, 1H), 8.76 (d, $J = 9.0$ Hz, 1H), 8.57 (m, 1H), 8.44 (d, $J = 9.0$ Hz, 1H), 8.25–8.19 (m, 3H), 7.95–7.92 (m, 3H), 7.79–7.77 (m, 2H), 7.65–7.61 (m, 2H), 6.95 (br s, 1H), 6.42–6.37 (m, 2H), 5.88 (d, $J = 13.9$ Hz, 1H), 5.64–5.60 (m, 2H), 5.54 (dd, $J = 10.5$, 1.2 Hz, 1H), 5.00 (d, $J = 13.5$ Hz, 1H), 4.96 (d, $J = 6.9$ Hz, 1H), 4.56–4.39 (m, 4H), 3.78 (m, 1H), 3.24 (app. t, $J = 12.2$ Hz, 1H), 2.90 (dt, $J = 10.8$, 5.9 Hz, 1H), 2.48 (m, 2H), 2.17 (m, 1H), 1.96 (d, $J = 2.9$ Hz, 1H), 1.60 (m, 2H); $^{13}C$ NMR ($CD_3OD$, 100 MHz) δ 151.1, 149.3, 143.0, 138.6, 134.8, 134.7, 134.6, 133.9, 133.9, 133.1, 133.0, 131.5, 131.3, 131.1, 130.5, 129.5, 129.2, 127.1, 126.6, 126.5, 125.7 (2C), 125.0 (2C), 121.9, 119.0, 117.9, 71.4, 69.9, 63.4, 57.4, 53.6, 49.9, 39.5, 27.3, 26.2, 23.4; MS–FAB$^+$ (*m*/*z*): 525; HRMS–FAB$^+$ (*m*/*z*): $M^+$ calcd for $C_{37}H_{37}N_2O$, 525.2906; found, 525.2930.

## Selected Experimental Procedures for Catalytic Enantioselective Michael Reactions

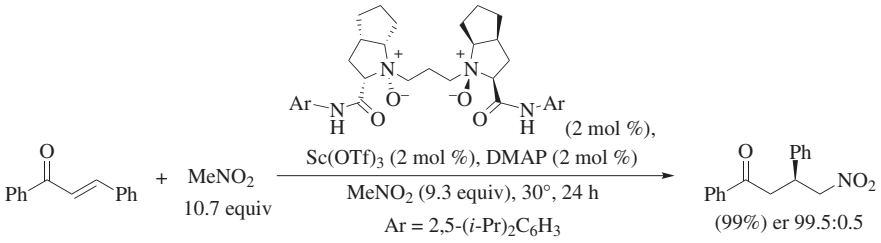



**(*S*)-(–)-2-Methyl-2-(3-oxocyclohexyl)propionic Acid, Methyl Ester [Oxazaborolidine-Catalyzed Mukaiyama–Michael Reaction].[56]** To a solution of freshly prepared (3a*S*,7*S*)-3,3-diphenyl-1-(*p*-tolyl)hexahydro-1*H*-pyrrolo[1,2-*c*][1,3,2]oxazaborol-7-ium triflamide (0.05 mmol, 25 mg, 20 mol %) in toluene (2 mL) were successively added a solution of triphenylphosphine oxide (0.0625 mmol, 17.4 mg, 25 mol %) in toluene (0.5 mL), 2-cyclohexen-1-one (0.25 mmol, 24.2 μL, 1 equiv), and 1-methoxy-2-methyl-1-(trimethylsilyloxy)propene (75.8 μL, 0.375 mmol, 1.5 equiv) at –20°. The reaction mixture was stirred at –20° for 16 h and then quenched by addition of 100 μL of $Et_3N$. The mixture was warmed to rt, and THF (5 mL) and aqueous 2 N HCl (1 mL) were added carefully. The resulting mixture was stirred at rt for 10 min and extracted with $CH_2Cl_2$ (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried ($Na_2SO_4$), and concentrated under vacuum. The residue was purified by flash column chromatography (hexanes/EtOAc) to afford the title compound (0.227 mmol, 45 mg, 91%, 96.5:3.5 er) as a colorless oil: $t_R$ (*S*) 11.6 min (major), $t_R$ (*R*) 9.8 min (minor) (Daicel Chiralpak-IA, hexanes/*i*-PrOH, 99:1, 1.0 mL/min, 290 nm); $[\alpha]_D^{25}$ – 20.0 (*c* 1.00, $CHCl_3$); IR (film) 2950, 1713, 1434, 1260, 1194, 1136 $cm^{-1}$; $^1H$ NMR ($CDCl_3$,

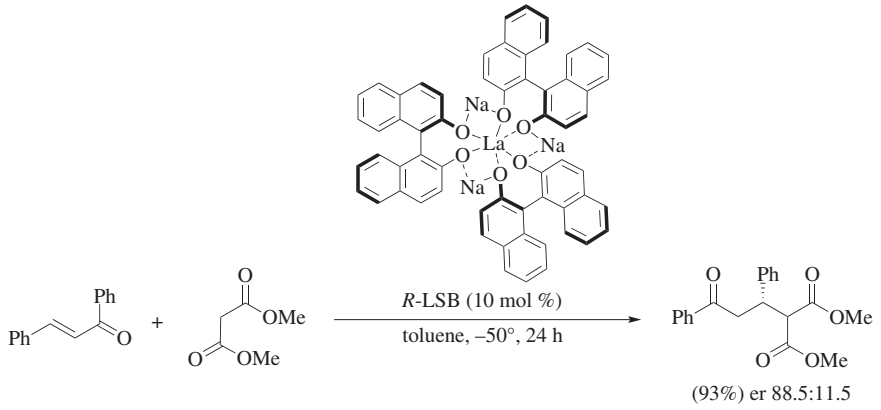
500 MHz) δ 3.63 (s, 3H), 2.37–1.96 (m, 6H), 1.77–1.70 (m, 1H), 1.59–1.50 (m, 1H), 1.38–1.30 (m, 1H), 1.13 (s, 3H), 1.11 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 211.1, 177.3, 51.8, 45.8, 45.2, 43.2, 41.1, 26.3, 25.0, 22.0, 21.7.




**(2*S*,3*S*)-2,3-Dimethyl-5-[2-oxo(1,3-oxazolidin-3-yl)]-1-pyrrolylpentane-1,5-dione [Cu(II)/Box-Catalyzed Mukaiyama–Michael Reaction].**[55] A dry 1-dram vial equipped with a magnetic stirrer was charged with (4*S*,4'*S*)-2,2'-(propane-2,2-diyl)bis-(4-*tert*-butyl-4,5-dihydrooxazole) copper(II) chloride complex (6.25 μmol, 3.2 mg, 0.05 equiv) and silver hexafluoroantimonate (12.5 μmol, 8.6 mg, 0.1 equiv) in an inert atmosphere ($N_2$) glove box. The flask was fitted with a septum, and brought out of the glove box, and $CH_2Cl_2$ (0.5 mL) was added by syringe. The mixture was stirred in the dark for 1 h resulting in a cloudy green mixture that was filtered through a plug of dry Celite directly into a flask containing (*E*)-3-(but-2-enoyl)oxazolidin-2-one (0.25 mmol, 52 μL, 2.0 equiv) in $CH_2Cl_2$ (0.2 mL) precooled to –20°. Neat hexafluoroisopropyl alcohol (0.125 mmol, 13 μL, 1.0 equiv) was added at this time. The resulting blue solution was then treated with (*Z*)-1-(1-trimethylsilyloxyprop-1-en-1-yl)-1*H*-pyrrole (0.125 mmol, 19.3 mg, 1.0 equiv). After 1 h, the reaction mixture was quenched with 2:1 (v/v) 3 M $NH_4OH$/sat. aq NaCl (1 mL). After warming to ambient temperature, the aqueous layer was extracted 3 times with EtOAc. The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated under vacuum. Flash chromatography on silica gel afforded the title compound (0.11 mmol, 30.4 mg, 88%, dr >99:1, 99.0:1.0 er): $R_f$ 0.10 (EtOAc/hexanes = 30/70); $t_R$ (*anti*-2*S*,3*S*) 30.1 min (major), $t_R$ (*anti*-2*R*,3*R*) 32.7 min (minor), $t_R$ (*syn*-isomers) 22.2 (major), 37.3 min (minor) (Daicel Chiralpak-AD, hexanes/*i*-PrOH (90:10), 1.0 mL/min, 254 nm); IR (neat) 1779, 1707 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.33 (br d, 2H), 6.30 (dd, $J$ = 2.4, 2.4 Hz, 2H), 4.40 (dd, $J$ = 8.0, 8.0 Hz, 2H), 4.00 (ddd, $J$ = 9.0, 8.0, 7.6 Hz, 2H), 3.22–3.16 (m, 1H), 3.16 (dd, $J$ = 17.0, 4.6 Hz, 1H), 2.82 (dd, $J$ = 17.0, 8.4 Hz, 1H), 2.63–2.53 (m, 1H), 1.28 (d, $J$ = 6.9 Hz, 3H), 1.06 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 173.6, 172.1, 153.4, 119.1, 113.2, 62.0, 42.5, 42.4, 37.9, 32.4, 18.4, 14.4; HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{14}H_{18}N_2O_4$, 301.1164; found: 301.1169. Anal. Calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52. Found: C, 60.70; H, 6.54.

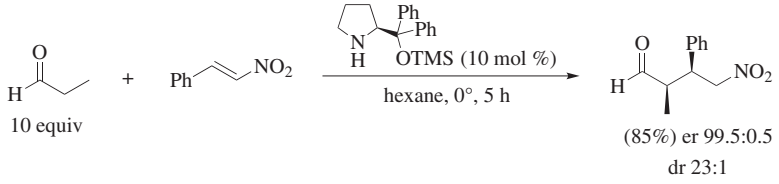



**(*S*)-4-Nitro-1,3-diphenylbutan-1-one. [Sc(III)/*N*,*N*-Dioxide Complex Catalyzed Michael Reaction].[105]** (1S,1′S,2S,2′S,3aS,3a′S,6aS,6a′S)-1,1′-(Propane-1,3-diyl)-bis [2-[(2,6-diisopropylphenyl)carbamoyl]octahydrocyclopenta[*b*]pyrrole-1-oxide]-Sc(III) triflate complex (0.2 mmol, 237.5 mg, 0.02 equiv) and some of the nitromethane (93 mmol, 5.0 mL, 9.3 equiv) were stirred in a test tube under nitrogen at 30° for 0.5 h. Chalcone (10 mmol, 2.08 g, 1.0 equiv) and DMAP (22 mg, 0.2 mmol, 0.02 equiv) were then added sequentially, followed by the remainder of the nitromethane (107 mmol, 5.75 mL, 10.7 eq, 20 equiv in total), and the mixture was stirred at 30° for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether 1:8 to 1:10) to afford the title compound (9.9 mmol, 2.67 g, 99%, 99.5:0.5 er) as a white solid: $t_R$ (*S*) 14.81 min (major), $t_R$ (*R*) 20.48 min (minor) (Daicel Chiralpak-ADH, hexanes/*i*-PrOH (90:10), 1.0 mL/min, 210 nm); $[\alpha]_D^{28}$ – 23.2 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48–7.44 (m, 2H), 7.38–7.16 (m, 5H), 4.86 (dd, *J* = 12.4, 8.0 Hz, 1H), 4.72 (dd, *J* = 12.4, 8.0 Hz, 1H), 4.26 (m, 1H), 3.32–3.54 (m, 2H).

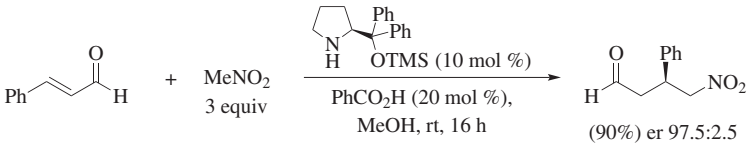



**(*S*)-Methyl 3,5-Diphenyl-2-methoxycarbonyl-5-oxopentanoate. [La/Na-BINOL Heterodinuclear Complex Catalyzed Michael Reaction].[50]** A THF solution of (*R*)-LSB (0.05 mmol, 1.0 mL, 0.05 M, 0.1 equiv) was concentrated

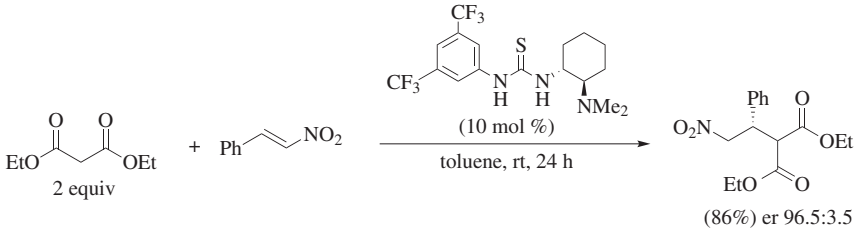
and the resulting (*R*)-LSB powder was redissolved in toluene (1.0 mL). To this solution was added *trans*-chalcone (0.5 mmol, 104.1 mg, 1.0 equiv) at rt and the mixture was stirred for 1 h at –50°. Dimethyl malonate (0.5 mmol, 57 μL, 1 equiv) was then added at –50°. After being stirred for 24 h at the same temperature, the reaction mixture was treated with 1 N HCl (2.0 mL) followed by extraction with EtOAc (3 x 10 mL). The combined organic extracts were washed with brine, dried ($Na_2SO_4$), and concentrated. Purification of the residue by flash chromatography on silica gel (hexane/acetone, 80:20) gave the title compound (0.46 mmol, 157 mg, 93%, 88.5:11.5 er) as a colorless solid: mp 78°; $[\alpha]_D^{24}$ + 25.64 (*c* 2.0, $CHCl_3$); IR (KBr) 1730, 1682, 1236 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 270 MHz) δ 7.91–7.88 (m, 2H), 7.56–7.17 (m, 8H), 4.20 (dt, *J* = 9.2, 5.3 Hz, 1H), 3.86 (d, *J* = 9.2 Hz, 1H), 3.73 (s, 3H), 3.71 (d, *J* = 5.3 Hz, 1H), 3.52 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.51 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 68 MHz) δ 197.5, 168.7, 168.1, 140.41, 136.8, 133.1, 128.5, 128.1, 127.9, 127.2, 125.6, 57.3, 52.7, 52.4, 42.3, 40.7; MS (*m*/*z*): $M^+$ 340, 309, 308, 105 (100). Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.40; H, 6.04.




**(2*R*,3*S*)-2-Methyl-4-nitro-3-phenylbutanal [*O*-TMS-Diphenylprolinol-Catalyzed Michael Reaction under Enamine Activation].[60]** Propanal (10 mmol, 0.75 mL, 10 equiv) was added to a solution of *trans*-β-nitrostyrene (1.0 mmol, 154 mg, 1.0 equiv) and (*S*)-2-[diphenyl(trimethylsilyloxy)methyl]pyrrolidine (0.1 mmol, 34 mg, 0.10 equiv) in hexane (1.0 mL) at 0°. After the mixture had been stirred for 5 h at 0°, the reaction was quenched by the addition of aqueous 1 N HCl (2.0 mL). The mixture was extracted with EtOAc (3 x 5 mL), the combined organic phases were dried ($Na_2SO_4$) and concentrated, and the residue was purified by preparative TLC ($CHCl_3$) to give the title compound (0.85 mmol, 183 mg, 85%, *syn* 94.0:6.0 er, *anti* 99.5:0.5 er) as a clear oil: $t_R$ (2*R*,3*S*) 19.7 min (major), $t_R$ (2*S*,3*R*) 14.5 min (minor) (Daicel Chiralcel-ODH, hexanes/*i*-PrOH, 10:1, 1.0 mL/min, 254 nm). The remaining analytical data matched that previously published[139]: $^1H$ NMR ($CDCl_3$, 500 MHz) δ 9.72 (d, *J* = 1.5 Hz, 1H), 7.36–7.29 (m, 3H), 7.17–7.16 (m, 2H), 4.80 (dd, *J* = 12.9, 5.5 Hz, 1H), 4.69 (dd, *J* = 12.9, 9.2 Hz, 1H), 3.81 (ddd, *J* = 9.2, 9.2, 5.5 Hz, 1H), 2.80–2.75 (m, 1H), 1.01 (d, *J* = 7.4 Hz, 3H); $^{13}C$-NMR ($CDCl_3$, 125 MHz) δ 202.2, 136.5, 129.1, 128.1, 128.0, 78.1, 48.4, 44.0, 12.1; HRMS (*m*/*z*): $[M + H]^+$ calcd for $C_{11}H_{13}NO_3$, 207.0817; found, 207.0812. Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.42; H, 6.27; N, 6.43.

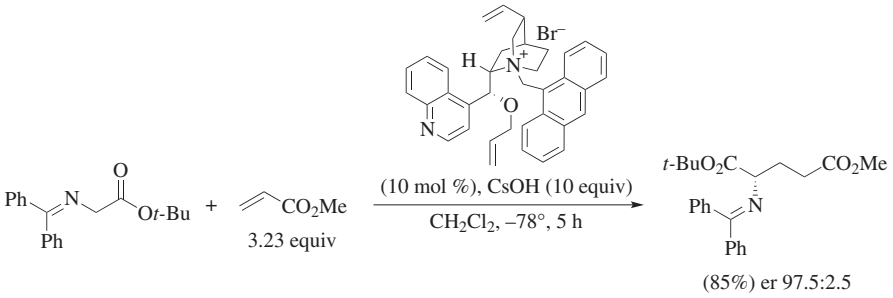



**(*S*)-4-Nitro-3-phenylbutanal [*O*-TMS-Diphenylprolinol-Catalyzed Michael Reaction under Iminium Activation].[153]** (*S*)-2- [Diphenyl(trimethylsilyloxy) methyl]pyrrolidine (0.06 mmol, 19.5 mg, 0.10 equiv) was added to a MeOH solution (1.2 mL) of cinnamaldehyde (0.6 mmol, 79.2 mg, 1.0 equiv), benzoic acid (0.12 mmol, 14.7 mg, 0.20 equiv), and nitromethane (1.8 mmol, 96 μL, 3.0 equiv) at rt. After being stirred at rt for 16 h, the mixture was quenched with sat. aq $NaHCO_3$ solution (2.0 mL). The organic materials were extracted with EtOAc (3 x 5 mL), and the combined organic fractions were dried over anhydrous $Na_2SO_4$, then concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc, 20:1 to 6:1) to afford the title compound (0.54 mmol, 104.3 mg, 90%, 97.5:2.5 er): $t_R$ (*S*) 44.7 min (major), $t_R$ (*R*) 43.1 min (minor) (GLC, Bodman Chiraldex Γ-TA, T (initial) 40°, gradient 10°/min, constant pressure 60 kPa); $[\alpha]_D^{22}$ − 23 (*c* 0.71, $CHCl_3$); IR (neat) 3032, 1723, 1548, 1380, 765, 702 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 9.70 (s, 1H), 7.40–7.20 (m, 5H), 4.68 (dd, $J$ = 7.6, 12.4 Hz, 1H), 4.62 (dd, $J$ = 7.6, 12.4 Hz, 1H), 4.08 (quint, $J$ = 7.2 Hz, 1H), 2.96 (dd, $J$ = 1.2, 2.0 Hz, 1H), 2.94 (dd, $J$ = 1.2, 2.0 Hz, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ 128.1, 199.1, 138.1, 129.2 (2C), 127.4 (2C), 79.4, 46.4, 37.9; HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{10}H_{11}NO_3$: 216.0631; found, 216.0645.




**(*S*)-Ethyl 2-Carboethoxy-4-nitro-3-phenylbutyrate [Takemoto's Thiourea-Catalyzed Michael Reaction].[86]** 1-[3,5-Bis(trifluoromethyl)phenyl]-3-[(1*R*,2*R*)-2-(dimethylamino)cyclohexyl]thiourea (0.02 mmol, 8.2 mg, 0.10 equiv) was added to a stirred solution of *trans*-β-nitrostyrene (0.20 mmol, 29.8 mg, 1.00 equiv) and diethyl malonate (0.40 mmol, 0.061 mL, 2.0 equiv) in dry toluene (0.40 mL) and under an argon atmosphere. After stirring for 24 h, the reaction mixture was concentrated under vacuum. The residue was purified by preparative TLC (hexane/$Et_2O$, 5:1) to afford

the title compound (0.172 mmol, 53.3 mg, 86%, 96.5:3.5 er) as colorless needles: mp 45–47°; $t_R$ (*S*) 11.1 min (major), $t_R$ (*R*) 13.9 min (minor) (Daicel Chiralpak-AD, hexanes/EtOH (10:1) 1.0 mL/min, 254 nm); $[\alpha]_D^{30}$ – 6.00 (*c* 1.00, $CHCl_3$); IR (film) 2989, 2938, 1731, 1557 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) δ 7.42–7.10 (m, 5H), 4.93 (dd, *J* = 13.1, 4.6 Hz, 1H), 4.86 (dd, *J* = 13.1, 9.2 Hz, 1H), 4.33–4.15 (m, 3H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.82 (d, *J* = 9.5 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 126 MHz) δ 167.4, 166. 7, 136.2, 128.8, 128.2, 127.9, 77.6, 62.0, 61.8, 54.9, 42.9, 13.9, 13.6; MS–FAB$^+$ (*m*/*z*): $[M + H]^+$ 310 (100). Anal. Calcd for $C_{15}H_{19}NO_6$: C, 58.24; H, 6.19; N, 4.53. Found: C, 58.43; H, 6.20; N, 4.56.




**(*S*)-1-(*tert*-Butyl) 5-Methyl 2-(Diphenylmethyleneamino)pentanedioate [Cinchonidinium Salt Catalyzed Michael Reaction].[206]** To a mixture of *tert*-butyl glycinate benzophenone imine (0.17 mmol, 50 mg, 1.0 equiv), *O*-(9)-allyl-*N*-9-anthracenylmethylcinchonidinium bromide (0.017 mmol, 10 mg, 0.10 equiv), and $CsOH \cdot H_2O$ (1.7 mmol, 250 mg, 10 equiv) in 0.4 mL $CH_2C1_2$, a solution of methyl acrylate (0.05 mL, 0.55 mmol, 3.23 equiv) in 0.1 mL $CH_2C1_2$ was added dropwise over 10 min at –78°. The reaction mixture was stirred vigorously for 5 h at –78° and then diluted with $Et_2O$ (30 mL). The organic phase was washed with $H_2O$ (2 x 10 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated under vacuum. Purification of the residue by silica gel chromatography (hexane/EtOAc, 20:1 to 5:1) afforded the title compound (0.144 mmol, 55 mg, 85%, 97.5:2.5 er) as a colorless oil: $t_R$ (*S*) 15.35 min (major), $t_R$ (*R*) 13.14 min (minor) (Regis Whelk-O1, hexanes/*i*-PrOH (80:20), 0.5 mL/min, 254 nm, rt); $[\alpha]_D^{23}$ – 110.5 (*c* 2.4, $CH_2Cl_2$); FTIR (film) 3061, 3056, 2977, 2950, 2933, 1735, 1624, 1446, 1368, 1316, 1277, 1254, 1195, 1150 $cm^{-1}$; $^1H$ NMR ($CDC1_3$, 400 MHz) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.45–7.25 (m, 6H), 7.18–7.16 (m, 2H), 3.95 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.59 (s, 3H), 2.39–2.35 (m, 2H), 2.24–2.18 (m, 2H), 1.43 (s, 9H); $^{13}C$ NMR ($CDC1_3$, 100 MHz) δ 173.3, 170.6, 170.5, 139.3, 136.3, 130.2, 128.6, 128.4, 128.3, 127.8, 127.6, 80.9, 64.6, 51.3, 30.3, 28.4, 27.8; MS–CI (*m*/*z*): $[M + H]^+$ 382, 280, 134; HRMS (*m*/*z*): $[M + H]^+$ calcd for $C_{23}H_{27}NO_4$, 382.2018; found, 382.2017.

**TABULAR SURVEY**

Tables are organized first by Michael donor type (1–5) and second by Michael acceptor (A–D). Vinylogous Michael reactions are found in Tables 1E, 3E, and 5E. Within each table, entries are organized according to increasing number of carbons of the Michael donor, not including protecting groups and substituents on heteroatoms. This system was adopted in order to group similar substrates together. For a given entry, references are listed according to publication date, showing the oldest ones first. Experiments involving recycling of the catalyst are listed first. Screening experiments are not included; only conditions giving the best yields and/or selectivities are listed. Products, catalysts, and ligands appear with the same structures and absolute configurations as provided in the original references. In those cases where an absolute configuration is not shown for the product(s), the configuration was not assigned by the original authors. Alkenyl substituents in the Tables (RCH=CH, PhCH=CH) have the E double bond configuration unless specifically designated as Z.

Typically reactions are equimolar in donor and acceptor, or with a slight excess of one of the reagents. The only exception is for those reactions proceeding under iminium or enamine activation, in which one of the reagents is usually, but not always, used in 3–10 fold excess. Reactant stoichiometry is discussed in more detail in the "Experimental Conditions" section.

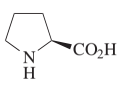
A substantial effort was made to include all reactions that appeared in the literature up to the end of 2012. However, in view of the difficulties in the delimitation of the subject, omissions are often unavoidable. Supplemental references are provided for articles published through the first half of 2015.

The following abbreviations, excluding those found in the "*The Journal of Organic Chemistry* Standard Abbreviations and Acronymns" list, are used in the Tabular Survey:

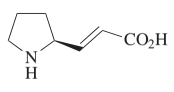
| | |
|---|---|
| 1-Ad | adamantan-l-yl |
| BEMP | 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine |
| bmim | 1-butyl-3-methylimidazolium |
| BOM | benzyloxymethyl |
| BTPP | (*tert*-butylimino)tris(pyrrolidino)phosphorane |
| 2-$C_4H_8O$ | furan-2-yl |
| 2-$C_4H_3S$ | thiophen-2-yl |
| 2-$C_4H_4N$ | pyrrol-2-yl |
| 2-$C_5H_4N$ | pyridin-2-yl |
| 5-$C_6H_4$ | cyclohexyl |
| 5-$C_5H_4$ | cyclopentyl |
| 2-$C_8H_6N$ | indol-2-yl |
| conv | conversion |
| CPME | cyclopentyl methyl ether |
| CSA | camphorsulfonic acid |

| | |
|---|---|
| DIPEA | diisopropylethylamine |
| HFIP | hexafluoroisopropyl alcohol |
| hmim | 1-hexyl-3-methylimidazolium |
| KHMDS | potassium bis(trimethylsilyl)amide |
| MMC | methylmethacrylate copolymer |
| MOC | methoxycarbonyl |
| MOPS | 3-(*N*-morpholino)propanesulfonic acid |
| MR | Merrifield Resin |
| MS | molecular sieves |
| MSCR | macroporous sulfonyl chloride resin |
| MW | microwave irradiation |
| NAP–MgO | NanoActive$^{TM}$ MgO Plus (590 $m^2$/gm) |
| NMM | *N*-methylmorpholine |
| Np | naphthyl |
| PE | polyethylene |
| PEG-800 | polyethylene glycol-800 |
| Piv | pivaloyl |
| PMP | 4-methoxyphenyl |
| PS | polystyrene |
| PTC | polystyrene triblock copolymer |
| PTSA | 4-toluenesulfonic acid |
| rr | regioisomer ratio |
| SC | styrene copolymer |
| TBATB | *tert*-butylammonium tetrahydroborate |
| TBBP | tetrabromobisphenol |
| TBDPS | *tert*-butyldiphenylsilyl |
| TES | triethylsilyl |
| TMG | 1,1,3,3-tetramethylguanidine |
| TMP | 2,2,6,6-tetramethylpiperidine |
| TOF | turnover frequency |
| TPAP | tetrapropylammonium perruthenate |
| TR | Tantagel Resin |

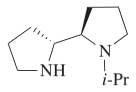
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES



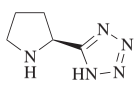
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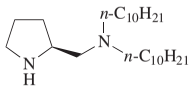
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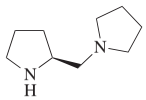
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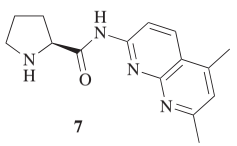
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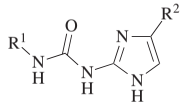
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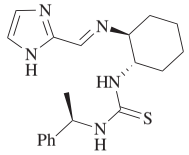
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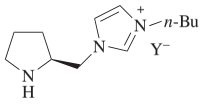
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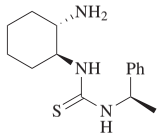
| | $R^1$ | $R^2$ |
|---|---|---|
| **8** | Ph | H |
| **9** | 3,5-$(CF_3)_2C_6H_3$ | H |
| **10** | Ph | *t*-Bu |



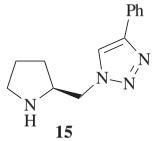
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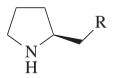
| | Y |
|---|---|
| **12** | Br |
| **13** | $BF_4$ |



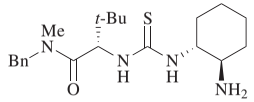
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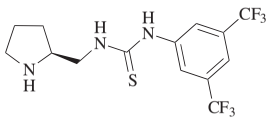
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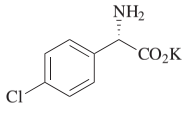
| | R |
|---|---|
| **16a** | TfHN |
| **16b** | HO |



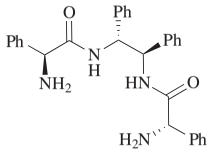
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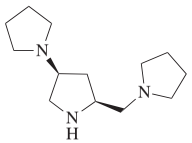
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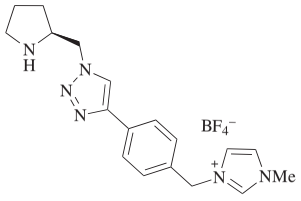
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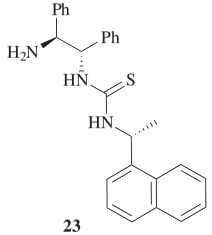
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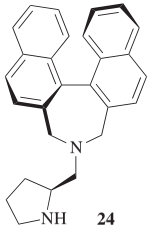
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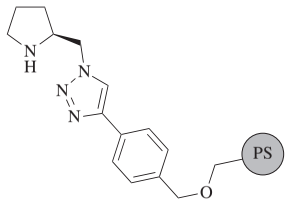
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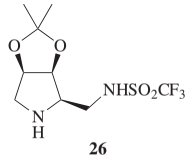
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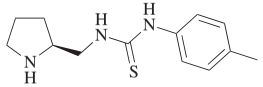
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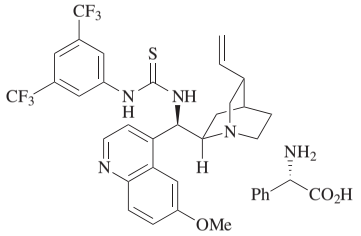
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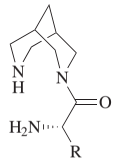
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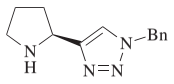
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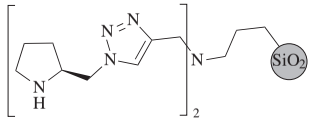
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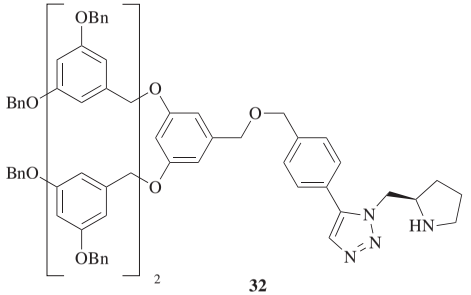
| | R |
|---|---|
| **29a** | Ph |
| **29b** | 4-$FC_6H_4$ |
| **29c** | Bn |



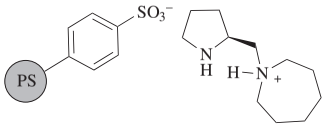
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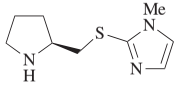
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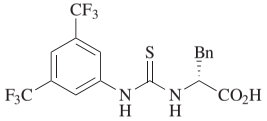
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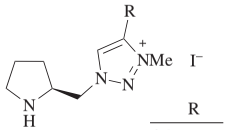
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**34**

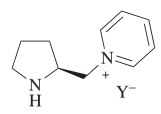


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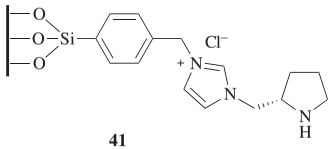


| | R |
|---|---|
| **36** | *n*-Bu |
| **37** | Ph |

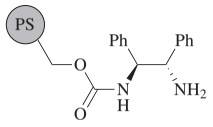
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



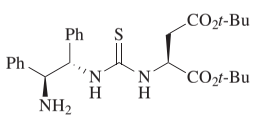
| | Y |
|---|---|
| **38** | Cl |
| **39** | $BF_4$ |
| **40** | $Tf_2N$ |



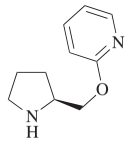
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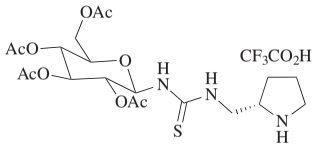
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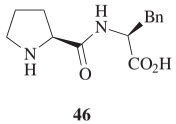
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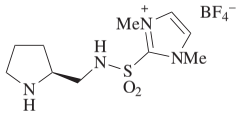
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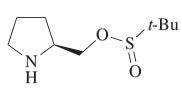
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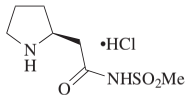
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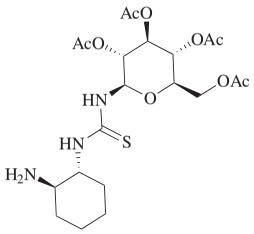
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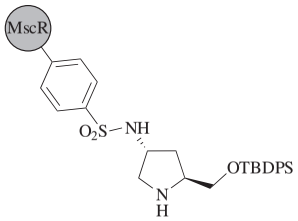
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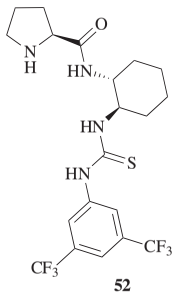
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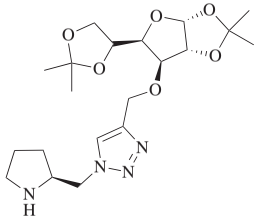
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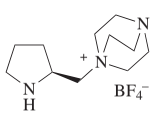
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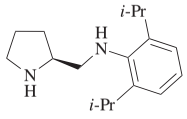
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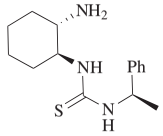
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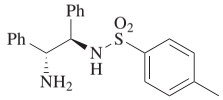
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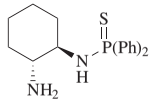
**55**



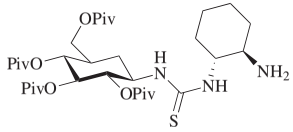
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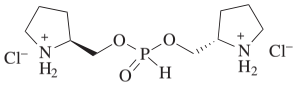
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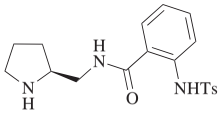
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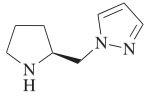
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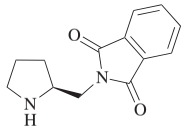
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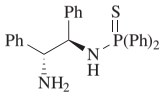
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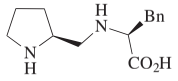
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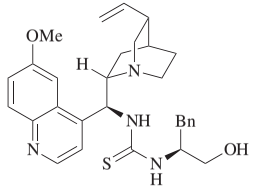
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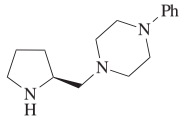
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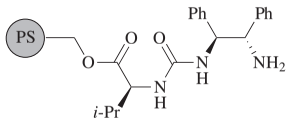
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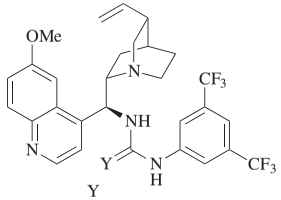
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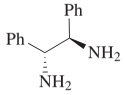
**67**



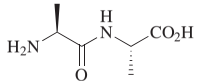
**68**



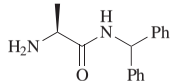
**69a** O
**69b** S



**70**

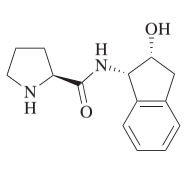


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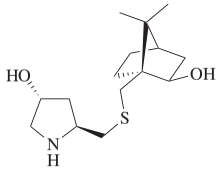


**72**

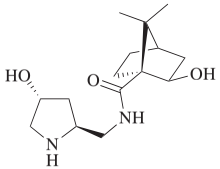
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



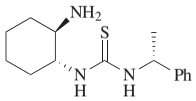
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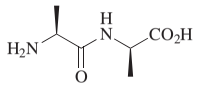
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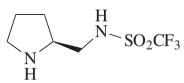
**75**



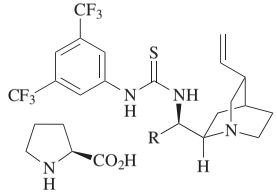
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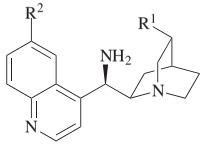
**77**



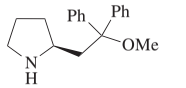
**78**



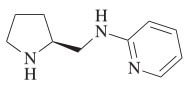
**79** R = 6-methoxyquinolin-4-yl



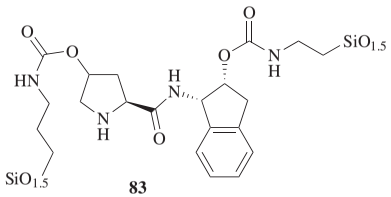
| | $R^1$ | $R^2$ |
|---|---|---|
| **80a** | Et | MeO |
| **80b** | $CH_2$=CH | H |
| **80c** | $CH_2$=CH | HO |
| **80d** | $CH_2$=CH | MeO |



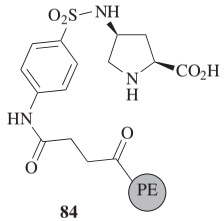
**81**



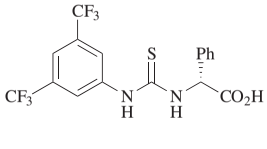
**82**



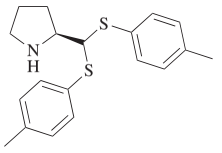
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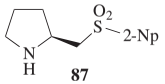
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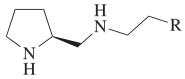
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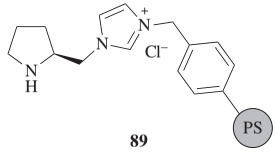
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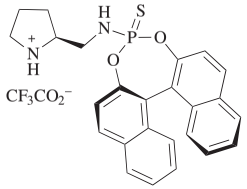
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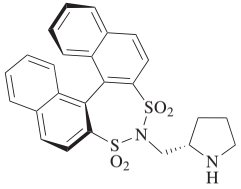
| | R |
|---|---|
| **88a** | $Me_2N$ |
| **88b** | *i*-Pr |



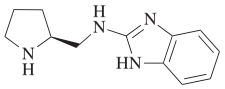
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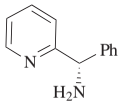
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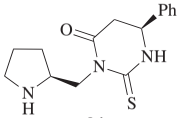
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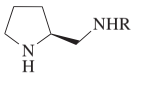
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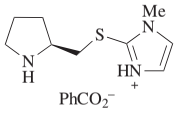
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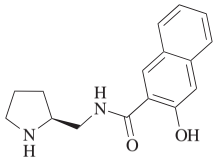
**94**



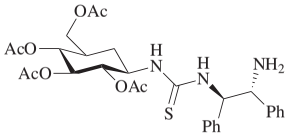
| R | |
|---|---|
| **95a** | *i*-$C_5H_{11}$ |
| **95b** | Ph |
| **95c** | 4-$MeOC_6H_4$ |
| **95d** | 4-$O_2NC_6H_4$ |
| **95e** | *n*-$C_4F_9SO_2$ |
| **95f** | 3,5-$(CF_3)_2C_6H_3SO_2$ |



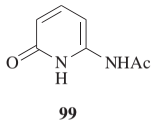
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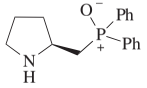
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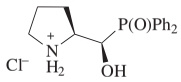
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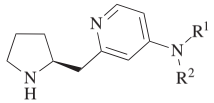
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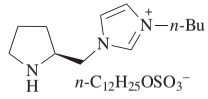
**100**



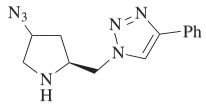
**101**



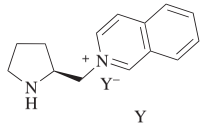
| | $R^1$ | $R^2$ |
|---|---|---|
| **102a** | Me | Me |
| **102b** | –$(CH_2)_4$– | |



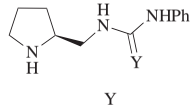
**103**



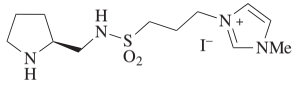
**104**



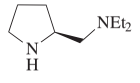
| Y | |
|---|---|
| **105a** | Br |
| **105b** | $PF_6$ |



| Y | |
|---|---|
| **106a** | O |
| **106b** | S |

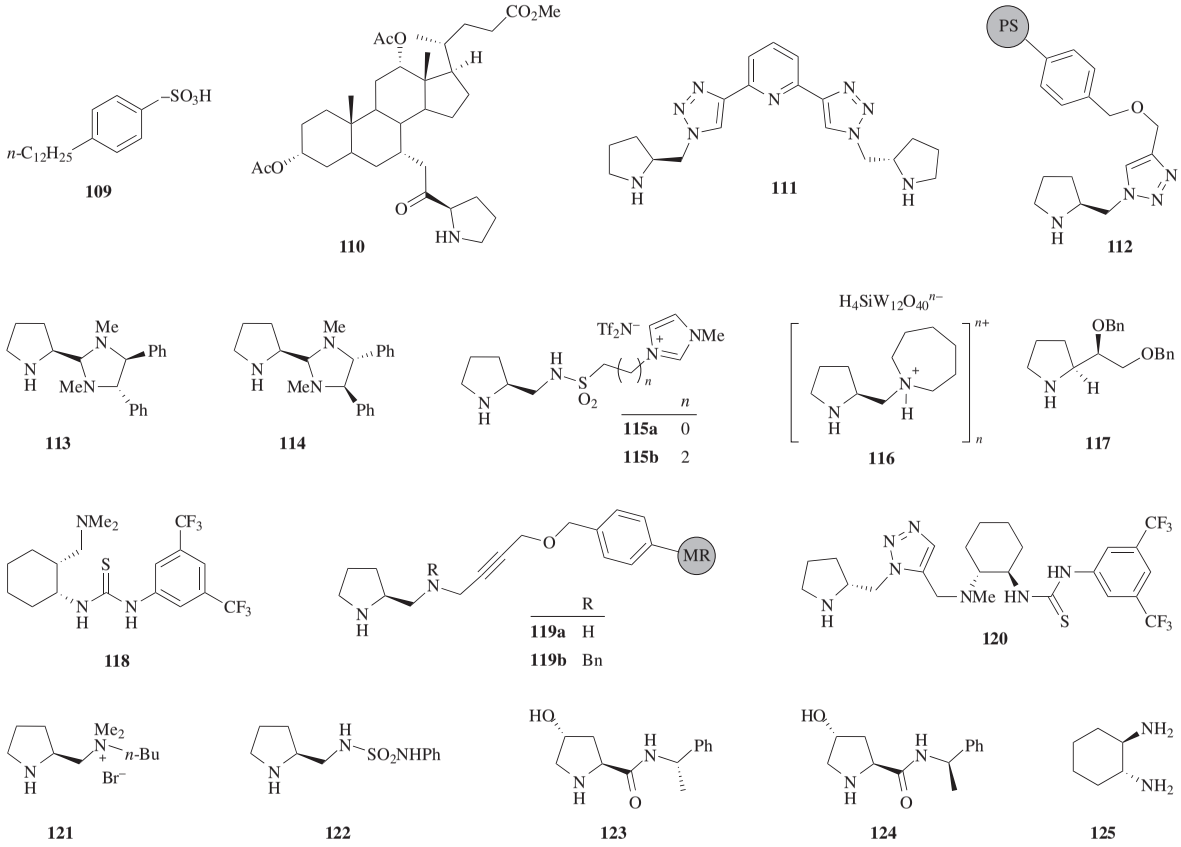


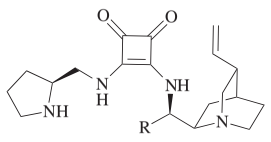
**107**



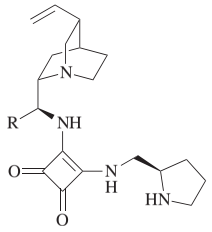
**108**

CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)

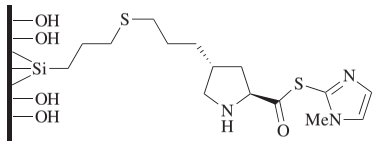




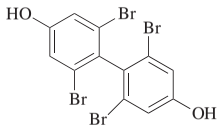
**126** R = quinolin-4-yl



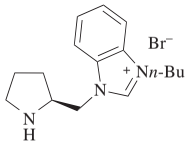
**127** R = quinolin-4-yl



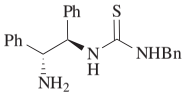
**128**



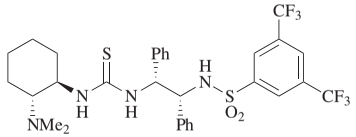
**129**



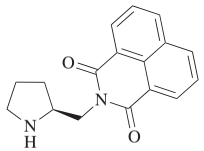
**130**



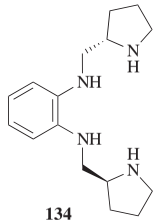
**131**



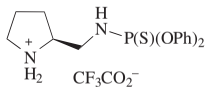
**132**



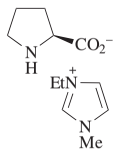
**133**



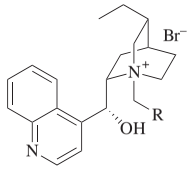
**134**



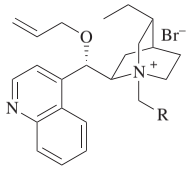
**135**



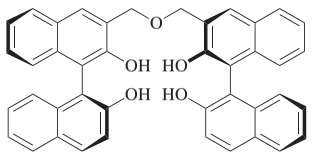
**136**



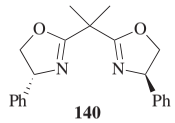
**137** R = anthracen-9-yl



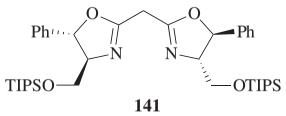
**138** R = anthracen-9-yl



**139**



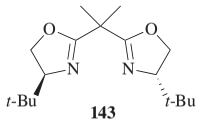
**140**



**141**

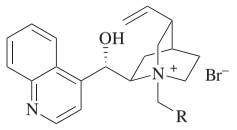
Antibody 38C2

**142**

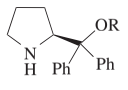


**143**

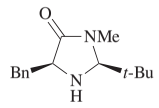
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



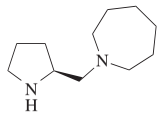
| R | |
|---|---|
| **144a** | 4-$CF_3C_6H_4$ |
| **144b** | 3,4,5-$(BnO)_3C_6H_2$ |



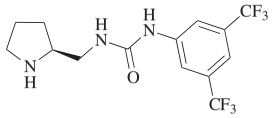
| R | |
|---|---|
| **145a** | Me |
| **145b** | TMS |
| **145c** | TES |
| **145d** | TBS |



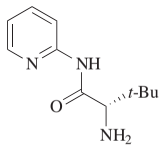
**146**



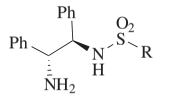
**147**



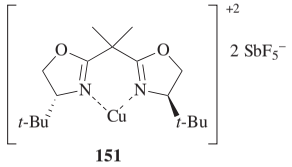
**148**



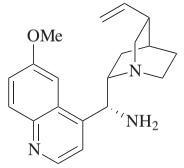
**149**



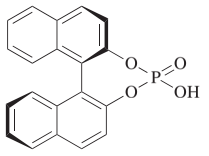
| R | |
|---|---|
| **150a** | 2,6-$Cl_2C_6H_3$ |
| **150b** | 3,5-$(CF_3)_2C_6H_3$ |



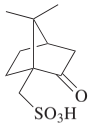
**151**



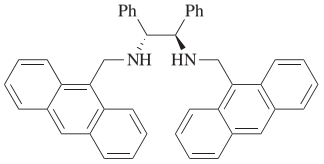
**152**



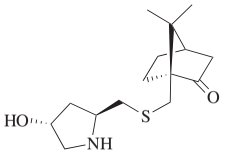
**153**



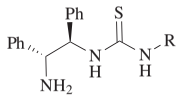
**154**



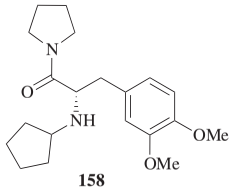
**155**



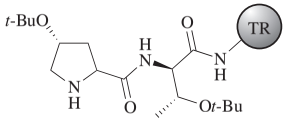
**156**



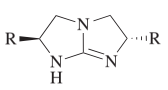
| R | |
|---|---|
| **157a** | Ph |
| **157b** | 3,5-$(CF_3)_2C_6H_3$ |



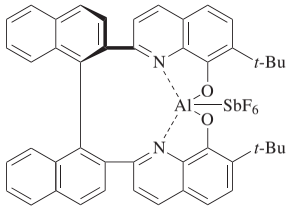
**158**



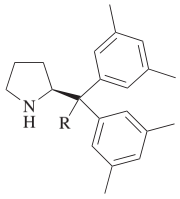
**159**



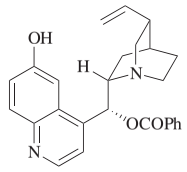
| R | |
|---|---|
| **160a** | *i*-Pr |
| **160b** | *t*-Bu |
| **160c** | Bn |



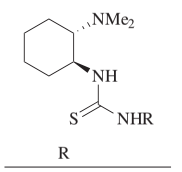
**161**



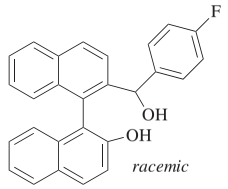
| | R |
|---|---|
| **162a** | H |
| **162b** | HO |



**163**

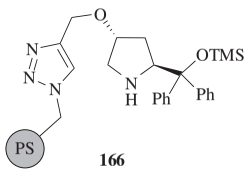


| | R |
|---|---|
| **164a** | 4-$FC_6H_4$ |
| **164b** | 3,5-$(CF_3)_2C_6H_3$ |

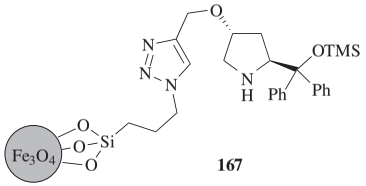


*racemic*

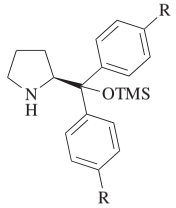
**165**



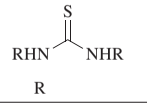
**166**



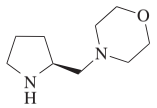
**167**



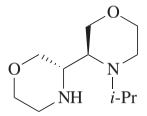
| | R |
|---|---|
| **168a** | $Me_2NCH_2$ |
| **168b** | $n$-$C_8H_{17}$ |



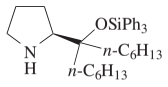
| | R |
|---|---|
| **169a** | Ph |
| **169b** | 3,5-$(CF_3)_2C_6H_3$ |



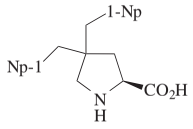
**170**



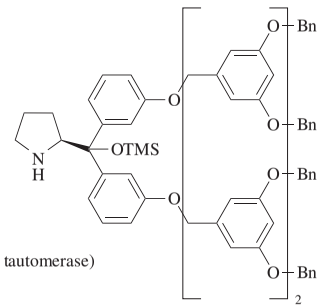
**171**



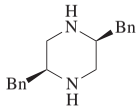
**172**



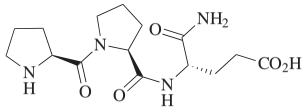
**173**



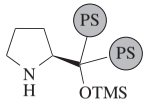
**178**



**174**



**175**

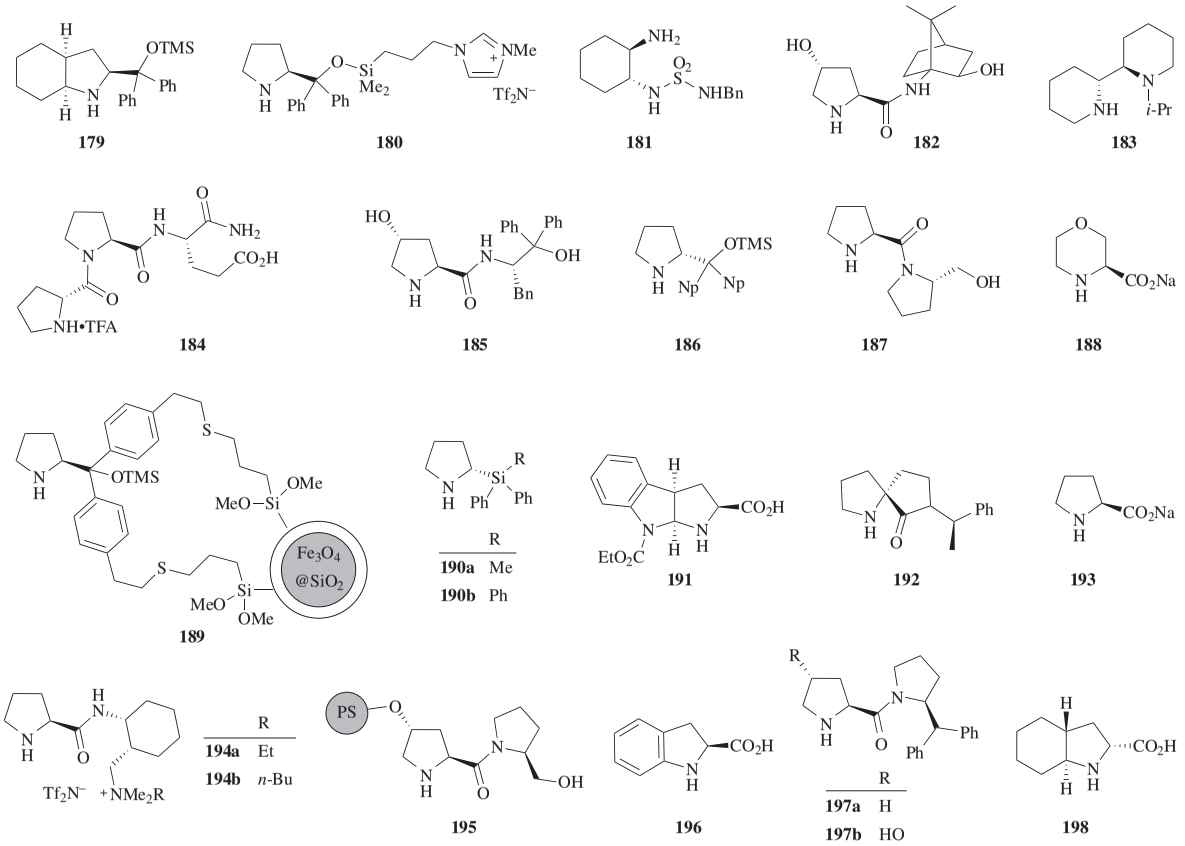


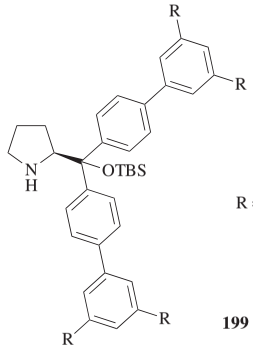
**176**

4-OT (4-oxalocrotonate tautomerase)

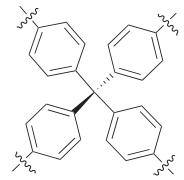
**177**

CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)

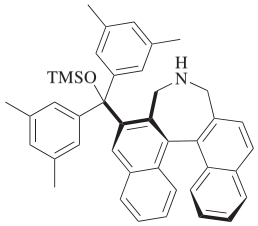




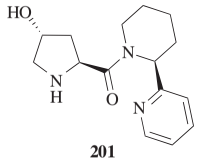
R =



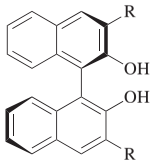
**199**



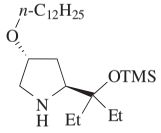
**200**



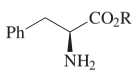
**201**



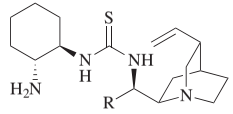
| | R |
|---|---|
| **202a** | H |
| **202b** | $Et_2NCH_2$ |



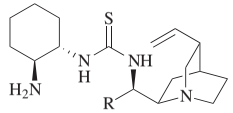
**203**



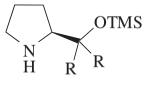
| | R |
|---|---|
| **204a** | H |
| **204b** | Li |



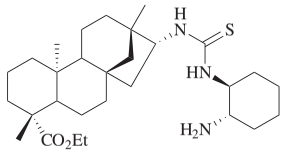
| | R |
|---|---|
| **205a** | quinolin-4-yl |
| **205b** | 6-methoxyquinolin-4-yl |



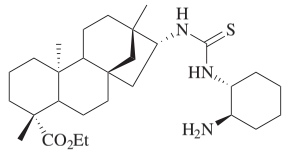
**206** R = 6-methoxyquinolin-4-yl



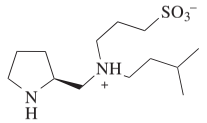
| | R |
|---|---|
| **207a** |  |
| **207b** | $n$-$C_6H_{13}$ |
| **207c** | 3,5-$(CF_3)_2C_6H_3$ |



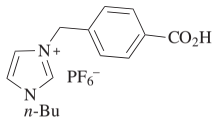
**208**



**209**

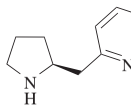


**210**

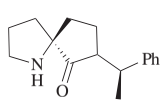


**211**

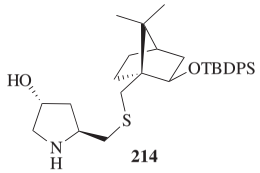
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



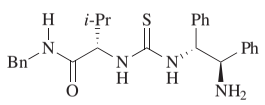
**212**



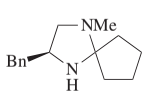
**213**



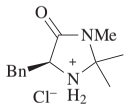
**214**



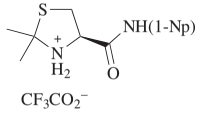
**215**



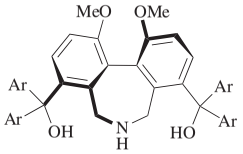
**216**



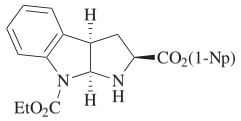
**217**



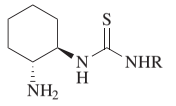
**218**



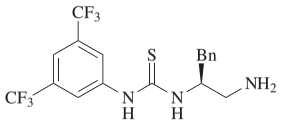
**219** Ar = 3,5-$F_2C_6H_3$



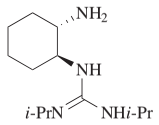
**220**



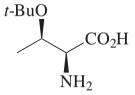
| | R |
|---|---|
| **221a** | 3,5-$(CF_3)_2C_6H_3$ |
| **221b** | 4-*n*-$C_8F_{17}C_6H_4$ |



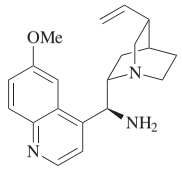
**222**



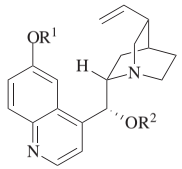
**223**



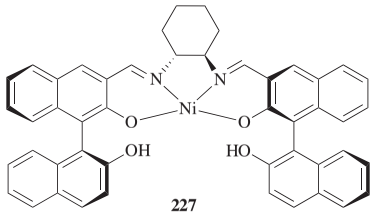
**224**



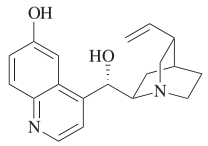
**225**



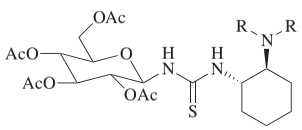
| | $R^1$ | $R^2$ |
|---|---|---|
| **226a** | H | H |
| **226b** | Na | H |
| **226c** | H | Bn |



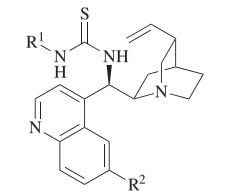
**227**



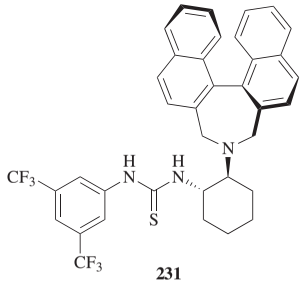
**228**



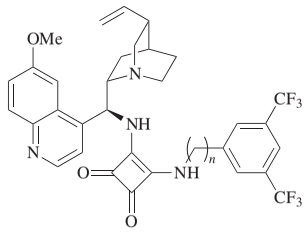
| | R |
|---|---|
| **229a** | Me |
| **229b** | *n*-Bu |



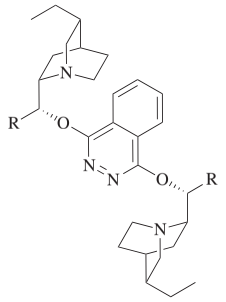
| | $R^1$ | $R^2$ |
|---|---|---|
| **230a** | 3,5-$(CF_3)_2C_6H_3$ | H |
| **230b** | $Ph_3C$ | MeO |



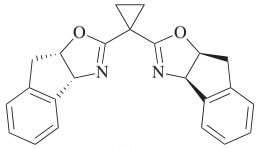
**231**



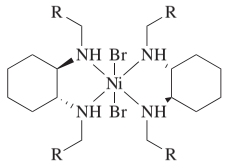
| | *n* |
|---|---|
| **232a** | 0 |
| **232b** | 1 |



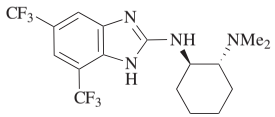
**233** R = 6-hydroxyquinolin-4-yl



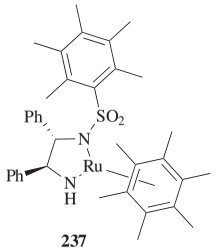
**234**



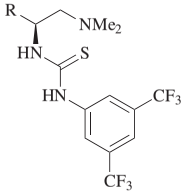
| | R |
|---|---|
| **235a** | Ph |
| **235b** | 4-$BrC_6H_4$ |



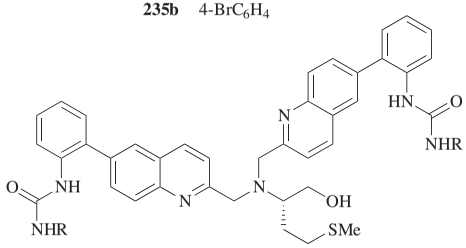
**236**



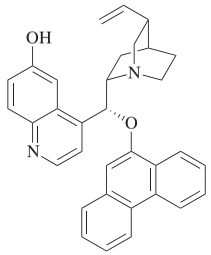
**237**



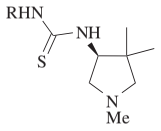
| | R |
|---|---|
| **238a** | *i*-Pr |
| **238b** | *t*-Bu |



**239** R = 3,5-$(CF_3)_2C_6H_3$

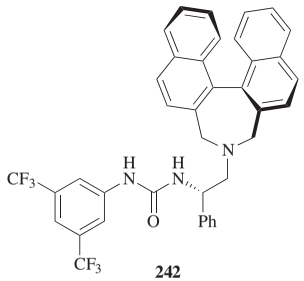


**240**

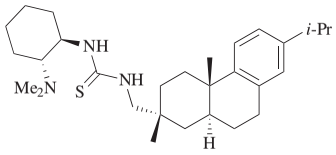


**241** R = 3,5-$(CF_3)_2C_6H_3$

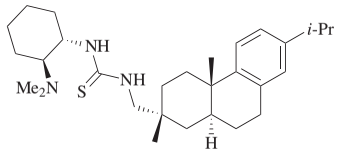
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



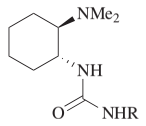
**242**



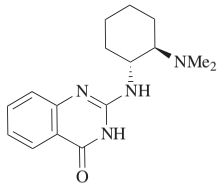
**243**



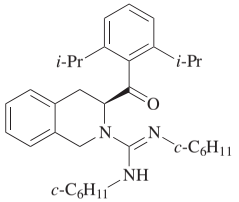
**244**



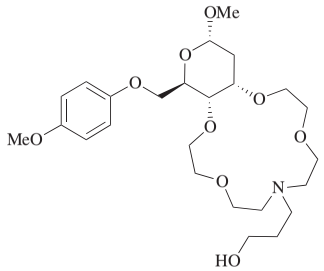
**245** R = 3,5-$(CF_3)_2C_6H_3$



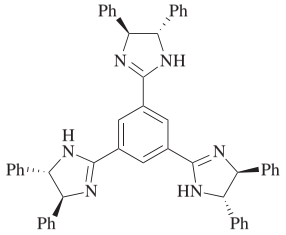
**246**



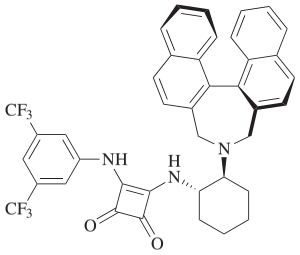
**247**



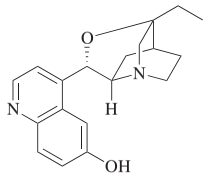
**248**



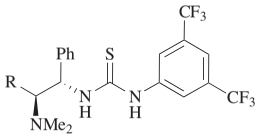
**249**



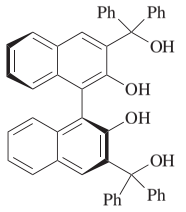
**250**



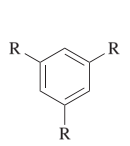
**251**



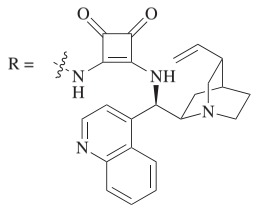
| | R |
|---|---|
| **252a** | Me |
| **252b** | Ph |

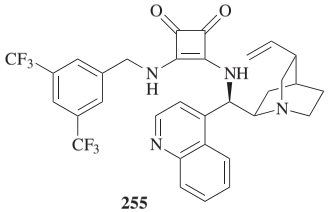


**253**

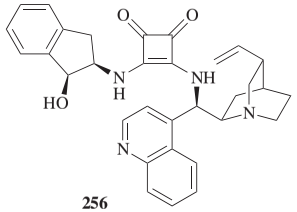


**254**

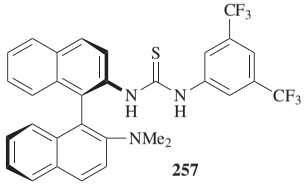




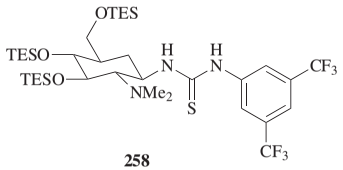
**255**



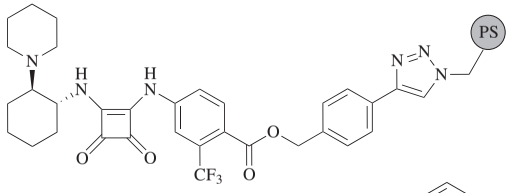
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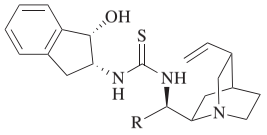
**257**



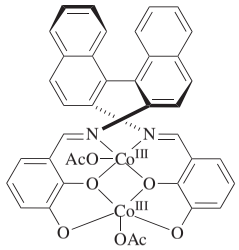
**258**



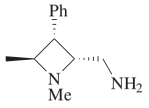
**259**



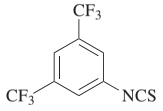
**260** R = 6-methoxyquinolin-4-yl



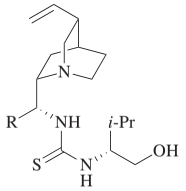
**261**



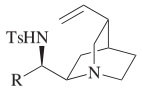
**262**



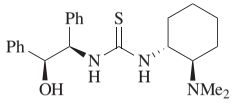
**263**



**264** R = 6-methoxyquinolin-4-yl

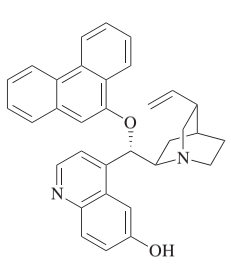


**265** R = 6-methoxyquinolin-4-yl

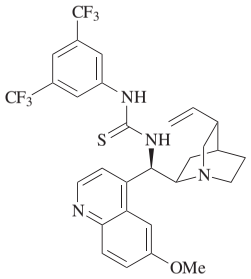


**266**

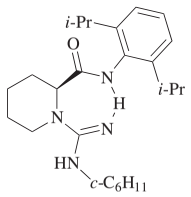
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



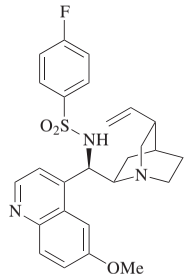
**267**



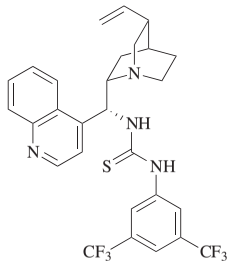
**268**



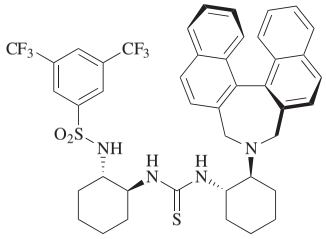
**269**



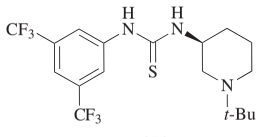
**270**



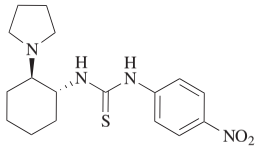
**271**



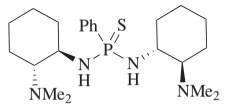
**272**



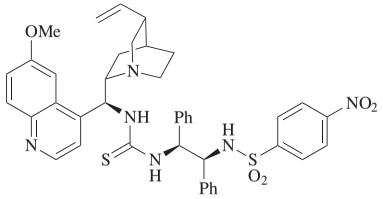
**273**



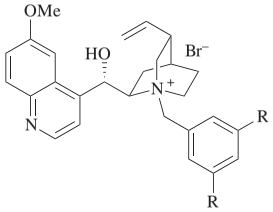
**274**



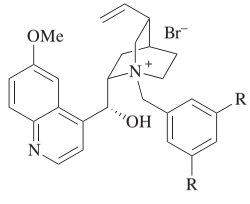
**275**



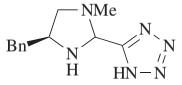
**276**



**277** R = 3,5-$(CF_3)_2C_6H_3$

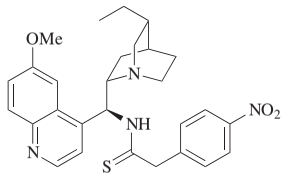


**278** R = 3,5-$(CF_3)_2C_6H_3$

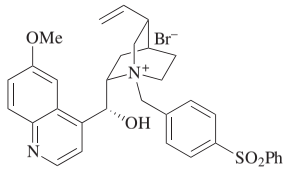


one diastereomer
*cis* assumed

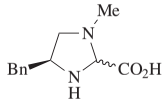
**279**



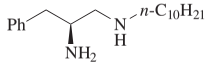
**280**



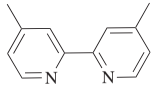
**281**



**282**



**283**



**284**



salmon testes DNA

**285**

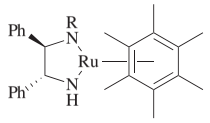
Artificial Bovine Pancreatic Peptide:
APLEPEXPGENATPEQMAQYAAELRRYINML

**286** X = L-3-pyridylalanine

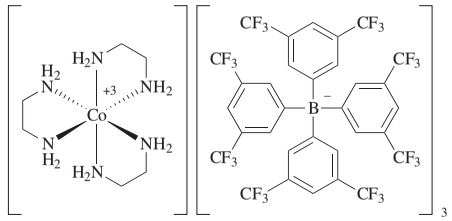


DNA d(TCA GGG CCC TGA)

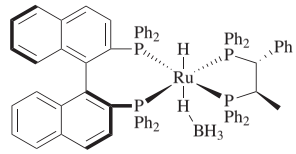
**287**



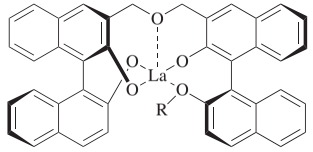
| | R |
|---|---|
| **288a** | Ms |
| **288b** | Ts |



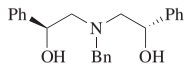
**289**



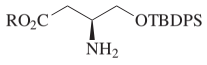
**290**



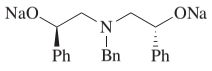
| | R |
|---|---|
| **291a** | H |
| **291b** | EtZn |



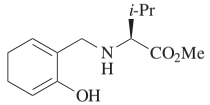
**292**



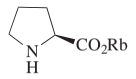
| | R |
|---|---|
| **293a** | H |
| **293b** | Li |



**294**

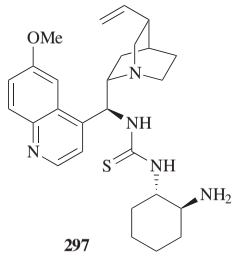


**295**

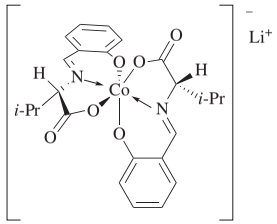


**296**

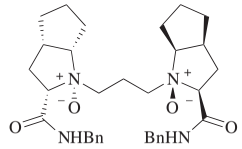
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



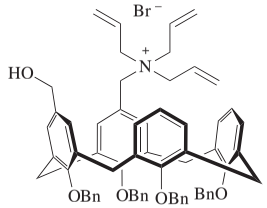

**297**



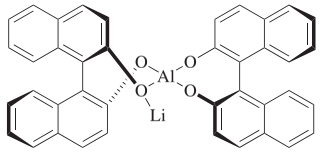

**298**



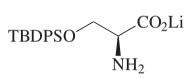

**299**



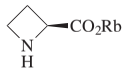

**300**



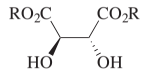

**301**



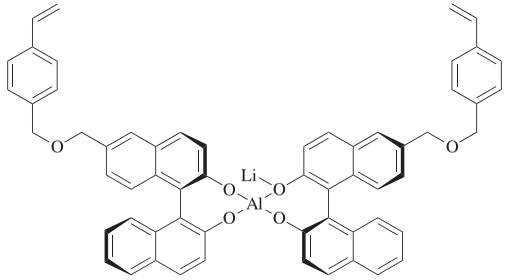

**302**



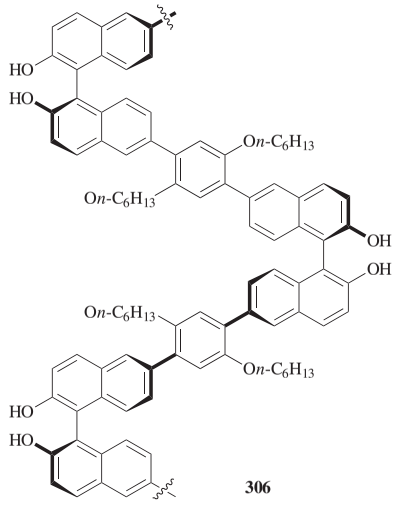

**303**



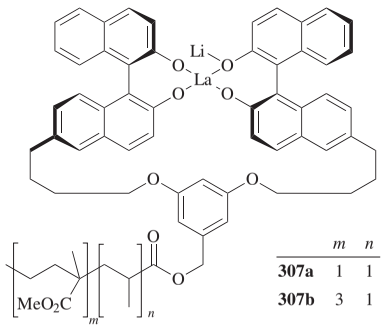

| R | |
|---|---|
| **304a** | Me |
| **304b** | *c*-$C_6H_{11}$ |
| **304c** | *c*-$C_6H_{11}CH_2$ |



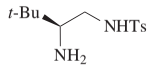

**305**



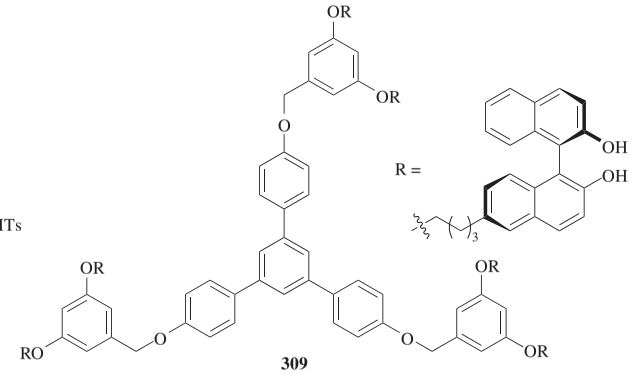

**306**



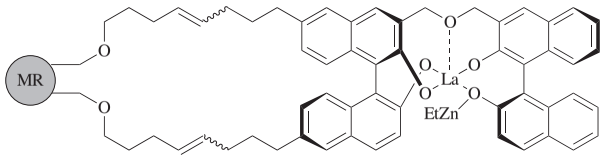

| | *m* | *n* |
|---|---|---|
| **307a** | 1 | 1 |
| **307b** | 3 | 1 |



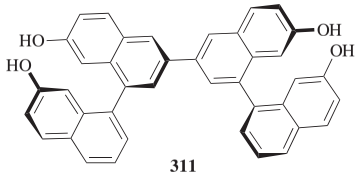

**308**



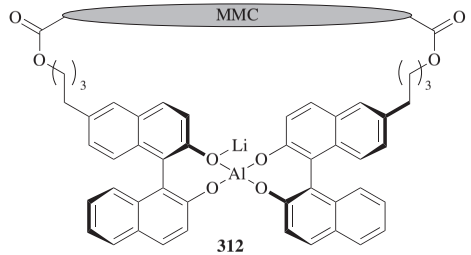

**309**



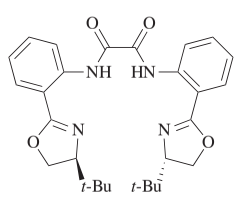

**310**



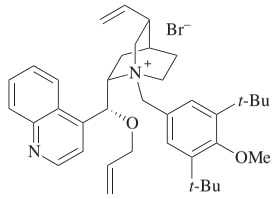

**311**




**312**

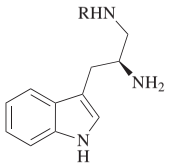



**313**

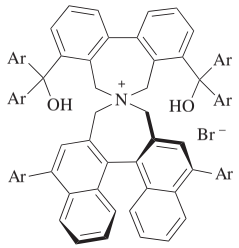



**314**

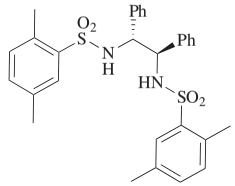
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



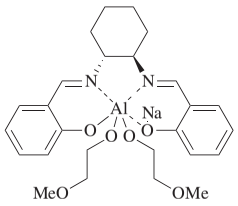
| | R |
|---|---|
| **315a** | *n*-Pr |
| **315b** | *t*-Bu |



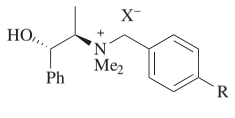
**316** Ar = 3,5-$Ph_2C_6H_3$



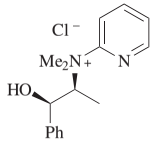
**317**



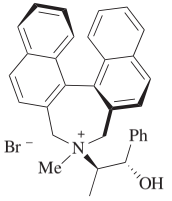
**318**



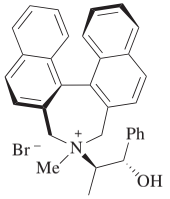
| | R | X |
|---|---|---|
| **319a** | MeO | Cl |
| **319b** | $O_2N$ | Br |



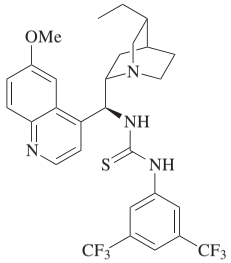
**320**



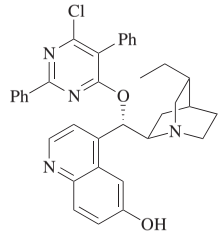
**321**



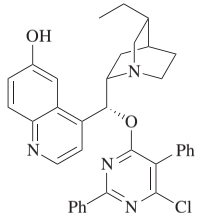
**322**



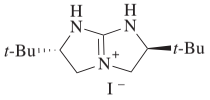
**323**



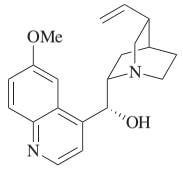
**324**



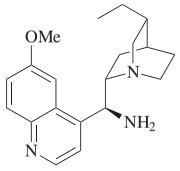
**325**



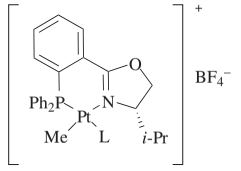
**326**



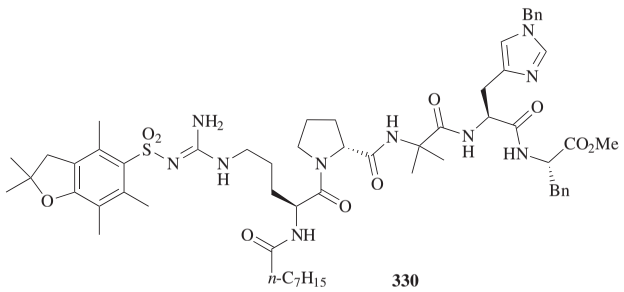
**327**



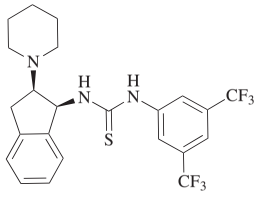
**328**



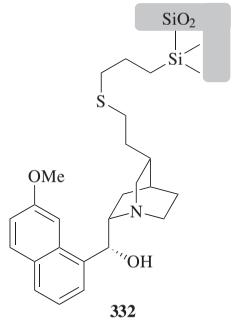
**329** L = $CH_2Cl_2$



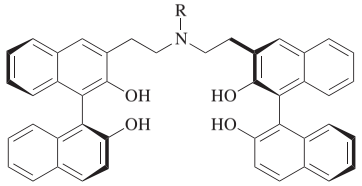
**330**



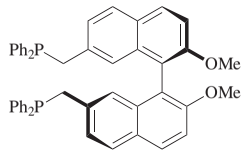
**331**



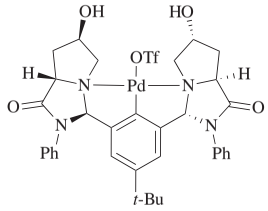
**332**



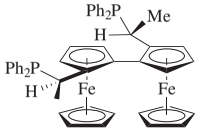
| | R |
|---|---|
| **333a** | H |
| **333b** | Me |
| **333c** | Et |



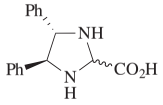
**334**



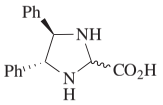
**335**



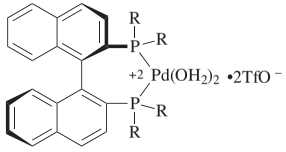
**336**



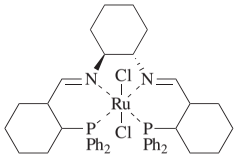
**337**



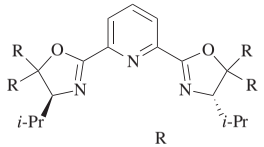
**338**



| | R |
|---|---|
| **339a** | Ph |
| **339b** | 4-MeC$_6$H$_5$ |

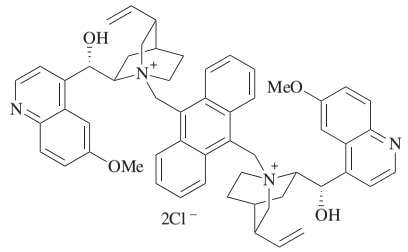


**340**

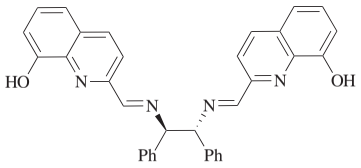


| | R |
|---|---|
| **341a** | H |
| **341b** | Ph |

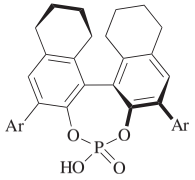
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



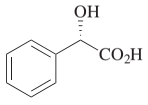

**342**



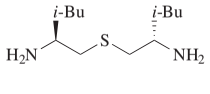

**343**



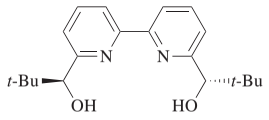

**344** Ar = 3,5-$(CF_3)_2C_6H_3$



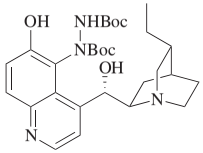

**345**



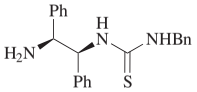

**346**



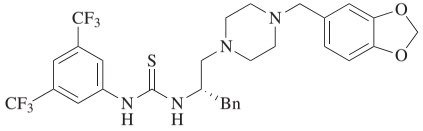

**347**



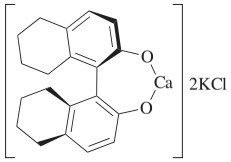

**348**



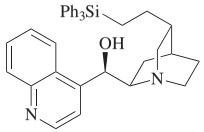

**349**



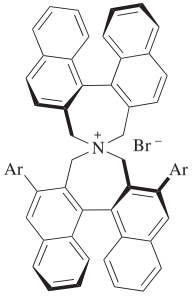

**350**



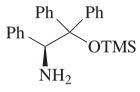

**351**



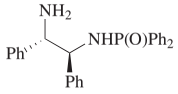

**352**



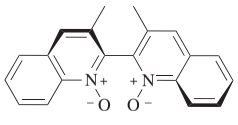

**358** Ar = 3,5-$(CF_3)_2C_6H_3$



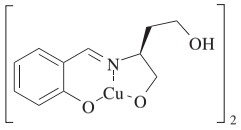

**353**



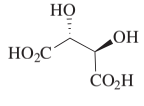

**354**



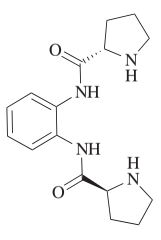

**355**



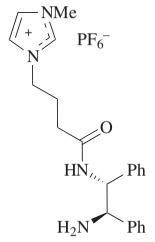

**356**



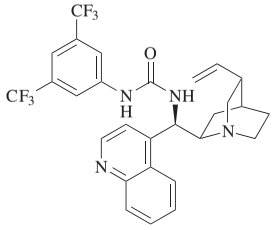

**357**



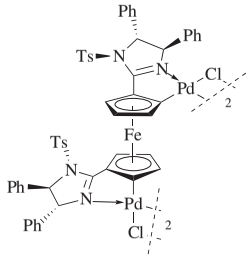
**359**



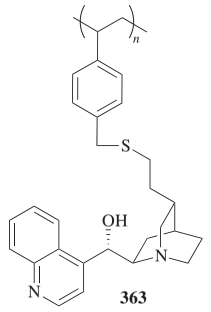
**360**



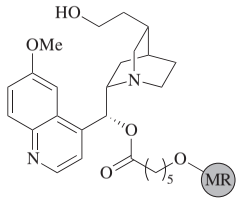
**361**



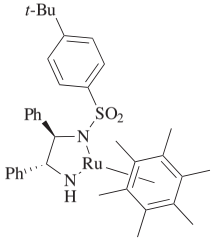
**362**



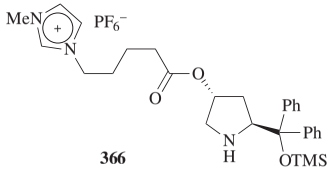
**363**



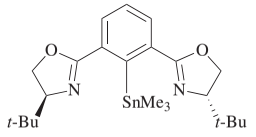
**364**



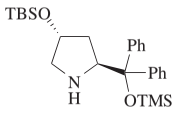
**365**



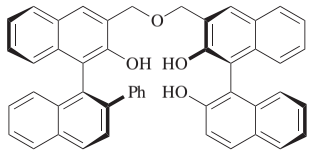
**366**



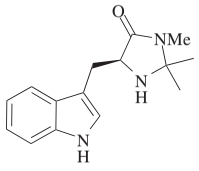
**367**



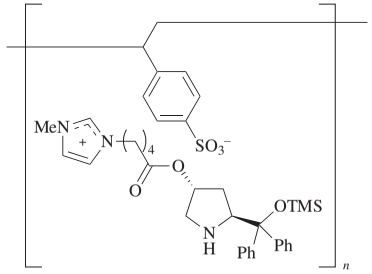
**368**



**369**

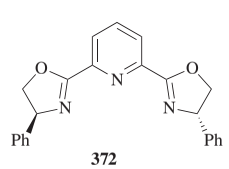


**370**

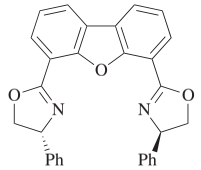


**371**

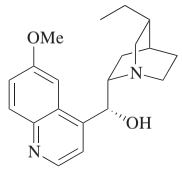
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



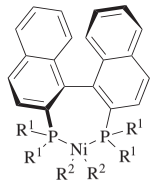
**372**



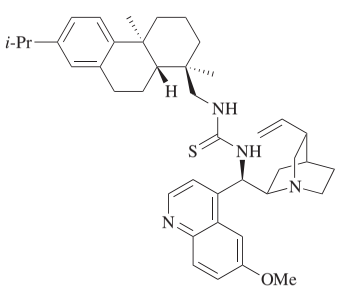
**373**



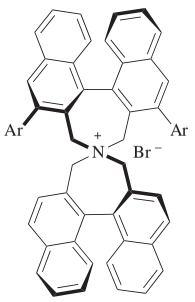
**374**



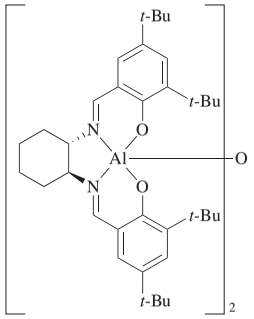
| | $R^1$ | $R^2$ |
|---|---|---|
| **375a** | 4-$MeC_6H_4$ | TfO |
| **375b** | 4-$MeC_6H_4$ | $BF_4$ |



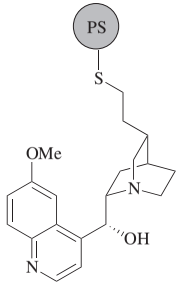
**376**



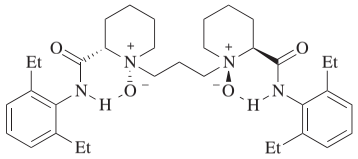
**377** Ar = 3,4,5-$F_3C_6H_2$



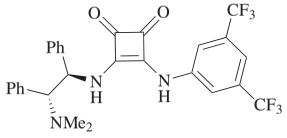
**378**



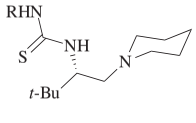
**379**



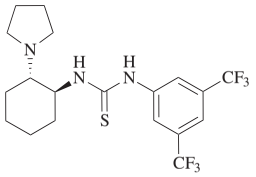
**380**



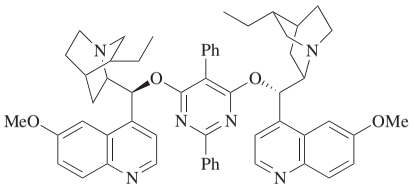
**381**



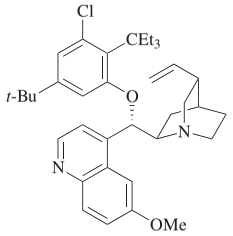
**382** R = 3,5-$(CF_3)_2C_6H_3$



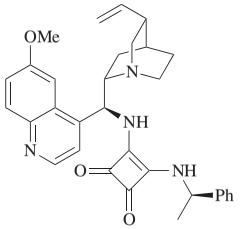
**383**



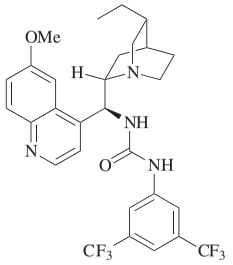
**384** $(DHQD)_2PYR$



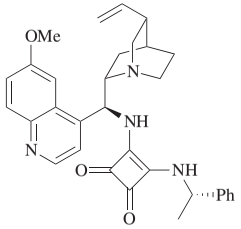
**385**



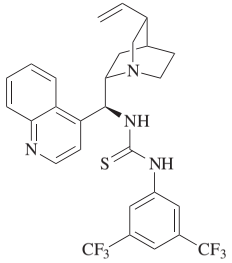
**386**



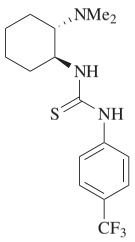
**387**



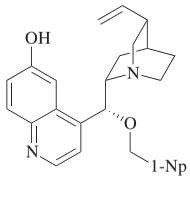
**388**



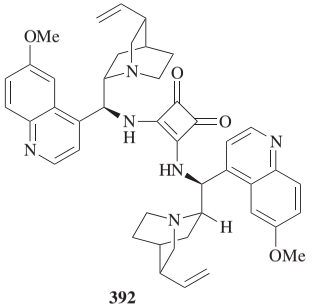
**389**



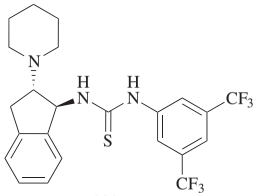
**390**



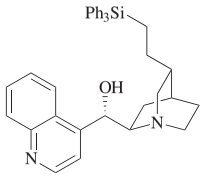
**391**



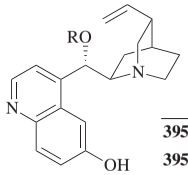
**392**



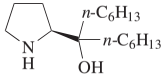
**393**



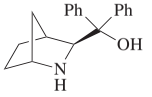
**394**



| | R |
|---|---|
| **395a** | Bn |
| **395b** | 2-Np |

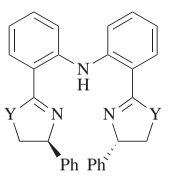


**396**

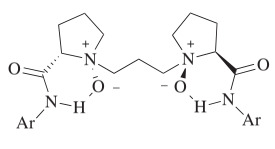


**397**

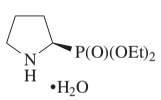
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



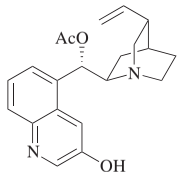
| | Y |
|---|---|
| **398a** | O |
| **398b** | S |



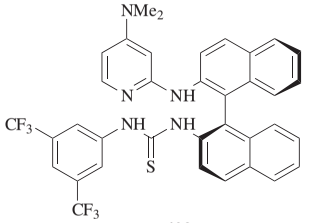
| | Ar |
|---|---|
| **399a** | Ph |
| **399b** | 2,6-$Et_2C_6H_3$ |



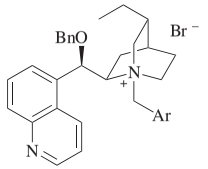
**400**



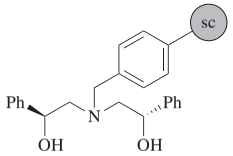
**401**



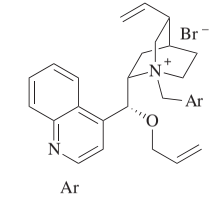
**402**



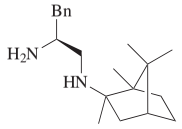
**403** Ar = anthracen-9-yl



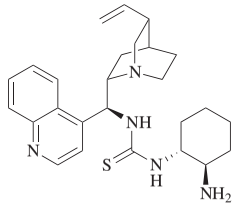
**404**



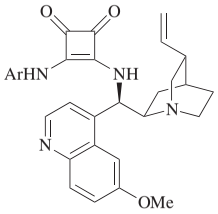
| | Ar |
|---|---|
| **405a** | 3,5-(*t*-BuO)$_2$-4-MeOC$_6$H$_2$ |
| **405b** | anthracen-9-yl |



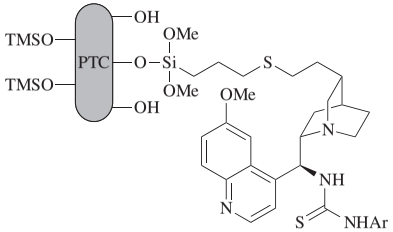
**406**



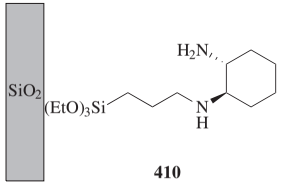
**407**



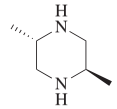
**408** Ar = 3,5-$(CF_3)_2C_6H_3$



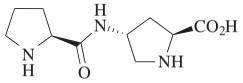
**409** Ar = 3,5-$(CF_3)_2C_6H_3$



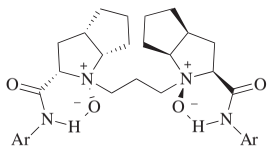
**410**



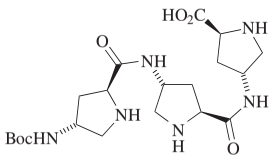
**411**



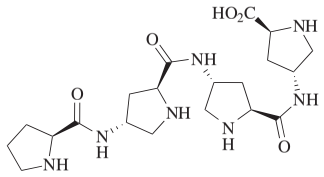
**412**



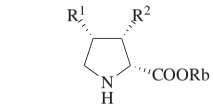
**413** Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$



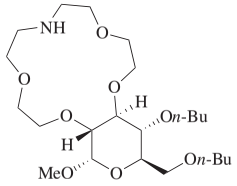
**414**



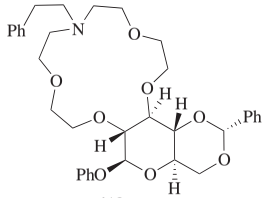
**415**



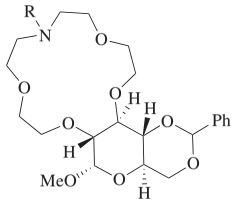
| | $R^1$ | $R^2$ |
|---|---|---|
| **416a** | TBSO | H |
| **416b** | TBSO | TBSO |
| **416c** | TBDPSO | TBDPSO |



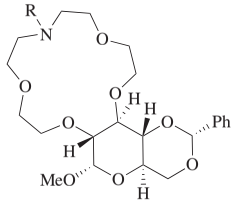
**417**



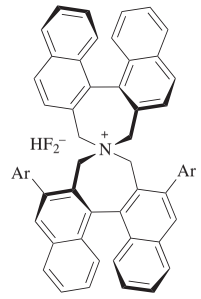
**418**



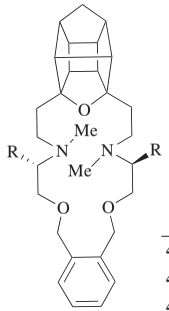
| | R |
|---|---|
| **419a** | H |
| **419b** | $(EtO)_2(O)PCH_2$ |
| **419c** | $(EtO)_2(O)P(CH_2)_2$ |
| **419d** | $(EtO)_2(O)P(CH_2)_3$ |
| **419e** | $(EtO)_2(O)P(CH_2)_4$ |
| **419f** | $(EtO)_2(O)P(CH_2)_5$ |



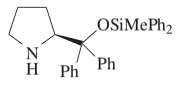
| | R |
|---|---|
| **420a** | H |
| **420b** | $HO(CH_2)_2$ |
| **420c** | $MeO(CH_2)_2$ |
| **420d** | $HO(CH_2)_3$ |
| **420e** | $Ph_2(O)P(CH_2)_4$ |



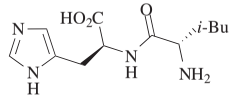
**421** Ar = 3,5-[3,5-(CF$_3$)$_2$C$_6$H$_3$]C$_6$H$_3$



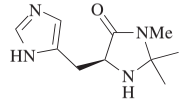
| | R |
|---|---|
| **422a** | *i*-Pr |
| **422b** | *i*-Bu |
| **422c** | Ph |



**423**

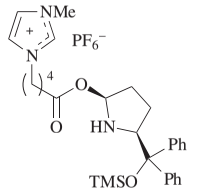


**424**

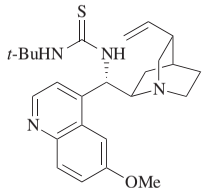


**425**

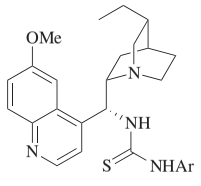
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



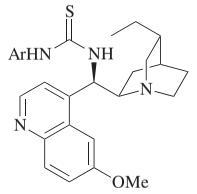
**426**



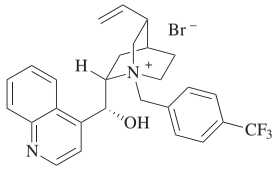
**427**



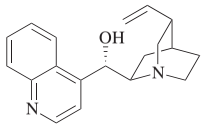
**428** Ar = 3,5-$(CF_3)_2C_6H_3$



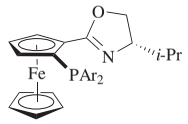
**429** Ar = 3,5-$(CF_3)_2C_6H_3$



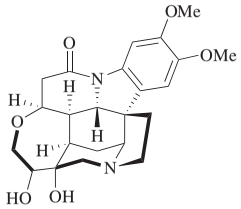
**430**



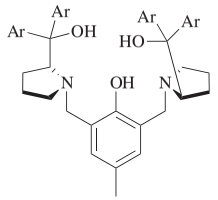
**431**



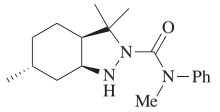
| | Ar |
|---|---|
| **432a** | $C_4H_4N$ |
| **432b** | 3,5-$(CF_3)_2C_6H_3$ |



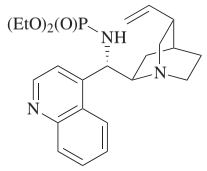
**433**



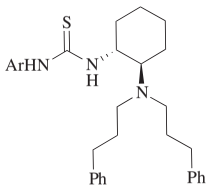
| | Ar |
|---|---|
| **434a** | Ph |
| **434b** | 2-Np |



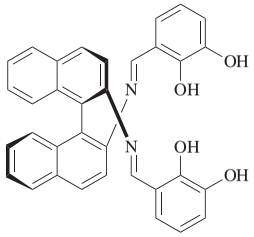
**435**



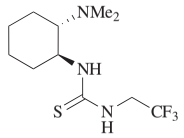
**436**



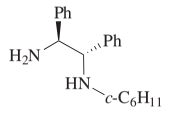
**437** Ar = 3,5-$(CF_3)_2C_6H_3$



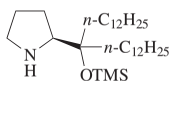
**438**



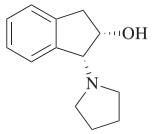
**439**



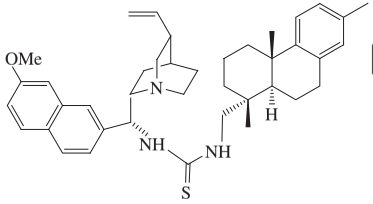
**440**



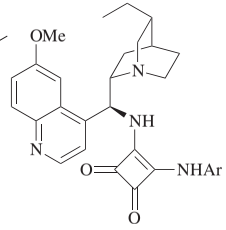
**441**



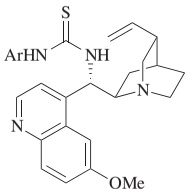
**442**



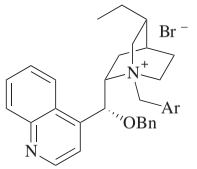
**443**



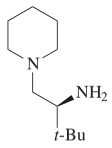
**444** Ar = 3,5-$(CF_3)_2C_6H_3$



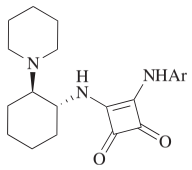
**445** Ar = 3,5-$(CF_3)_2C_6H_3$



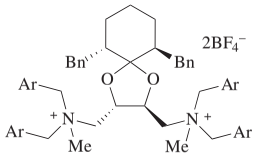
**446** Ar = anthracen-9-yl



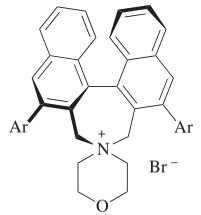
**447**



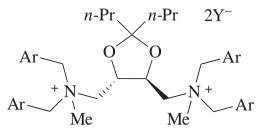
**448** Ar = 3,5-$(CF_3)_2C_6H_3$



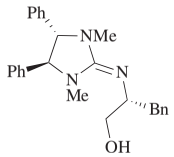
**449** Ar = 4-$MeC_6H_4$



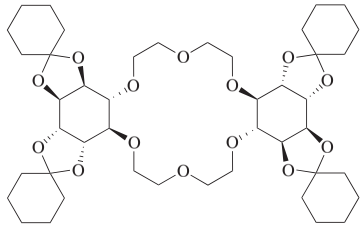
**450** Ar = 3,5-(3,4,5-$F_3C_6H_2)_2C_6H_3$



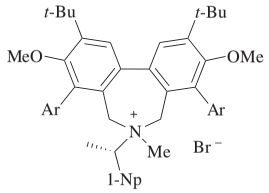
| | Y | Ar |
|---|---|---|
| **451a** | I | 4-$MeC_6H_4$ |
| **451b** | $BF_4$ | 4-$MeC_6H_4$ |



**452**

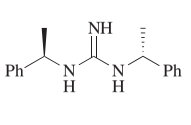


**453**

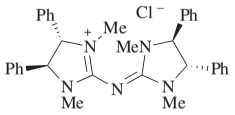


**454** Ar = 3,5-$(CF_3)_2C_6H_3$

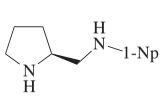
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



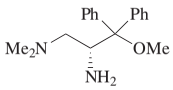
**455**



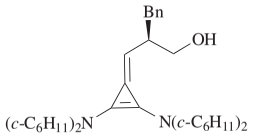
**456**



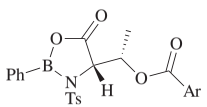
**457**



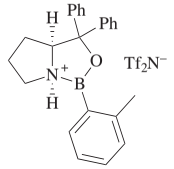
**458**



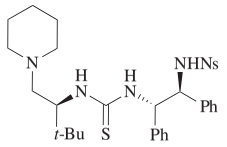
**459**



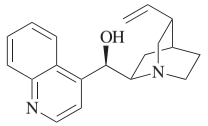
| Ar | |
|---|---|
| **460a** | 2-Np |
| **460b** | 4-PhC$_6$H$_4$ |



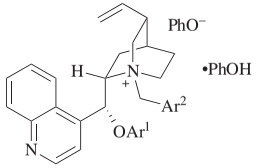
**461**



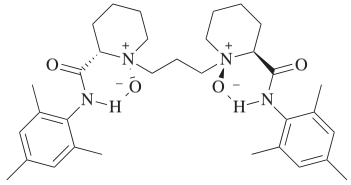
**462**



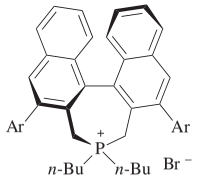
**463**



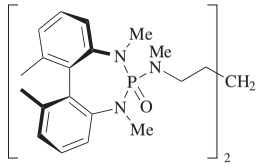
**464** Ar$^1$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$CH$_2$
Ar$^2$ = anthracen-9-yl



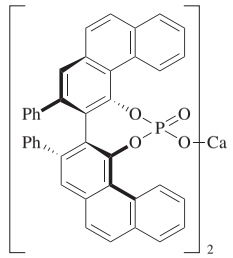
**465**



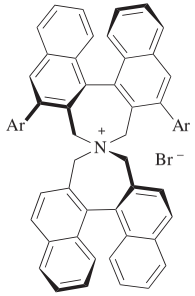
**466** Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$



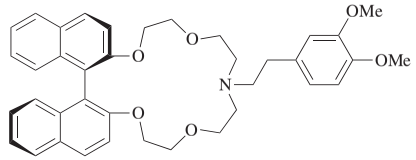
**467**



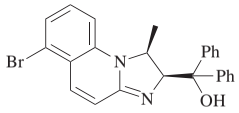
**468**



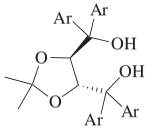
**469** R = 3,5-[3,5-$(CF_3)_2C_6H_3]_2C_6H_3$



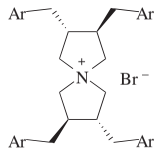
**470**



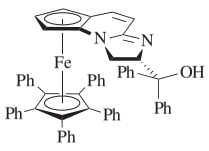
**471**



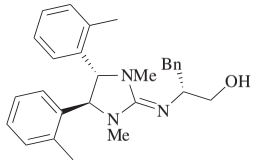
| | Ar |
|---|---|
| **472a** | Ph |
| **472b** | 1-Np |



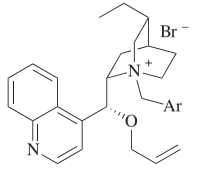
**473** Ar = 4-$CF_3C_6H_4$



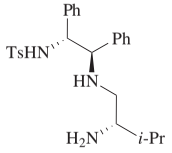
**474**



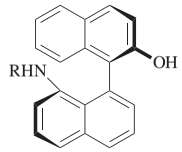
**475**



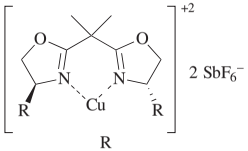
**476** Ar = anthracen-9-yl



**477**

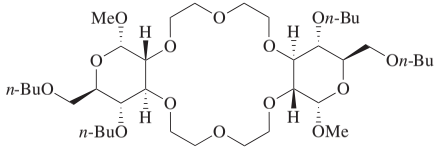


| | R |
|---|---|
| **478a** | H |
| **478b** | Ac |
| **478c** | Piv |
| **478d** | (1-Ad)CO |

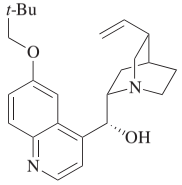


| | R |
|---|---|
| **479a** | Ph |
| **479b** | 1-Np |
| **479c** | 2-Np |

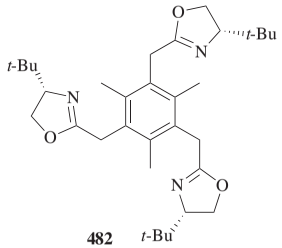
CHART 1. CATALYSTS AND LIGANDS USED IN TABLES (*Continued*)



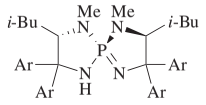
**480**



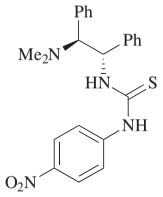
**481**



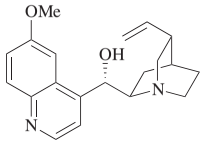
**482**



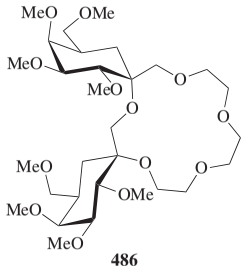
**483** Ar = 4-$FC_6H_4$



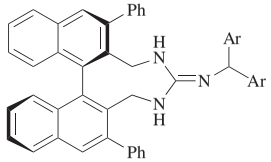
**484**



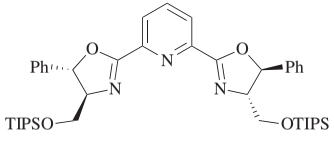
**485**



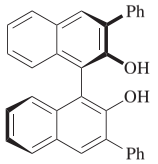
**486**



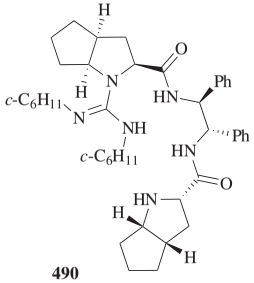
**487** Ar = 3,4,5-$(MeO)_3C_6H_2$



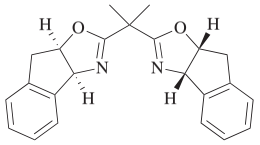
**488**



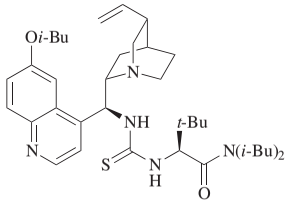
**489**



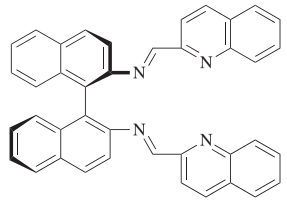
**490**



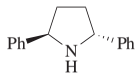
**491**



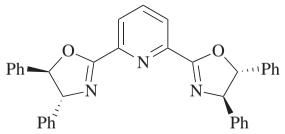

**492**



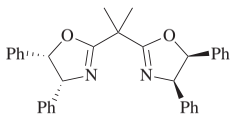

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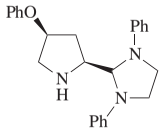

**494**



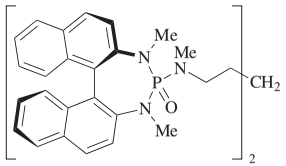

**495**




**496**

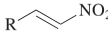
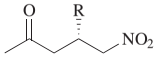
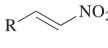
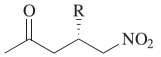
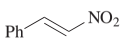
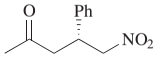
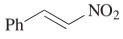
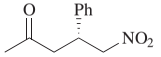
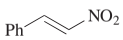
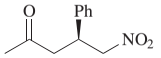
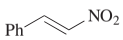
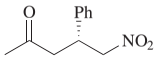
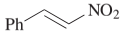
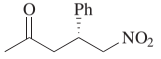


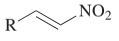

**497**

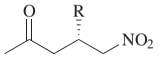



**498**

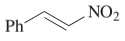
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS
A. NITROALKENES AS ACCEPTORS

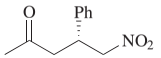
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **1** (20 mol %), DMSO, rt |  R: *i*-Pr (80) er 50.0:50.0; Ph (80) er 50.0:50.0 | 249 |
| |  | **1** (15 mol %), DMSO, rt, 2–24 h |  R: *i*-Pr (87) —; *i*-PrCH=CH (85) —; Ph (97) 53.5:46.5 | 136 |
| |  | **1** (20 mol %), MeOH, rt, 2 d |  (93) er 56.0:44.0 | 137 |
| |  | **2** (15 mol %), DMSO, rt, 2–24 h |  (68) er 70.0:30.0 | 136 |
| |  | **3** (15 mol %), additive (*x* mol %), $CHCl_3$, rt, 15 h |  Additive: none 0 (29) 64.5:35.5; PTSA 15 (74) 61.5:38.5; HCl 15 (82) 62.5:37.5 | 250, 251 |
| |  | **5** (10 mol %), TFA (10 mol %), brine, rt, 24 h |  (87) er 66.0:34.0 | 252 |
| |  | **6** (20 mol %), THF, rt |  (81) er 67.5:32.5 | 253 |



**11** (15 mol %), toluene, rt  254

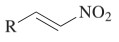
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3S$ | 48 | (57) | 92.0:8.0 |
| Ph | 40 | (55) | 93.5:6.5 |
| 4-$BrC_6H_4$ | 48 | (62) | 91.5:8.5 |
| 4-$MeOC_6H_4$ | 48 | (46) | 93.0:7.0 |

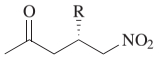


Catalyst (15 mol %), TFA (5 mol %), rt, 12 h 

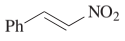
| Catalyst | | er |
|---|---|---|
| **12** | (77) | 72.5:27.5 |
| **13** | (83) | 71.5:28.5 |

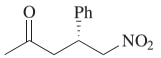
255



**14** (15 mol %), AcOH (15 mol %), $H_2O$ (2 eq), toluene, rt  256

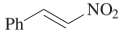
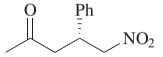
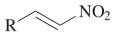
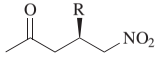
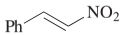
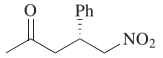
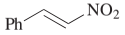
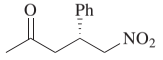
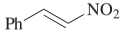
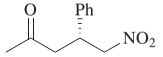
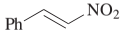
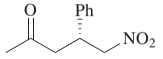
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3S$ | 25 | (87) | 96.0:4.0 |
| Ph | 16 | (85.5) | 93.0:7.0 |
| 4-$BrC_6H_4$ | 15 | (93) | 92.0:8.0 |
| 4-$MeOC_6H_4$ | 71 | (87) | 93.5:6.5 |

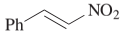


**15** (10 mol %), solvent, rt  257

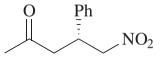
| Solvent | Time (h) | | er |
|---|---|---|---|
| $CHCl_3$ | 40 | (83) | 75.0:25.0 |
| $H_2O$ | 11 | (89) | 82.5:17.5 |
| TFA (2.5 mol %) | 17 | (93) | 72.5:27.5 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

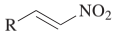
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **16b** (20 mol %), *i*-PrOH, 0°, 8 h |  (96) er 77.5:22.5 | 258 |
| |  | **17** (*x* mol %), $PhCO_2H$ (*y* mol %), toluene, rt, 48 h |  | 144 |
| | | R: Me; *x* 15; *y* 2; (70); er 99.0:1.0 | | |
| | | R: *n*-Bu; *x* 15; *y* 2; (78); er 97.5:2.5 | | |
| | | R: *i*-Bu; *x* 15; *y* 2; (81); er 97.0:3.0 | | |
| | | R: 2-$C_4H_3O$; *x* 10; *y* 10; (88); er 99.5:0.5 | | |
| | | R: 2-$C_4H_3S$; *x* 10; *y* 10; (94); er 98.0:2.0 | | |
| | | R: Ph; *x* 10; *y* 10; (93); er 99.5:0.5 | | |
| | | R: 4-$MeOC_6H_4$; *x* 10; *y* 10; (88); er 99.5:0.5 | | |
| | | R: 4-$MeC_6H_4$; *x* 10; *y* 10; (87); er 98.5:1.5 | | |
| |  | **18** (20 mol %), *n*-$PrCO_2H$ (10 mol %), neat, rt |  (80) er 74.0:26.0 | 259 |
| |  | **19** (20 mol %), 3-xylene, 0°, 12 h |  (57) er 84.5:15.5 | 260 |
| |  | **20** (15 mol %), 4-TsOH (15 mol %), rt, 10 h |  (99) er 86.5:13.5 | 260 |
| |  | **21** (20 mol %), $(CF_3SO)_2NH$ (20 mol %), *i*-PrOH, 0°, 20 h |  (24) er 76.5:23.5 | 261 |



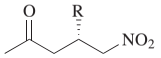
**22** (15 mol %), TFA (5 mol %), rt, 36 h



(95) er 70.0:30.0 262

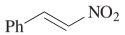


**23** (15 mol %), $H_2O$ (2 eq), AcOH (15 mol %), toluene, rt

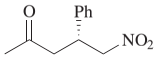


263

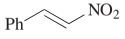
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3S$ | 50 | (98) | 95.0:5.0 |
| Ph | 48 | (98) | 95.5:4.5 |
| 4-$BrC_6H_4$ | 40 | (99) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 61 | (84) | 95.5:4.5 |



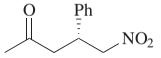
**24** (10 mol %), TFA (10 mol %) brine, rt, 6 h



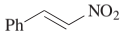
(89) er 58.0:42.0 119



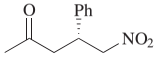
**25** (10 mol %), $Me_2PEG$ (10 mol %), $H_2O$, rt, 24 h



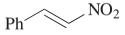
(40) er 63.0:37.0 264



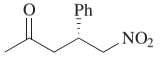
**26** (15 mol %), $CHCl_3$, rt, 16 h



(68) er 60.0:40.0 265



**27** (10 mol %), $PhCO_2H$ (10 mol %), $H_2O$, 35°, 64 h



(65) er 78.5:21.5 266

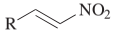
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

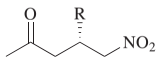
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$

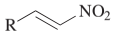




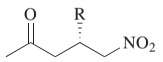
**28** (5 mol %), benzene, rt, 8 d



| R | | er | |
|---|---|---|---|
| Ph | (63) | 97.5:2.5 | 267 |
| 2-$BrC_6H_4$ | (63) | 99.0:1.0 | |
| 4-$BrC_6H_4$ | (59) | 97.0:3.0 | |
| 3-$ClC_6H_4$ | (55) | 97.5:2.5 | |
| 4-$ClC_6H_4$ | (57) | 97.5:2.5 | |
| 4-$MeOC_6H_4$ | (55) | 98.0:2.0 | |
| 2-$O_2NC_6H_4$ | (69) | 98.5:1.5 | |
| 4-$MeC_6H_4$ | (61) | 97.0:3.0 | |

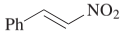
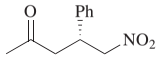
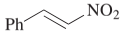
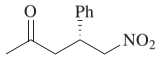
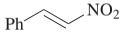
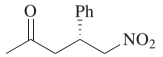
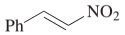
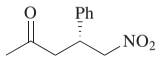
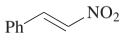
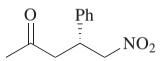
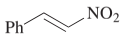
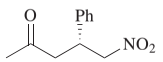
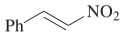
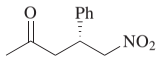
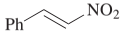
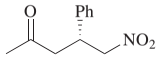
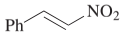
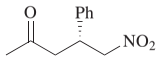


**29** (10 mol %), TBBP (10 mol %), neat, rt



268

| R | Time (h) | | er |
|---|---|---|---|
| *i*-Pr | 54 | (30) | 90.5:9.5 |
| 2-$C_3H_4O$ | 24 | (89) | 98.0:2.0 |
| Ph | 24 | (85) | 97.5:2.5 |
| 4-$BrC_6H_4$ | 24 | (88) | 96.5:3.5 |
| 2-$ClC_6H_4$ | 24 | (96) | 97.5:2.5 |
| 3-$ClC_6H_4$ | 24 | (90) | 96.0:4.0 |
| 2,4-$Cl_2C_6H_4$ | 24 | (80) | 96.5:3.5 |
| 2-$MeOC_6H_4$ | 24 | (92) | 98.0:2.0 |
| 3-$MeOC_6H_4$ | 24 | (88) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 24 | (90) | 98.0:2.0 |
| 2-$O_2NC_6H_4$ | 24 | (95) | 95.0:5.0 |
| 4-$NCC_6H_4$ | 24 | (83) | 95.0:5.0 |
| 1-Np | 24 | (99) | 96.5:3.5 |

| | | | | |
|---|---|---|---|---|
|  | **30** (10 mol %), TFA (1.7 mol %), neat, 0°, 36 h |  | (68) er 79.0:21.0 | 269 |
|  | **31** (10 mol %), rt |  | (95) er 70.0:30.0 | 270 |
|  | **32** (10 mol %), TFA (2.5 mol %), rt |  | (65) er 69.0:31.0 | 271 |
|  | **33** (10 mol %), toluene, rt, 36 h |  | (21) er 60.0:40.0 | 272 |
|  | **34** (20 mol %), 2-$HOC_6H_4CO_2H$ (20 mol %), *i*-PrOH, rt |  | (82) er 78.0:22.0 | 273 |
|  | **34** (5 mol %), **35** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h |  | (95)[a] er 82.0:18.0 | 274 |
|  | **36** (10 mol %), TFA (2 mol %), neat, 17 h |  | (85) er 76.0:24.0 | 275 |
|  | Catalyst (15 mol %), TFA (5 mol %), neat, rt |  | | 276 |
|  | **41** (10 mol %), neat, rt, 36 h |  | (92) er 76.0:24.0 | 277 |

| Catalyst | Time (h) | | er |
|---|---|---|---|
| **39** | 72 | (82) | 67.5:32.5 |
| **40** | 36 | (90) | 70.0:30.0 |

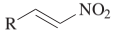
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

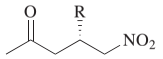
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





**42** (30 mol %),
$PhCO_2H$ (*x* mol %),
toluene, 4 d

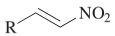


278

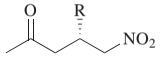
Catalyst Recycling (R = Ph)

| Run | Temp | | er |
|---|---|---|---|
| 1 | rt | (60) | 91.0:9.0 |
| 2 | rt | (58) | 92.0:8.0 |
| 3 | rt | (56) | 92.0:8.0 |

| R | Temp | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | rt | (30) | 96.0:4.0 |
| Ph | 50° | (65) | 91.0:9.0 |
| 4-$MeOC_6H_4$ | rt | (28) | 93.0:7.0 |

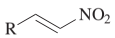


**42** (30 mol %),
$PhCO_2H$ (20 mol %),
toluene, rt, 4 d

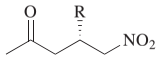


| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (30) | 96.0:4.0 |
| Ph | (60) | 91.5:8.5 |
| 2,4-$Cl_2C_6H_3$ | (73) | 91.0:9.0 |

279

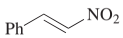


**43** (15 mol %),
AcOH (15 mol %),
$H_2O$ (2 eq),
toluene, rt, 48 h

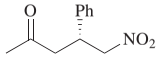


| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (94) | 96.0:4.0 |
| Ph | (100) | 95.5:4.5 |
| 4-$FC_6H_4$ | (99) | 94.0:6.0 |
| 4-$MeOC_6H_4$ | (69) | 95.5:4.5 |
| 4-$O_2NC_6H_4$ | (94) | 94.0:6.0 |

280

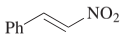


**44** (15 mol %),
2-NpOH (5 mol %),
THF, rt, 48 h

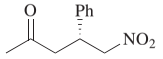


(85) er 78.5:21.5

281

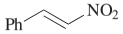


**45** (20 mol %),
$Et_3N$ (20 mol %),
*n*-$PrCO_2H$ (10 mol %), rt

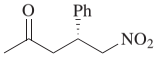


(75) er 70.0:30.0

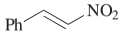
282



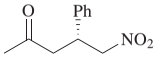
**46** (30 mol %), NaOH (30 mol %), $H_2O$, rt



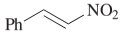
(23) er 60.0:40.0 283



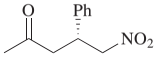
**47** (10 mol %), *i*-PrOH, rt, 36 h



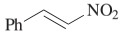
(75) er 57.0:43.0 284



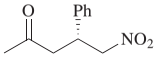
**48** (10 mol %) neat, rt, 16 h



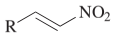
(95) er 73.5:26.5 285



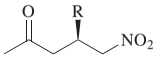
**49** (10 mol %), $Et_3N$ (10 mol %), *i*-PrOH/EtOH (1:1), rt, 24 h



(87) er 74.0:26.0 286



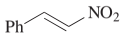
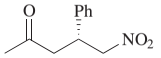
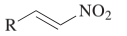
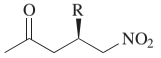
**50** (5 mol %), AcOH, $CH_2Cl_2$, rt



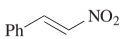
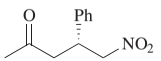
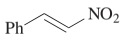
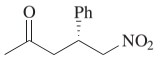
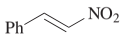
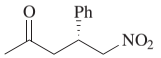
287

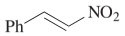
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 15 | (80) | 98.0:2.0 |
| Ph | 60 | (91) | 96.0:4.0 |
| 4-$BrC_6H_4$ | 36 | (91) | 96.5:3.5 |
| 2-$ClC_6H_4$ | 36 | (93) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 36 | (92) | 97.5:2.5 |
| 2,4-$Cl_2C_6H_3$ | 60 | (91) | 95.5:4.5 |
| 4-$FC_6H_4$ | 36 | (92) | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 60 | (91) | 96.5:3.5 |
| 2-$O_2NC_6H_4$ | 60 | (92) | 96.0:4.0 |
| 3-$O_2NC_6H_4$ | 30 | (90) | 94.0:6.0 |
| 4-$O_2NC_6H_4$ | 20 | (94) | 95.0:5.0 |
| 4-$MeC_6H_4$ | 60 | (92) | 96.5:3.5 |
| 4-$CF_3C_6H_4$ | 96 | (76) | 95.5:4.5 |
| 4-$NCC_6H_4$ | 60 | (92) | 95.5:4.5 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

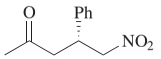
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **51** (10 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), $H_2O$, rt, 72 h |  (39) er 95.0:5.0 | 288 |
| |  | **52** (20 mol %), $Et_2O$, rt, 48 h |  | 289 |

| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (95) | 78.0:22.0 |
| 2-$C_4H_3S$ | (91) | 92.0:8.0 |
| Ph | (96) | 90.5:9.5 |
| 4-$ClC_6H_4$ | (97) | 77.5:22.5 |
| 3-$FC_6H_4$ | (98) | 75.0:25.0 |
| 3,4-$(MeO)_2C_6H_3$ | (87) | 80.5:19.5 |
| 3,4,5-$(MeO)_3C_6H_2$ | (98) | 72.0:28.0 |
| 4-$MeC_6H_4$ | (95) | 86.0:14.0 |
| 1-Np | (99) | 88.0:12.0 |
| 6-MeO-1-$C_{10}H_6$ | (62) | 79.5:20.5 |

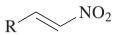
| | | | | |
|---|---|---|---|---|
| |  | **53** (10 mol %), neat, rt, 24 h |  (93) er 81.5:18.5 | 290 |
| |  | **54** (20 mol %), [bmim][$BF_4$], rt, 90 h |  (81) er 70.0:30.0 | 291 |
| |  | **55** (10 mol %), rt |  (77) er 67.0:33.0 | 292 |



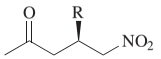
**56** (5 mol %),
4-$O_2NC_6H_4CO_2H$
(15 mol %), THF, rt, 72 h



(90) er 99.5:0.5 293



**57** (20 mol %),
4-$HO_2CC_6H_4CO_2H$
(20 mol %), toluene, rt



294

| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (96) | 99.0:1.0 |
| 2-$C_4H_3S$ | (98) | 98.0:2.0 |
| Ph | (99) | 97.5:2.5 |
| 2-$BrC_6H_4$ | (87) | 98.5:1.5 |
| 4-$BrC_6H_4$ | (99) | 98.0:2.0 |
| 2-$ClC_6H_4$ | (90) | 98.5:1.5 |
| 4-$ClC_6H_4$ | (94) | 98.0:2.0 |
| 3-$FC_6H_4$ | (92) | 97.0:3.0 |
| 4-$FC_6H_4$ | (87) | 98.0:2.0 |
| 2-$MeOC_6H_4$ | (94) | 99.0:1.0 |
| 4-$MeOC_6H_4$ | (85) | 98.5:1.5 |
| 3,4-$(MeO)_2C_6H_3$ | (91) | 98.5:1.5 |
| 3,4,5-$(MeO)_3C_6H_2$ | (84) | 98.0:2.0 |
| 3,4-$(OCH_2O)C_6H_3$ | (91) | 98.5:1.5 |
| 2-$O_2NC_6H_4$ | (99) | 98.5:1.5 |
| 3-$O_2NC_6H_4$ | (90) | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | (92) | 98.0:2.0 |
| 1-Np | (97) | 97.0:3.0 |
| 6-MeO-1-$C_{10}H_6$ | (88) | 96.5:3.5 |

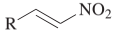
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

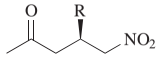
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



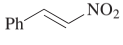


**58** (20 mol %), $C_6H_5OH$ (10 mol %), toluene

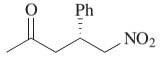


295

| R | Temp (°) | Time (h) | | er |
|---|---|---|---|---|
| Et | rt | 72 | (81) | 91.5:8.5 |
| 2-$C_4H_3O$ | 0 | 96 | (86) | 97.0:3.0 |
| 2-$C_4H_3S$ | 0 | 120 | (96) | 97.5:2.5 |
| Ph | 0 | 72 | (>99) | 96.5:3.5 |
| 2-$BrC_6H_4$ | 0 | 96 | (99) | 98.5:1.5 |
| 4-$BrC_6H_4$ | 0 | 120 | (96) | 97.0:3.0 |
| 2-$ClC_6H_4$ | 0 | 84 | (99) | 98.0:2.0 |
| 4-$ClC_6H_4$ | 0 | 69 | (95) | 96.5:3.5 |
| 2,4-$Cl_2C_6H_3$ | 0 | 96 | (98) | 98.5:1.5 |
| 2-$MeOC_6H_4$ | 0 | 120 | (82) | 96.5:3.5 |
| 3-$MeOC_6H_4$ | 0 | 96 | (95) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 0 | 120 | (80) | 97.0:3.0 |
| 2-$O_2NC_6H_4$ | 0 | 108 | (25) | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | 0 | 84 | (72) | 98.0:2.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 0 | 42 | (99) | 97.5:2.5 |
| 4-$MeC_6H_4$ | 0 | 144 | (91) | 96.5:3.5 |
| 2-$CF_3C_6H_4$ | 0 | 42 | (97) | 96.5:3.5 |
| 3-$CF_3C_6H_4$ | 0 | 108 | (93) | 97.0:3.0 |
| $BnCH_2$ | 20 | 72 | (82) | 93.5:6.5 |
| PhCH=CH | 20 | 72 | (85) | 96.5:3.5 |
| 1-Np | 0 | 168 | (90) | 98.5:1.5 |

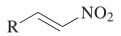


**60** (10 mol %), $NaHCO_3$ (50 mol %), [bmin][$BF_4$], rt, 48 h

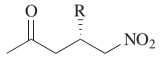


(97) er 96.5:3.5

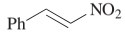
296



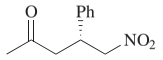
**61** (10 mol %), $PhCO_2H$ (10 mol %), brine, rt, 12 h



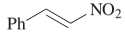
| R | | er | |
|---|---|---|---|
| Ph | (94) | 90.5:9.5 | 297 |
| 4-$MeOC_6H_4$ | (86) | 90.0:10.0 | |



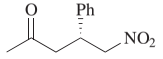
**62** (10 mol %), TFA (2 mol %), neat, rt, 24 h



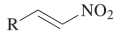
(67) er 69.5:30.5 298



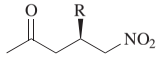
**63** (10 mol %), 2,4-$(O_2N)_2C_6H_3CO_2H$ (10 mol %), toluene, rt, 72 h



(85) er 70.5:29.5 299



**64** (20 mol %), toluene, 20°



300

| R | Time (h) | | er |
|---|---|---|---|
| Et | 72 | (85) | 98.5:1.5 |
| *n*-Pr | 67 | (86) | 98.5:1.5 |
| *i*-Bu | 72 | (95) | 99.0:1.0 |
| 2-$C_4H_3O$ | 21 | (98) | 99.0:1.0 |
| 2-$C_4H_3S$ | 36 | (>99) | 99.0:1.0 |
| *c*-$C_6H_{11}$ | 72 | (75) | 99.0:1.0 |
| Ph | 36 | (>99) | 99.0:1.0 |
| 2-$BrC_6H_4$ | 24 | (99) | 99.5:0.5 |
| 2-$ClC_6H_4$ | 21 | (>99) | 99.5:0.5 |
| 4-$ClC_6H_4$ | 24 | (95) | 99.0:1.0 |
| 2-$MeOC_6H_4$ | 59 | (99) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 36 | (94) | 99.5:0.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 36 | (90) | 99.0:1.0 |
| 2-$O_2NC_6H_4$ | 21 | (95) | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | 16 | (>99) | >99.5:0.5 |
| 2-$CF_3C_6H_4$ | 36 | (91) | >99.5:0.5 |
| $BnCH_2$ | 108 | (>99) | 98.5:1.5 |
| (*E*)-PhCH=CH | 48 | (90) | 99.0:1.0 |
| 1-Np | 20 | (>99) | 99.5:0.5 |

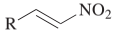
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

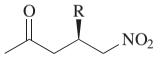
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



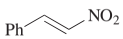


**64** (5 mol %), 4-$O_2NC_6H_4OH$ (10 mol %), toluene, 20°

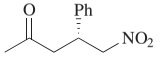


300

| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 49 | (93) | 99.0:1.0 |
| 2-$C_4H_3S$ | 60 | (87) | 99.0:1.0 |
| Ph | 31 | (>99) | 99.5:0.5 |
| 2-$BrC_6H_4$ | 40 | (97) | >99.5:0.5 |
| 2-$ClC_6H_4$ | 41 | (>99) | >99.5:0.5 |
| 4-$ClC_6H_4$ | 36 | (90) | 99.0:1.0 |
| 2-$MeOC_6H_4$ | 49 | (92) | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 60 | (99) | 99.0:1.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 60 | (86) | 99.5:0.5 |
| 2-$O_2NC_6H_4$ | 75 | (67) | 99.5:0.5 |
| 4-$O_2NC_6H_4$ | 22 | (>99) | 99.5:0.5 |
| 2-$CF_3C_6H_4$ | 60 | (90) | >99.5:0.5 |
| 1-Np | 48 | (94) | 99.0:1.0 |

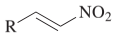


**65** (5 mol %), MeOH, rt

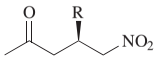


(94) er 75.5:24.5

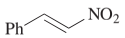
301



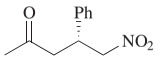
**66** (10 mol %), toluene, 4 Å MS, 5°, 8 d



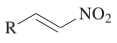
| R | | er | |
|---|---|---|---|
| 2-$C_4H_3O$ | (80) | 99.5:0.5 | 302 |
| Ph | (83) | 99.0:1.0 | |
| 4-$BrC_6H_4$ | (71) | 99.5:0.5 | |
| 2-$ClC_6H_4$ | (76) | 99.5:0.5 | |
| 4-$ClC_6H_4$ | (75) | 99.5:0.5 | |
| 4-$FC_6H_4$ | (73) | 99.5:0.5 | |
| 4-$MeOC_6H_4$ | (79) | 99.5:0.5 | |
| 2-$O_2NC_6H_4$ | (92) | 99.5:0.5 | |
| 3-$O_2NC_6H_4$ | (91) | 99.5:0.5 | |
| 4-$O_2NC_6H_4$ | (77) | 99.5:0.5 | |
| 4-$MeC_6H_4$ | (91) | 99.5:0.5 | |
| 4-$CF_3C_6H_4$ | (75) | 99.5:0.5 | |
| 4-$NCC_6H_4$ | (82) | 99.5:0.5 | |



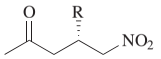
**67** (10 mol %), $CCl_3CO_2H$ (10 mol %), brine, rt, 28 h



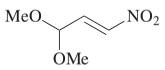
(74) er 62.5:37.5 303



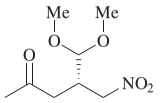
**68** (30 mol %), $PhCO_2H$ (20 mol %), toluene, rt, 4 d



| R | | er | |
|---|---|---|---|
| 2-$C_4H_3O$ | (99) | 98.5:1.5 | 279 |
| Ph | (99) | 95.5:4.5 | |

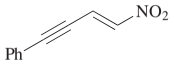
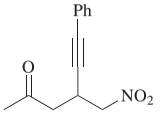
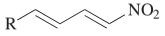
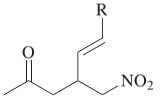


**16a** (10 mol %), *i*-PrOH, rt

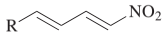
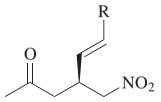


(56) er 85.0:15.0 116

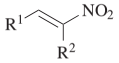
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

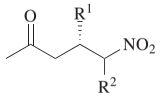
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$  |  | **59** (15 mol %), $PhCO_2H$ (5 mol %), $CH_2Cl_2$, rt, 6 d |  (85) er 97.0:3.0 | 304 |
|  | | **59** (15 mol %), $PhCO_2H$ (5 mol %), $CH_2Cl_2$, rt, 6 d |  | 304 |

| R | | er |
|---|---|---|
| Ph | (75) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | (70) | 95.5:4.5 |
| 2-$O_2NC_6H_4$ | (78) | 92.0:8.0 |

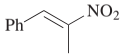
| | | | 305 |
|---|---|---|---|
|  | **70** (15 mol %), AcOH (*x* mol %), $CHCl_3$, 80° |  | |

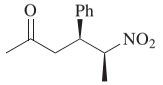
| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| Ph | 0 | 48 | (99) | 99.0:1.0 |
| 4-$ClC_6H_4$ | 0 | 48 | (86) | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 0 | 24 | (77) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 10 | 24 | (92) | 99.5:0.5 |
| 2-$O_2NC_6H_4$ | 0 | 24 | (58) | 96.0:4.0 |
| 2-$O_2NC_6H_4$ | 10 | 24 | (95) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | 10 | 48 | (94) | 98.0:2.0 |



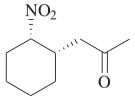
**5** (20 mol %), THF, rt  253

| $R^1$ | $R^2$ | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|
| Ph | H | 17 | (61) | — | 78.0:22.0 |
| Ph | Me | 26 | (54) | 62:38 | 85.0:15.0 |
| 2-$CF_3C_6H_4$ | H | 48 | (97) | — | 86.0:14.0 |

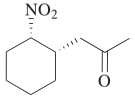


**64** (20 mol %), toluene, 20°, 7 d  (98) *syn/anti* = 85:15, er 96.5:3.5 300



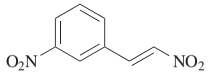
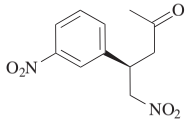
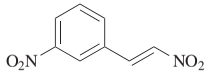
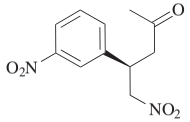
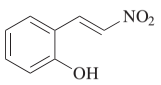
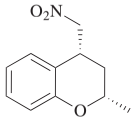
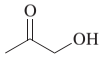
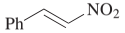
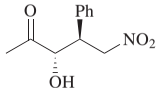
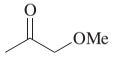
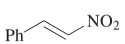
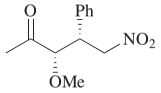
**1** (15 mol %), DMSO, rt, 2–24 h  (95) dr 10:1, er 59.5:40.5 136

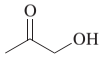


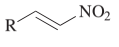
Catalyst (15 mol %), TFA (5 mol %), rt, 24 h  255

| Catalyst | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| **12** | (57) | 83:17 | 89.5:10.5 | 90.5:9.5 |
| **13** | (92) | 85:15 | 88.0:12.0 | 90.0:10.0 |

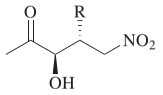
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **4** (15 mol %), EtOH/*i*-PrOH (1:1), 20°, 48 h |  (72) er 66.5:33.5 | 306, 307 |
| |  | **7** (20 mol %), **10** (20 mol %), $CDCl_3$, rt, 48 h |  (99) er 84.0:16.0 | 308 |
| |  | 1. **69b** (5 mol %), *ent*-**1** (5 mol %), 0.5 M in $CH_2Cl_2$, rt, 5 h<br>2. $Et_3SiH$, $BF_3{\bullet}OEt_2$, 0.1 M in $CH_2Cl_2$, −10° to rt, 2 h |  (93) dr >99.5:0.5<br>er 97.0:3.0 | 309 |
|  |  | **3** (15 mol %), microwaves (15 W), 28°, 4 h |  (83) *anti*/*syn* = 89:11<br>er 99.0:1.0 | 310 |
|  |  | *ent*-**3** (15 mol %), $CHCl_3$, rt, 2 d |  (75) *syn*/*anti* = 83:17<br>er 84.5:15.5 | 311, 251 |



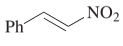


*ent*-**3** (15 mol %), $CHCl_3$, rt, 7 d

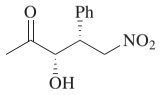


311, 251

| R | | *anti*/*syn* | er (*anti*) |
|---|---|---|---|
| 2-$C_4H_3S$ | (66) | 78:22 | 98.1:1.9 |
| Ph | (79) | 83:17 | 98.8:1.2 |
| 4-$ClC_6H_4$ | (81) | 87:13 | 98.9:1.1 |
| 2,4-$Cl_2C_6H_4$ | (85) | 91:9 | 99.3:0.7 |
| 2,6-$Cl_2C_6H_4$ | (83) | 84:16 | 99.0:1.0 |
| 3,4-$Cl_2C_6H_4$ | (66) | 88:12 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | (65) | 81:19 | 98.7:1.3 |
| 4-$MeC_6H_4$ | (68) | 84:16 | 98.8:1.2 |
| 2-$CF_3C_6H_4$ | (84) | 95:5 | 99.3:0.7 |
| 1-Np | (68) | 78:22 | 99.2:0.8 |

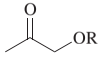


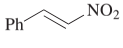
**5** (20 mol %), THF, rt, 17 h



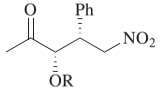
(81) *syn*/*anti* = 69:31

253





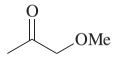
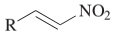
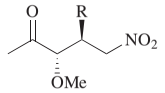
**16b** (20 mol %), *i*-PrOH, 0°



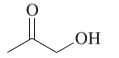
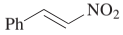
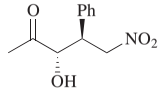
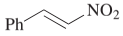
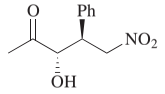
258

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| H | 48 | (46) | 3:1 | 73.0:27.0 |
| TBS | 18 | (89) | 14:1 | 93.0:7.0 |

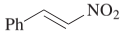
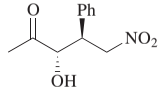
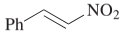
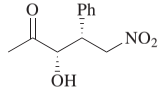
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

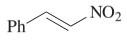
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **17** (20 mol %), $PhCO_2H$ (*x* mol %), toluene, rt |  | 144 |

| R | *x* | | rr | dr | er |
|---|---|---|---|---|---|
| *i*-Bu | 2 | (78) | 5:1 | 10:1 | 93.0:7.0 |
| Ph | 0 | (75) | >30:1 | 6:1 | 97.0:3.0 |

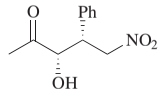
| | | | | |
|---|---|---|---|---|
|  |  | **64** (20 mol %), toluene, 20° |  (90) *syn/anti* = 26:74<br>er (*syn*) 94.0:6.0<br>er (*anti*) 99.0:1.0 | 300 |
| |  | **71** (30 mol %), $H_2O$ (10 eq), NMP/DMSO (1:1) |  | 312 |

| Temp (°) | Time (d) | | *syn/anti* | er |
|---|---|---|---|---|
| –20 | 2 | (23) | 1:2 | 70.0:30.0 |
| 4 | 3 | (60) | 1:2 | 64.5:34.5 |

| | | | |
|---|---|---|---|
|  | **72** (30 mol %), $H_2O$ (10 eq), 4-TsOH (15 mol %) NMP, 4° |  (83) *syn/anti* = 1:2<br>er 63.5:36.5 | 313 |
|  | **73** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (20 mol %), $CH_2Cl_2$, rt, 2 d |  (64) *syn/anti* = 65:35<br>er (*syn*) 70.5:29.5<br>er (*anti*) 67.5:32.5 | 314 |



Catalyst (20 mol %), $PhCO_2H$ (20 mol %), neat, rt, 12h

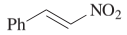


315

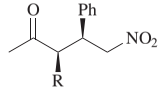
| Catalyst | | dr | er |
|---|---|---|---|
| **74** | (76) | 50:50 | 62.5:37.5 |
| **75** | (76) | 70:30 | 78.0:22.0 |

$C_{3-5}$



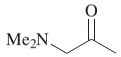


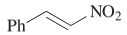
**79** (5 mol %), benzene, rt



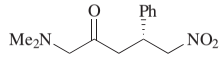
267

| R | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| MeO | 4 | (51) | 82:18 | 95.0:5.0 |
| Et | 3.5 | (72) | 90:10 | 97.0:3.0 |





Catalyst (15 mol %), $CHCl_3$, rt, 3 d



251

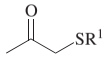
| Catalyst | | er |
|---|---|---|
| **1** | (24) | 81.5:18.5 |
| **3** | (52) | 81.0:19.0 |
| **6** | (83) | 87.5:12.5 |

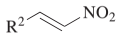
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

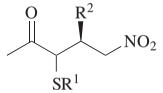
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



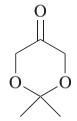


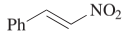
**76** (15 mol %), $PhCO_2H$ (15 mol %), toluene, 0–20°, 72 h



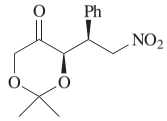
316

| $R^1$ | $R^2$ | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| Ph | *i*-Pr | (36) | 36:64 | 94.0:6.0 | 98.5:1.5 |
| Ph | 2-$C_4H_3O$ | (65) | 40:60 | 93.0:7.0 | 92.0:8.0 |
| Ph | Ph | (58) | 61:39 | 94.5:5.5 | 95.0:5.0 |
| Ph | 3-$BrC_6H_4$ | (62) | 27:73 | 92.0:8.0 | 88.0:12.0 |
| Ph | 4-$BrC_6H_4$ | (56) | 25:75 | 91.5:8.5 | 88.0:12.0 |
| Ph | 4-$ClC_6H_4$ | (51) | 30:70 | 90.5:9.5 | 89.0:11.0 |
| Ph | 4-$FC_6H_4$ | (62) | 20:80 | 92.0:8.0 | 95.0:5.0 |
| Ph | 2-$MeOC_6H_4$ | (63) | 60:40 | 96.0:4.0 | 95.0:5.0 |
| Ph | 4-$MeOC_6H_4$ | (68) | 70:30 | 91.0:9.0 | 91.5:8.5 |
| Ph | 4-$O_2NC_6H_4$ | (71) | 43:57 | 87.5:12.5 | 93.0:7.0 |
| Ph | 1-Np | (54) | 68:32 | 96.0:4.0 | 95.0:5.0 |
| Ph | 2-Np | (63) | 65:35 | 98.0:2.0 | 90.5:9.5 |
| 4-$MeC_6H_4$ | Ph | (60) | 35:65 | 92.5:7.5 | 94.0:6.0 |



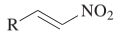


**77** (45 mol %), $H_2O$ (10 eq), NMP/DMSO (1:1), –20°, 3 d

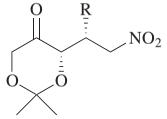


(30) *syn*/*anti* = 12:1
er 96.0:4.0

312



**78** (*x* mol %), $H_2O$ (*y* eq), *i*-PrOH, rt, 6–28 d

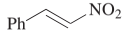


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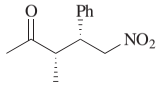
| R | *x* | *y* | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Me | 20 | 2 | (52) | >97:3 | 92.5:7.5 |
| $TBSOCH_2$ | 20 | 2 | (60) | >98:2 | — |
| $AcOCH_2$ | 20 | 2 | (15) | 97:3 | 93.0:7.0 |
| Et | 30 | 0 | (48) | 97:3 | 91.5:8.5 |
| 2-$C_4H_3O$ | 25 | 0 | (25) | 74:26 | 80.0:20.0 |
| Ph | 25 | 0 | (33) | 92:8 | 88.5:11.5 |
| 2-$ClC_6H_4$ | 25 | 0 | (16) | 88:12 | 90.5:9.5 |
| 3-$ClC_6H_4$ | 25 | 0 | (12) | 86:14 | 87.5:12.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 25 | 0 | (14) | 93:7 | 85.5:14.5 |

$C_4$



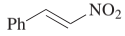


**1** (15 mol %), DMSO, rt, 2–24 h

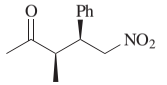


(85) rr >20:1, *syn*/*anti* = 3:1, er 55.0:45.0

136

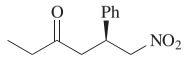


**3** (15 mol %), additive (*x* mol %), $CHCl_3$, rt



**I**

+

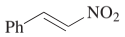
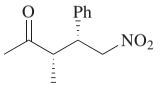
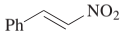
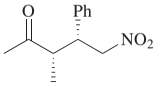
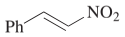
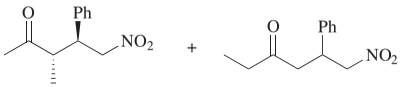
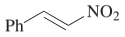
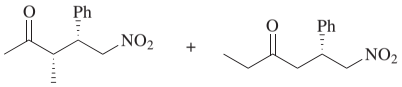
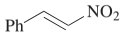
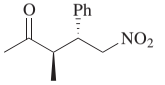


**II**

250, 251

| Additive | *x* | Time (d) | | **I**/**II** | *syn*/*anti* (**I**) | er **I** | er **II** |
|---|---|---|---|---|---|---|---|
| none | 0 | 3 | (61) | 43:57 | 85:15 | 66.0:34.0 | 85.0:15.0 |
| PTSA | 15 | 4 | (99) | 70:30 | 82:18 | 74.0:26.0 | 78.0:22.0 |
| HCl | 15 | 6 | (55) | 74:26 | 80:20 | 75.5:24.5 | 74.5:25.5 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **5** (20 mol %), THF, rt, 2 d |  (90) *syn*/*anti* = 88:12 er 84.0:16.0 | 253 |
| |  | **16b** (20 mol %), *i*-PrOH, 0°, 72 h |  (47) *syn*/*anti* = 1.1:1 er 76.5:23.5 | 258 |
| |  | **17** (20 mol %), $PhCO_2H$ (2 mol %), toluene, rt |  (78) rr 2:1, dr 15:1 (major regioisomer) er (major regioisomer) 98.5:1.5 er (minor regioisomer) 97.5:2.5 | 144 |
| |  | **18** (20 mol %), *n*-$PrCO_2H$ (10 mol %), neat, rt |  **I** **II** (90), **I**/**II** = 54:46 *syn*/*anti* **I** = 99:1 er **I** 85.0:15.0, er **II** 85.5:14.5 | 259 |
| |  | **23** (15 mol %), $H_2O$ (2 eq), AcOH (15 mol %), toluene, rt, 72 h |  (88) *anti*/*syn* = 86:14 er >99.5:0.5 | 263 |

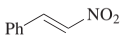
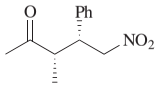
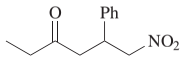
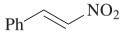
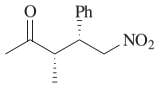
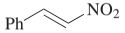
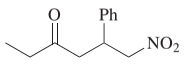
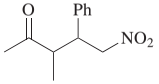
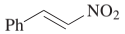
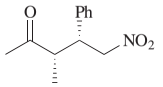
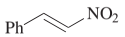
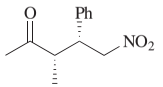
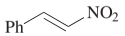
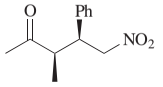
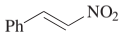
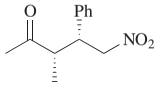
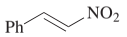
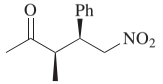
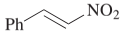
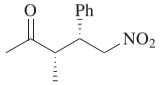
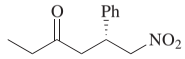
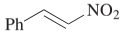
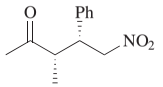
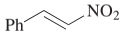
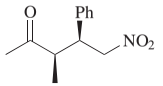
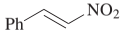
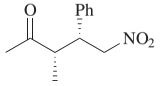
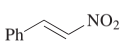
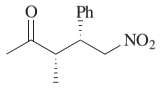
| | | | | |
|---|---|---|---|---|
|  | **25** (10 mol %), $Me_2PEG$ (10 mol %), $H_2O$, rt, 24 h |  +  | (64) *syn*/*anti* = 89:11<br>er 85.0:15.0 (31) | 264 |
|  | **26** (15 mol %), $CHCl_3$, rt, 16 h |  | (65) *syn*/*anti* >97.5:2.5<br>er 92.0:8.0 | 265 |
|  | **29** (10 mol %), TBBP (10 mol %), neat, rt, 24 h |  +  | (55) er 99.5:0.5 (35) | 268 |
|  | **32** (10 mol %), TFA (2.5 mol %), rt |  | (60) *syn*/*anti* = 8:1<br>er 84.0:16.0 | 271 |
|  | **44** (15 mol %), 2-naphthol (5 mol %), THF, rt, 48 h |  | (63) *syn*/*anti* = 96:4<br>er 95.4:4.5 | 281 |
|  | **64** (20 mol %), toluene, 20° |  | (82) *syn*/*anti* = 77:23<br>er (*syn*) 99.0:1.0<br>er (*anti*) 85.5:14.5 | 300 |
|  | **65** (5 mol %), MeOH, rt |  | (67) *syn*/*anti* = 93:7<br>er 87.0:13.0 | 301 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

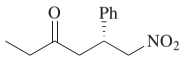
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **72** (30 mol %), $H_2O$ (10 eq), 4-TsOH (15 mol %), NMP, rt |  (45) *syn*/*anti* = 5:1 er 83.5:16.5 | 313 |
| |  | **73** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (20 mol %), $CH_2Cl_2$, rt, 2 d |  (60) *syn*/*anti* = 90:10 er (*syn*) 57.5:42.5 er (*anti*) 52.5:47.5 +  (40) er 88.0:12.0 | 314 |
| |  | Catalyst (20 mol %), $PhCO_2H$ (20 mol %), neat, rt |  | 315 |
| | | | Catalyst / Time (d) / dr / er: **74** 4 (52) 99:1 76.0:24.0; **75** 2 (45) 99:1 81.5:18.5 | |
| |  | **79** (5 mol %), benzene, rt, 3.5 d |  (78) *syn*/*anti* = 96:4 er 95.0:5.0 | 267 |
| |  | **80a** (20 mol %), $PhCO_2H$ (20 mol %), $H_2O$, neat, rt, 3 d |  (71) *syn*/*anti* = 4.8:1 er 98.0:2.0 | 318 |



**81** (5 mol %), 2-$MeC_6H_4CO_2H$, *n*-hexane, rt, 90 h



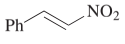
+



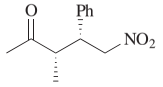
(46) *syn*/*anti* = 96:4
er 95.0:5.0

(16)
er 92.0:8.0

319

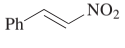


**82** (10 mol %), $PhCO_2H$ (10 mol %), EtOH, rt, 48 h

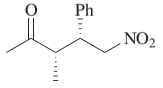


(91) *syn*/*anti* = 97:3
er 99.5:0.5

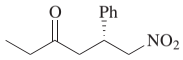
320



**83** (16 mol %), 4-$O_2NC_6H_4CO_2H$ (9.5 mol %), $H_2O$, rt, 7 d



+

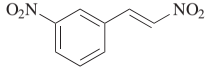


**I** **II**

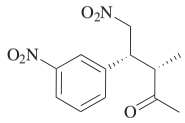
321

Catalyst Recycling

| Run | Conv. (%) | **I**/**II** | *syn*/*anti* **I** | er **I** |
|---|---|---|---|---|
| 1 | 99 | 84:16 | 80:20 | 88.0:22.0 |
| 2 | 40 | 86:14 | 76:24 | 85.0:15.0 |

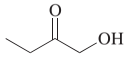


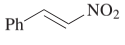
**4** (15 mol %), EtOH/*i*-PrOH (1:1), 20°, 24 h



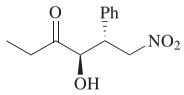
(71) *syn*:*anti* = 10:1
er 66.0:34.0

307





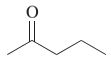
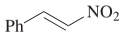
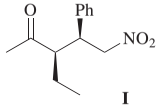
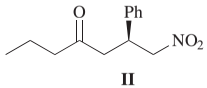
**3** (15 mol %), $CHCl_3$, 60°, 7 d



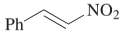
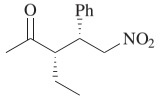
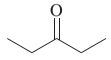
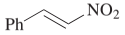
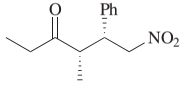
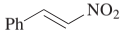
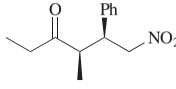
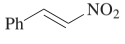
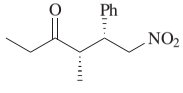
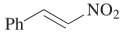
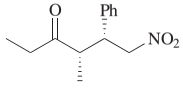
(21) *anti*/*syn* = 92:8
er 99.0:1.0

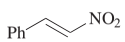
251

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

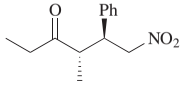
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **3** (15 mol %), additive (*x* mol %), $CHCl_3$, 6–7 d |  **I** +  **II** | 250, 251 |

| Additive | *x* | Temp (°) | | **I/II** | *syn/anti* **I** | er **I** | er **II** |
|---|---|---|---|---|---|---|---|
| none | 0 | rt | (46) | 33:67 | 78:22 | 68.5:31.5 | 76.5:23.5 |
| PTSA | 15 | 60 | (81) | 40:60 | 70:30 | 68.0:32.0 | 70.0:30.0 |
| HCl | 15 | 60 | (95) | 33:67 | 68:32 | 67.0:33.0 | 69.0:31.0 |

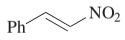
| | | | | |
|---|---|---|---|---|
| |  | **34** (5 mol %), **35** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h |  (91)[a] *syn/anti* = 89:11 er 87.0:13.0 | 274 |
|  |  | **1** (20 mol %), MeOH, rt, 4 d |  (74) *syn/anti* = 94:6 er 88.0:12.0 | 137 |
| |  | **3** (15 mol %), HCl (15 mol %), $CHCl_3$, 60°, 7 d |  (65) *syn/anti* = 84:16 er 83.5:16.5 | 250, 251 |
| |  | **5** (20 mol %), THF, rt, 5 d |  (27) *syn/anti* = 92:8 er 83.5:16.5 | 253 |
| |  | **16b** (20 mol %), *i*-PrOH, 0°, 36 h |  (85) *syn/anti* = 50:1 er 96.5:3.5 | 258 |



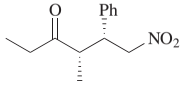
**17** (20 mol %), $PhCO_2H$ (2 mol %), toluene, rt



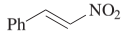
(65) dr 20:1, er 99.5:0.5 — 144



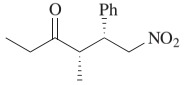
**32** (10 mol %), TFA (2.5 mol %), rt



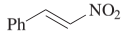
(58) *syn*/*anti* = 7:4, er (*syn*) 86.0:14.0, er (*anti*) 83.0:17.0 — 271



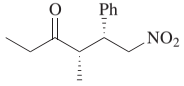
**44** (15 mol %), 2-$HOC_{10}H_7$ (5 mol %), THF, rt, 48 h



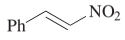
(58) *syn*/*anti* = 92:8, er 96.4:3.5 — 281



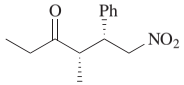
**65** (5 mol %), MeOH, rt



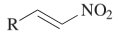
(75) *syn*/*anti* = 98:2, er 97.0:3.0 — 301



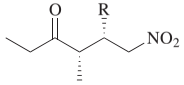
**67** (10 mol %), $CCl_3CO_2H$ (10 mol %), brine, rt, 4 d



(64) *syn*/*anti* = 97:3, er 93.5:6.5 — 303



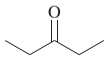
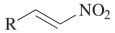
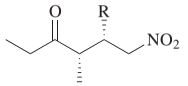
**73** (20 mol %), NMP, rt, 4 d



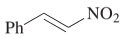
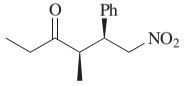
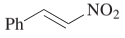
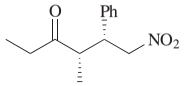
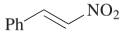
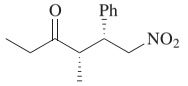
322

| R | Conv. (%) | *syn*/*anti* | er |
|---|---|---|---|
| Ph | 90 | 91:9 | 89.0:11.0 |
| 4-$ClC_6H_4$ | 93 | 95:5 | 89.0:11.0 |
| 3,5-$Cl_2C_6H_3$ | 95 | 97:3 | 86.5:13.5 |
| 4-$MeOC_6H_4$ | 92 | 92:8 | 86.5:13.5 |
| 4-$MeC_6H_4$ | 98 | 93:7 | 87.0:13.0 |
| 4-$CF_3C_6H_4$ | >99 | 97:3 | 75.0:25.0 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

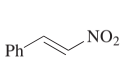
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **73** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (20 mol %), NMP, rt |  | 314 |

| R | Time (d) | | *syn/anti* | er |
|---|---|---|---|---|
| Ph | 1 | (76) | 95:5 | 89.0:11.0 |
| 2-$ClC_6H_4$ | 1 | (75) | 97:3 | 89.0:11.0 |
| 4-$ClC_6H_4$ | 1.5 | (75) | 92:8 | 89.5:10.5 |
| 3,5-$Cl_2C_6H_3$ | 1.5 | (83) | 97:3 | 89.0:11.0 |
| 4-$MeOC_6H_4$ | 1.5 | (74) | 93:7 | 90.5:9.5 |
| 4-$MeC_6H_4$ | 1.5 | (64) | 91:9 | 88.0:12.0 |
| 2-$CF_3C_6H_4$ | 1.5 | (75) | 99:1 | 79.5:20.5 |

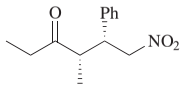
| | | | | |
|---|---|---|---|---|
|  | **79** (5 mol %), benzene, rt, 7 d |  | (47) *syn/anti* = 88:12 er 95.0:5.0 | 267 |
|  | **80a** (20 mol %), $PhCO_2H$ (20 mol %), $H_2O$, neat, rt, 8 d |  | (87) *syn/anti* = 10:1 er 99.5:0.5 | 318 |
|  | **83** (16 mol %), 4-$O_2NC_6H_4CO_2H$ (9.5 mol %), $H_2O$, rt |  | | 321 |

Catalyst Recycling

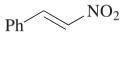
| Run | Time (h) | Conv. (%) | *syn/anti* | er |
|---|---|---|---|---|
| 1 | 5 | 97 | 79:21 | 88.0:22.0 |
| 2 | 7 | 60 | 76:24 | 80.0:20.0 |



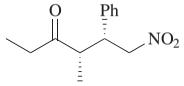
**84** (5 mol %), $CHCl_3$/MeOH (1:1), rt, 48 h



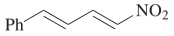
(61) *syn*/*anti* > 98:2, er 93.0:7.0 — 323



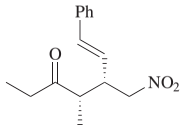
**87** (15 mol %), neat, 27°, 5 d



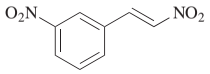
(35) dr >99:1, er 97.0:3.0 — 324



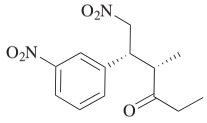
**34** (5 mol %), **85** (5 mol %), $CH_2Cl_2$, rt, 48 h



(82) *syn*/*anti* = 97:3, er 90.0:10.0 — 325

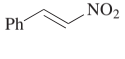


**4** (15 mol %), EtOH/*i*-PrOH (1:1), 20°, 72 h

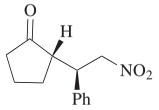


(68) *syn*/*anti* > 19:1, er 82.5:17.5 — 306, 307



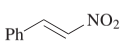
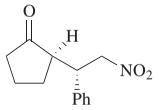


Catalyst (20 mol %), THF, rt

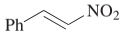
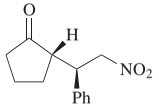
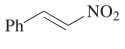
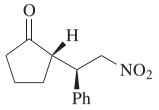
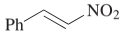
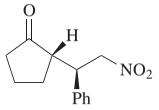


| Catalyst | Time (d) | | *syn*/*anti* | er (*syn*) | er (*anti*) | |
|---|---|---|---|---|---|---|
| **1** | 3 | (88) | — | 64.5:35.5 | — | 253 |
| **6** | — | (78) | 4:1 | 89.0:11.0 | 85.5:14.5 | 253, 138 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **3** (15 mol %), HCl (15 mol %), $CHCl_3$, 6 d |  | 250, 251 |

| Temp | | *syn*/*anti* | er |
|---|---|---|---|
| rt | (6) | 69:31 | 75.0:25.0 |
| 60° | (46) | 34:66 | 58.5:41.5 |

| | | | | |
|---|---|---|---|---|
|  | **5** (20 mol %), THF, rt, 3 d |  | (46) *syn*/*anti* = 86:14 er 87.0:13.0 | 253 |
|  | **5** (10 mol %), TFA (10 mol %), brine, rt, 96 h |  | (75) *syn*/*anti* = 77:23 er 90.0:10.0 | 252 |
|  | Catalyst (15 mol %), TFA (5 mol %), rt |  | | 255 |

| Catalyst | Time (h) | | dr (*syn*/*anti*) | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| **12** | 80 | (61) | 75:25 | 91.5:8.5 | 90.0:10.0 |
| **13** | 60 | (87) | 63:37 | 89.5:10.5 | 91.0:9.0 |

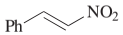
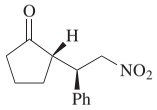
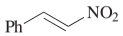
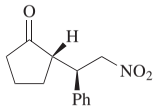
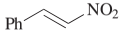
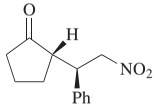
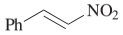
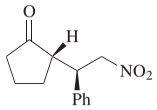
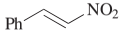
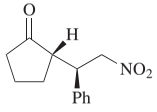
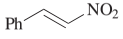
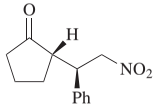
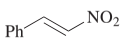
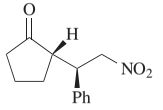
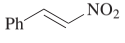
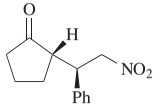
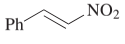
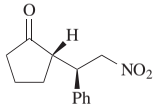
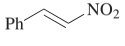
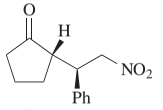
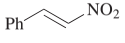
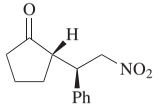
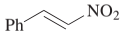
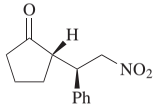
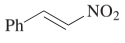
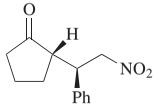
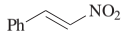
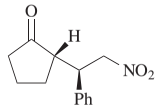
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|---|---|---|---|---|
|  | **15** (10 mol %), TFA (2.5 mol %), rt, 23 h |  | (72) *syn*/*anti* = 60:40<br>er (*syn*) 90.0:10.0<br>er (*anti*) 89.0:11.0 | 326 |
|  | **16b** (20 mol %), *i*-PrOH, 0°, 72 h |  | (7) | 258 |
|  | **18** (20 mol %), *n*-$PrCO_2H$ (10 mol %), neat, rt |  | (27) *syn*/*anti* = 75:25<br>er (*syn*) 85.5:14.5<br>er (*anti*) 79.0:21.0 | 259 |
|  | **19** (20 mol %), 4-xylene, 0°, 12 h |  | (52) *syn*/*anti* = 83:17<br>er 91.5:8.5 | 260 |
|  | **20** (15 mol %), 4-TsOH (15 mol %), rt, 10 h |  | (99) *syn*/*anti* = 80:20<br>er 96.5:3.5 | 260 |
|  | **21** (20 mol %), $(CF_3SO)_2NH$ (20 mol %), *i*-PrOH, 0°, 20 h |  | (<10) *syn*/*anti* = 66:34<br>er 78.0:22.0 | 261 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **22** (15 mol %), TFA (5 mol %), rt, 60 h |  | (63) *syn*/*anti* = 5:3<br>er (*syn*) 90.5:9.5<br>er (*anti*) 88.5:11.5 | 262 |
| |  | **24** (10 mol %), TFA (10 mol %) brine, rt, 20 h |  | (78) *syn*/*anti* = 77:23<br>er 87.5:12.5 | 119 |
| |  | **30** (10 mol %), TFA (1.7 mol %), neat, 0°, 30 h |  | (85) *syn*/*anti* = 80:20<br>er 91.5:8.5 | 269 |
| |  | **31** (10 mol %), rt, neat |  | (55) *syn*/*anti* = 23:14<br>er (*syn*) 71.5:28.5<br>er (*anti*) 78.0:22.0 | 270 |
| |  | **33** (10 mol %), toluene, rt, 24 h |  | (39) *syn*/*anti* = 70:30<br>er 81.0:19.0 | 272 |
| |  | **34** (5 mol %), **35** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h |  | (67)[a] er 93.5:6.5 | 274 |
| |  | **36** (10 mol %), TFA (2 mol %), neat, 45 h, rt |  | (84) dr 67:33<br>er 91.0:9.0 | 275 |

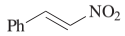


Catalyst (15 mol %),
TFA (5 mol %),
neat, rt, 36 h

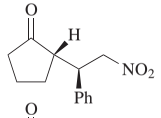


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| Catalyst | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|
| **39** | (<10) | — | — | — |
| **40** | (69) | 53:47 | 81.0:19.0 | 91.0:9.0 |

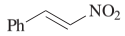


**41** (10 mol %), neat, rt, 36 h

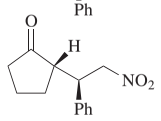


(87) *syn*/*anti* = 75:25
er 70.5:29.5

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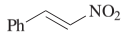


**42** (30 mol %),
$PhCO_2H$ (20 mol %),
toluene, rt, 4 d

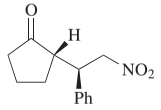


(82) *syn*/*anti* = 4:1
er (*syn*) 98.5:1.5
er (*anti*) 81.0:19.0

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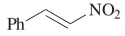


**45** (20 mol %),
$Et_3N$ (20 mol %),
*n*-$PrCO_2H$ (10 mol %), rt

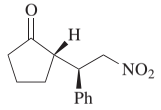


(70) *syn*/*anti* = 75:25
er (*syn*) 89.5:10.5
er (*anti*) 88.5:11.5

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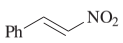
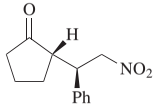
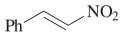
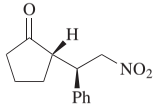
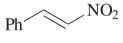
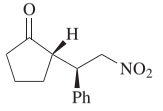
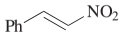
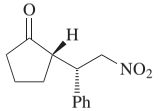
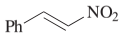
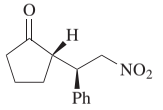
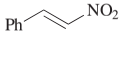
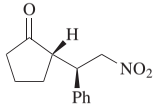
**47** (10 mol %),
*i*-PrOH, rt, 36 h

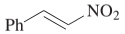


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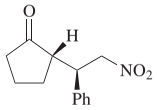
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TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **48** (10 mol %), neat, rt, 30 h |  (80) *syn*/*anti* = 62:38<br>er (*syn*) 84.5:15.5<br>er (*anti*) 83.0:17.0 | 285 |
| |  | **53** (10 mol %), neat, rt, 24 h |  (95) *syn*/*anti* = 34:66<br>er (*syn*) 92.5:7.5<br>er (*anti*) 91.5:8.5 | 290 |
| |  | **54** (20 mol %),<br>[bmim][$BF_4$], rt, 22 h |  (95) *syn*/*anti* = 75:25<br>er 89.5:10.5 | 291 |
| |  | **58** (20 mol %),<br>$C_6H_5OH$ (10 mol %),<br>toluene, 0°, 96 h |  (>99) *syn*/*anti* = 40:60<br>er (*syn*) 96.0:4.0<br>er (*anti*) 99.0:1.0 | 295 |
| |  | **60** (10 mol %),<br>$NaHCO_3$ (50 mol %),<br>[bmin]$BF_4$, rt, 40 h |  (99) *syn*/*anti* = 75:25<br>er 78.0:22.0 | 296 |
| |  | **65** (5 mol %), MeOH, rt |  (78) *syn*/*anti* = 80:20<br>er 79.0:21.0 | 301 |

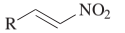


**68** (30 mol %),
$PhCO_2H$ (20 mol %),
toluene, rt, 4 d

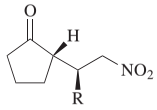


(99) *syn*/*anti* = 4:1
er (*syn*) 98.0:2.0
er (*anti*) 94.0:6.0

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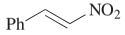


**61** (10 mol %),
$PhCO_2H$ (10 mol %),
brine, rt

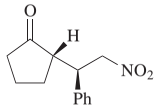


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 13 | (85) | 75:25 | 92.0:8.0 |
| 4-$MeOC_6H_4$ | 16 | (74) | 77:23 | 90.5:9.5 |
| 4-$O_2NC_6H_4$ | 14 | (72) | 75:25 | 91.5:8.5 |

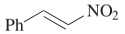


**62** (10 mol %),
TFA (2 mol %),
neat, rt, 20 h

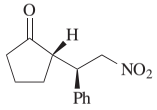


(97) *syn*/*anti* = 97:3
er 98.0:2.0

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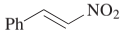


**67** (10 mol %),
$CCl_3CO_2H$ (10 mol %),
brine, rt, 2 d

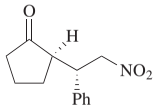


(69) *syn*/*anti* = 70:30
er 76.0:24.0

303



**71** (30 mol %), $H_2O$ (10 eq),
NMP/DMSO (1:1),
rt, 3 d



(35) *syn*/*anti* = 1:1
er (*syn*) 82.0:18.0
er (*anti*) 89.5:10.5

312

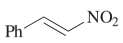
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

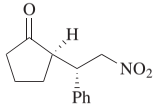
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_5$



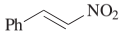


**79** (5 mol %), benzene, rt, 5 d

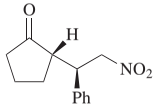


(63) *syn*/*anti* = 77:23; er 96.0:4.0

267

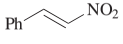


**81** (20 mol %), 2-$MeC_6H_4CO_2H$ (20 mol %), *n*-hexane, rt, 48 h

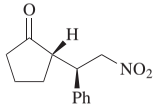


(91) *syn*/*anti* = 65:35; er (*syn*) 96.5:3.5; er (*anti*) 96.5:3.5

319

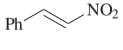


**82** (10 mol %), $PhCO_2H$ (10 mol %), EtOH, rt, 64 h

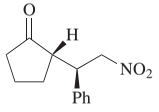


(71) *syn*/*anti* = 99:1; er 77.5:22.5

320



**86** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 26 h

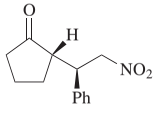


(80) *syn*/*anti* = 90:10; er 99.0:1.0

327

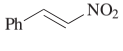


**87** (15 mol %), neat, 27°, 5 d

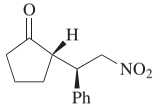


(70) *syn*/*anti* = 85:15; er (*syn*) 93.0:7.0; er (*anti*) 92.5:7.5

324

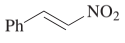


Catalyst (20 mol %), TsOH (20 mol %), DMF, rt, 24 h

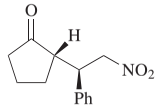


328

| Catalyst | | *syn*/*anti* | er |
|---|---|---|---|
| **88a** | (51) | 7:1 | 64.5:35.5 |
| **88b** | (33) | 2:1 | 74.5:25.5 |

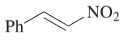


**89** (10 mol %), neat

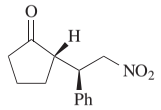


| Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 0° | 48 | (84) | 81:19 | 75.5:24.5 |
| rt | 24 | (96) | 75:25 | 73.0:27.0 |

329

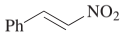


**90** (20 mol %), $Et_3N$ (20 mol %), $PhCO_2H$ (10 mol %), rt, 12 h

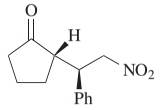


(85) *syn*/*anti* = 86:14
er (*syn*) 96.0:4.0
er (*anti*) 99.5:0.5

330

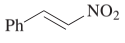


**91** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 48 h

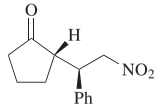


(21) *syn*/*anti* = 73:27
er (*syn*) 86.5:13.5
er (*anti*) 94.0:6.0

331

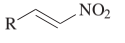


**92** (30 mol %), 4-$MeOC_6H_4CO_2H$ (30 mol %), brine, rt, 24 h

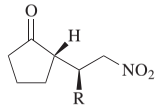


(81) *syn*/*anti* = 88:12
er 95.5:4.5

332



**93** (10 mol %), 2,4-$(O_2N)_2C_6H_4SO_3H$ (2.5 mol %), 4-*n*-$C_{12}H_{25}C_6H_3SO_3Na$ (10 mol %), 2 M in $CHCl_3$, rt



| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 30 | (89) | 57:43 | 90.5:9.5 |
| Ph | 24 | (76) | 81:19 | 93.5:6.5 |
| 4-$MeOC_6H_4$ | 24 | (85) | 88:12 | 88.5:11.5 |
| 4-$MeC_6H_4$ | 21 | (72) | 76:24 | 94.0:6.0 |

333

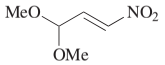
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

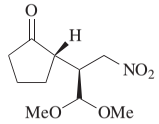
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_5$



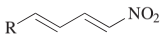



**16a** (10 mol %), THF, rt

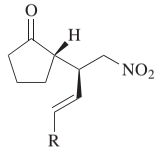



(30) *syn/anti* > 20:1
er 93.5:6.5

116

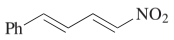



**34** (5 mol %),
**85** (5 mol %),
$CH_2Cl_2$, rt

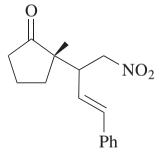



325

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| Ph | 24 | (87) | 95:5 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 18 | (91) | 97:3 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | 36 | (84) | 90:10 | 96.5:3.5 |

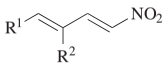



**59** (15 mol %),
$PhCO_2H$ (5 mol %),
$H_2O$ (200 mol %),
toluene, rt

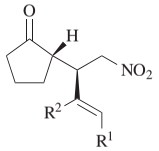



(97) *syn/anti* = 63:37
er (*syn*) 98.5:1.5

304

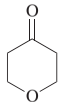


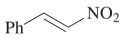
**94** (10 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
$H_2O$ (2 eq), toluene, rt



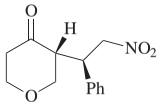
334

| $R^1$ | $R^2$ | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|
| Ph | H | 48 | (90) | 56:44 | 93.0:7.0 |
| Ph | Me | 48 | (93) | 80:20 | 96.5:3.5 |
| 4-$ClC_6H_4$ | H | 48 | (90) | 70:30 | 95.0:5.0 |
| 4-$MeOC_6H_4$ | H | 72 | (83) | 70:30 | 94.0:6.0 |
| 2-$O_2NC_6H_4$ | H | 48 | (76) | 85:15 | 96.0:4.0 |



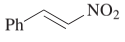


**16b** (20 mol %),
*i*-PrOH, 0°, 24 h

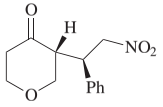


(87) *syn/anti* = 50:1
er 99.0:1.0

258

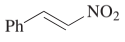


**24** (10 mol %),
TFA (10 mol %)
brine, rt, 16 h

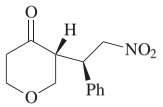


(95) *syn/anti* = 93:7
er 96.5:3.5

119

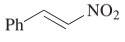


**25** (10 mol %),
$Me_2PEG$ (10 mol %),
$H_2O$, rt, 24 h

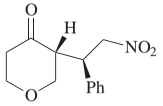


(62) *syn/anti* = 94:6
er 92.5:7.5

264



**26** (15 mol %),
$CHCl_3$, rt, 16 h



(65) *syn/anti* > 97.5:2.5

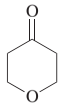
265

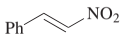
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

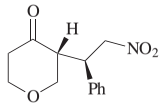
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_5$

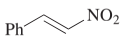




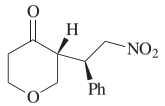
**27** (10 mol %), $PhCO_2H$ (10 mol %), *n*-hexane, rt, 12 h



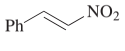
| Solvent | Temp | Time (h) | | *syn*/*anti* | er | |
|---|---|---|---|---|---|---|
| *n*-hexane | rt | 12 | (92) | 98:2 | 95.0:5.0 | 335 |
| $H_2O$ | 35° | 42 | (80) | 99:1 | 94.0:6.0 | 266 |



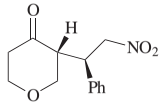
**34** (20 mol %), 2-$HOC_6H_4CO_2H$ (20 mol %), *i*-PrOH, rt



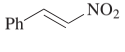
(91) *syn*/*anti* = 97:3, er 99.5:0.5 — 273



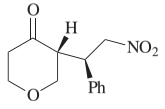
**34** (5 mol %), **35** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h



(87) *syn*/*anti* = 95:5, er 79.5:20.5 — 274

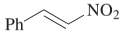


Catalyst (15 mol %), TFA (5 mol %), neat, 36 h

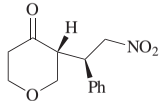


276

| Catalyst | Temp | | *syn*/*anti* | er |
|---|---|---|---|---|
| **38** | rt | (76) | 94:6 | 94.5:5.5 |
| **39** | 4° | (90) | 94:6 | 96.0:4.0 |



**41** (10 mol %), neat, rt, 36 h



(88) *syn*/*anti* = 95:5, er 97.5:2.5 — 277

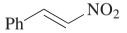
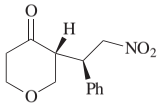
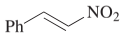
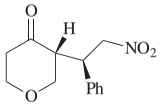
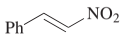
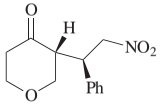
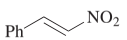
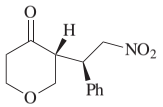
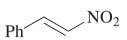
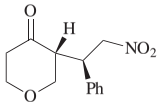
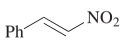
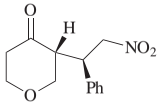
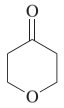
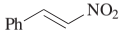
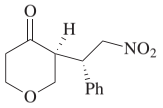
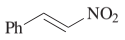
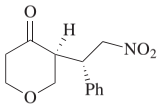
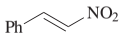
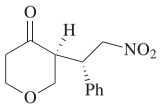
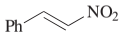
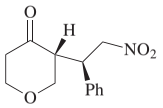
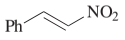
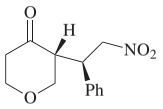
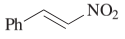
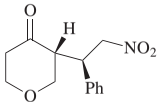
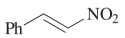
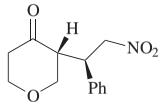
| | | | | |
|---|---|---|---|---|
|  | **47** (10 mol %), *i*-PrOH, rt, 36 h |  | (94) *syn*/*anti* = 94:6 er 96.0:4.0 | 284 |
|  | **53** (10 mol %), neat, rt, 24 h |  | (89) *syn*/*anti* = 99:1 er 97.5:2.5 | 290 |
|  | **54** (20 mol %), [bmim][$BF_4$], rt, 17 h |  | (100) *syn*/*anti* = 99:1 er 98.0:2.0 | 291 |
|  | **60** (10 mol %), $NaHCO_3$ (50 mol %), [bmim][$BF_4$], rt, 17 h |  | (98) *syn*/*anti* = 98:2 er 95.5:4.5 | 296 |
|  | **62** (10 mol %), TFA (2 mol %), neat, rt, 15 h |  | (94) *syn*/*anti* = 98:2 er 95.5:4.5 | 298 |
|  | **65** (5 mol %), MeOH, rt |  | (91) *syn*/*anti* = 99:1 er 98.5:1.5 | 301 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$  |  | **72** (30 mol %), $H_2O$ (10 eq), NMP/DMSO (9:1), rt |  (72) *syn/anti* = 31:1 er 95.0:5.0 | 313 |
| |  | **77** (45 mol %), $H_2O$ (10 eq), NMP/DMSO (1:1), –20°, 3 d |  (95) *syn/anti* = 15:1 er 95.0:5.0 | 312 |
| |  | **79** (5 mol %), benzene, rt, 4 d |  (75) *syn/anti* = 90:10 er 97.0:3.0 | 267 |
| |  | **80a** (15 mol %), $PhCO_2H$ (15 mol %), $H_2O$, neat, rt, 10 d |  (91) *syn/anti* = 10:1 er 89.0:11.0 | 318 |
| |  | **82** (10 mol %), $PhCO_2H$ (10 mol %), EtOH, rt, 24 h |  (98) *syn/anti* = 87:23 er >99.5:0.5 | 320 |
| |  | **86** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 27 h |  (79) *syn/anti* = 99:1 er 98.0:2.0 | 327 |

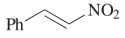


Catalyst (20 mol %), TsOH (20 mol %), DMF, rt, 24 h

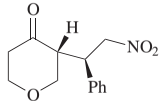


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| Catalyst | | *syn*/*anti* | er |
|---|---|---|---|
| **88a** | (99) | 19:1 | 92.5:7.5 |
| **88b** | (90) | 20:1 | 96.0:4.0 |

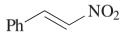


**89** (10 mol %), neat, rt, 24 h

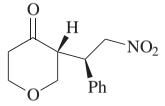


(91) *syn*/*anti* = 93:7, er 97.5:2.5

329

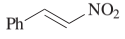


Catalyst (20 mol %), toluene, rt, 48 h

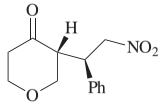


336

| Catalyst | | *syn*/*anti* | er |
|---|---|---|---|
| **95a** | (74) | 15:1 | 90.0:10.0 |
| **95b** | (96) | 11:1 | 94.5:5.5 |
| **95c** | (81) | 15:1 | 84.0:16.0 |

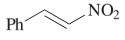


**95e** (10 mol %), $H_2O$, rt, 24 h

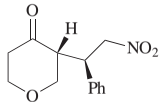


(56) dr 50:1, er 97.5:2.5

339



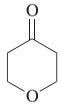
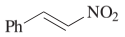
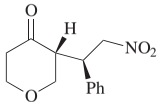
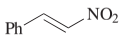
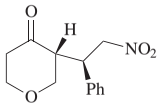
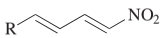
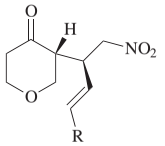
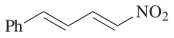
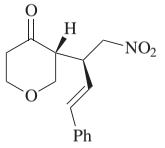
**95f** (15 mol %), *i*-PrOH, rt, 4 d



(90) *syn*/*anti* = 91:9, er 96.5:3.5

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TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **96** (20 mol %), PEG-800, rt, 12 h |  (87) *syn/anti* = 95:5 er 99.5:0.5 | 339 |
| |  | **97** (10 mol %), $PhCO_2H$ (10 mol %), 0.5 M in $CH_2Cl_2$, rt, 48 h |  (60) *syn/anti* = 97:3 er 75.0:25.0 | 340 |
| |  | **34** (5 mol %), **85** (5 mol %), $CH_2Cl_2$, rt |  | 325 |
| |  | **94** (10 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), $H_2O$ (2 eq), toluene, rt, 48 h |  (74) *syn/anti* = 73:27 er 96.5:3.5 | 334 |

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| Ph | 24 | (84) | 89:11 | 98.5:1.5 |
| 4-$ClC_6H_4$ | 18 | (89) | 88:12 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 36 | (82) | 89:11 | 96.5:3.5 |

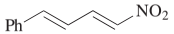
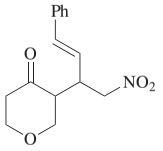
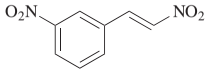
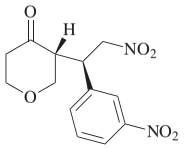
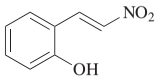
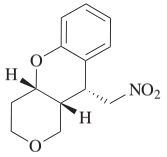
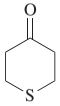
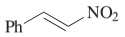
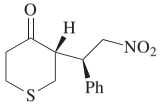
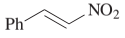
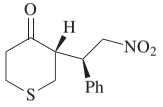
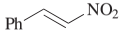
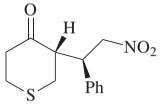
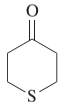
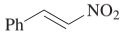
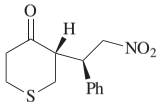
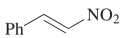
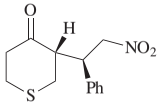
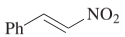
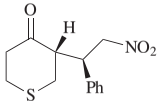
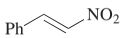
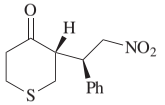
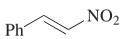
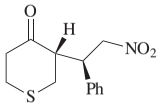
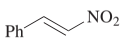
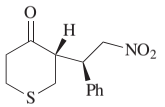
| | | | | |
|---|---|---|---|---|
|  | **98** (15 mol %), $PhCO_2H$ (5 mol %), $H_2O$ (200 mol %), toluene, rt |  | (98) *syn*/*anti* = 50:50<br>er (*syn*) 99.5:0.5 | 304 |
|  | **4** (15 mol %), EtOH/*i*-PrOH (1:1), 20°, 24 h |  | (100) *syn*/*anti* = 6:1<br>er 77.0:23.0 | 306 |
|  | 1. *ent*-**1** (5 mol %), **69b** (5 mol %), 0.5 M in $CH_2Cl_2$, rt, 5 h<br>2. $Et_3SiH$, $BF_3$•$OEt_2$, 0.1 M in $CH_2Cl_2$, −10° to rt, 2 h |  | (68) dr >99.5:0.5<br>er >99.5:0.5 | 309 |
|  | | | | |
|  | **1** (15 mol %), DMSO, rt, 2–24 h |  | (92) *syn*/*anti* > 20:1<br>er 55.0:45.0 | 136 |
|  | **5** (10 mol %), TFA (10 mol %), brine/toluene (5:1), rt, 96 h |  | (67) *syn*/*anti* = 97:3<br>er 93.5:6.5 | 252 |
|  | **16b** (20 mol %), *i*-PrOH, 0°, 12 h |  | (95) *syn*/*anti* = 30:1<br>er 98.5:1.5 | 258 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **23** (15 mol %), $H_2O$ (2 eq), AcOH (15 mol %), toluene, rt, 72 h |  (89) *syn*/*anti* = 83:17, er 99.0:1.0 | 263 |
|  | | **24** (10 mol %), TFA (10 mol %), brine, THF, rt, 18 h |  (92) *syn*/*anti* = 96:4, er 96.0:4.0 | 119 |
|  | | **26** (15 mol %), $CHCl_3$, rt, 16 h |  (45) *syn*/*anti* > 97.5:2.5, er 97.0:3.0 | 265 |
|  | | **27** (10 mol %), $PhCO_2H$ (10 mol %), $H_2O/CH_2Cl_2$ (10:1), 35°, 11 h |  (90) *syn*/*anti* = 98:2, er 94.5:5.5 | 266 |
|  | | **34** (20 mol %), 2-$HOC_6H_4CO_2H$ (20 mol %), *i*-PrOH, rt |  (91) *syn*/*anti* = 87:13, er 94.0:6.0 | 273 |
|  | | **34** (5 mol %), **35** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h |  (86) *syn*/*anti* = 97:3, er 89.0:11.0 | 274 |

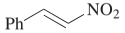
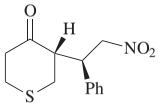
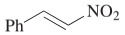
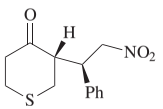
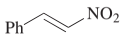
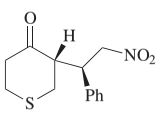
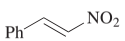
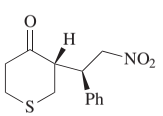
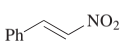
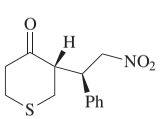
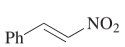
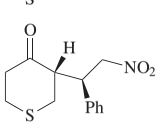
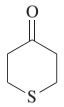
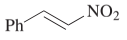
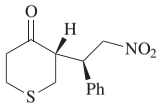
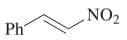
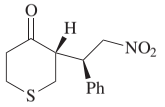
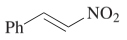
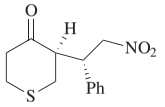
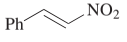
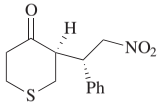
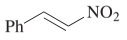
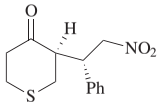
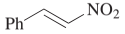
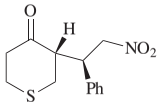
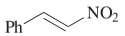
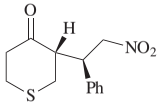
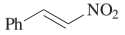
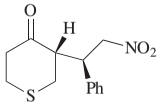
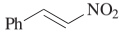
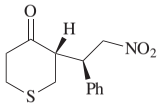
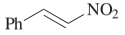
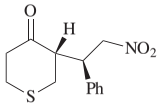
| | | | | |
|---|---|---|---|---|
|  | **41** (10 mol %), neat, rt, 36 h |  | (85) *syn*/*anti* = 96:4<br>er 96.5:3.5 | 277 |
|  | **46** (30 mol %),<br>NaOH (30 mol %),<br>$H_2O$, rt |  | (65) *syn*/*anti* = 94:6<br>er 79.5:20.5 | 283 |
|  | **47** (10 mol %),<br>*i*-PrOH, rt, 32 h |  | (85) *syn*/*anti* = 96:4<br>er 96.0:4.0 | 284 |
|  | **48** (10 mol %), neat, rt, 30 h |  | (89) *syn*/*anti* = 98:2<br>er 96.0:4.0 | 285 |
|  | **53** (10 mol %), neat, rt, 24 h |  | (87) *syn*/*anti* = 99:1<br>er 99.0:1.0 | 290 |
|  | **54** (20 mol %),<br>[bmim][$BF_4$], rt, 48 h |  | (96) *syn*/*anti* = 91:9<br>er 93.5:6.5 | 291 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **60** (10 mol %), $NaHCO_3$ (50 mol %), [bmim][$BF_4$], rt, 40 h |  (99) *syn/anti* = 96:4 er 90.5:9.5 | 296 |
| |  | **65** (5 mol %), MeOH, rt |  (89) *syn/anti* = 98:2 er 98.0:2.0 | 301 |
| |  | **72** (30 mol %), $H_2O$ (10 eq), 4-TsOH (*x* mol %), solvent, rt |  | 313 |

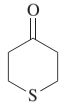
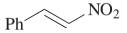
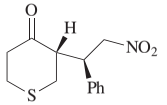
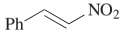
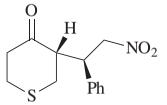
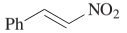
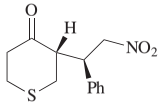
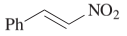
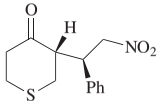
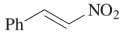
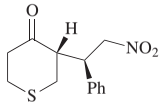
| *x* | Solvent | | *syn/anti* | er |
|---|---|---|---|---|
| 0 | NMP/DMSO (9:1) | (63) | >38:1 | 99.0:1.0 |
| 15 | NMP | (45) | 38:1 | 99.5:0.5 |

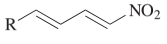
| | | | | |
|---|---|---|---|---|
| |  | **77** (45 mol %), $H_2O$ (10 eq), NMP/DMSO (1:1), 4°, 2 d |  (66) *syn/anti* = 25:1 er 99.0:1.0 | 312 |
| |  | **79** (5 mol %), benzene, rt, 3.5 d |  (76) *syn/anti* = 96:4 er 99.5:0.5 | 267 |

| | | | | |
|---|---|---|---|---|
|  | **80a** (10 mol %), $PhCO_2H$ (10 mol %), $H_2O$, toluene, rt, 11 d |  | (88) *syn*/*anti* = 11:1 er 84.5:15.5 | 318 |
|  | **86** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 29 h |  | (76) *syn*/*anti* = 98:2 er 97.5:2.5 | 327 |
|  | **88a** (20 mol %), TsOH (20 mol %), DMF, rt, 24 h |  | (78) *syn*/*anti* = 19:1 er 99.5:0.5 | 328 |
|  | **89** (10 mol %), neat, rt, 24 h |  | (87) *syn*/*anti* = 96:4 er 96.5:3.5 | 329 |
|  | Catalyst (20 mol %), toluene, rt, 48 h |  | | 336 |

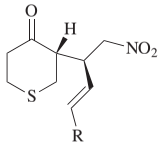
| Catalyst | | *syn*/*anti* | er |
|---|---|---|---|
| **95a** | (71) | 9:1 | 86.5:13.5 |
| **95b** | (90) | 9:1 | 85.5:14.5 |
| **95c** | (86) | 10:1 | 79.5:20.5 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **95f** (15 mol %), *i*-PrOH, rt, 4 d |  (92) *syn*/*anti* = 98:2 er 96.0:4.0 | 338 |
| |  | **96** (20 mol %), PEG-800, rt, 12 h |  (70) *syn*/*anti* = 96:4 er 95.0:5.0 | 339 |
| |  | **97** (10 mol %), $PhCO_2H$ (10 mol %), 0.5 M in $CH_2Cl_2$, rt, 10 h |  (77) *syn*/*anti* = 97:3 er 90.0:10.0 | 340 |
| |  | **100** (15 mol %), toluene, rt, 40 h |  (87) *syn*/*anti* > 99:1 er 96.5:3.5 | 341 |
| |  | **101** (5 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), 1 M KOH (50 μL), neat, rt |  (87) *syn*/*anti* = 95:5 er 92.5:7.5 | 342 |

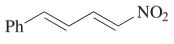


**34** (5 mol %),
**85** (5 mol %),
$CH_2Cl_2$, rt

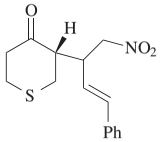


| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 24 | (85) | 99:1 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 18 | (89) | 93:7 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 36 | (84) | 91:9 | 97.5:2.5 |

325

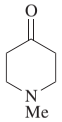


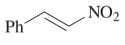
**98** (15 mol %),
$PhCO_2H$ (5 mol %),
$H_2O$ (200 mol %),
toluene, rt



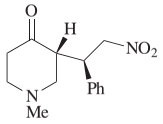
(92) *syn*/*anti* = 55:45
er 94.0:6.0

304



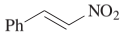


**16b** (20 mol %),
*i*-PrOH, 0°, 24 h

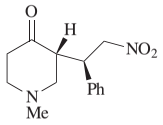


(83) *syn*/*anti* = 50:1
er 98.0:2.0

258

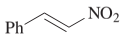


**62** (10 mol %),
TFA (2 mol %),
neat, rt, 15 h

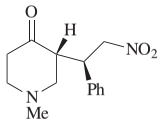


(95) *syn*/*anti* = 95:5
er 93.0:7.0

298



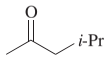
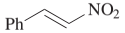
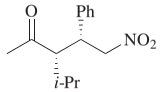
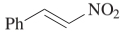
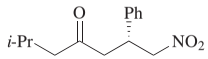
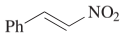
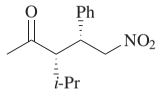
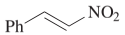
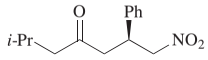
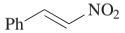
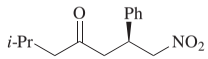
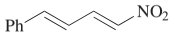
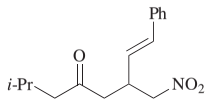
**95e** (10 mol %),
$H_2O$, rt, 12 h



(87) dr 50:1
er 84.0:16.0

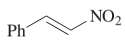
337

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

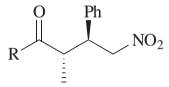
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_6$ | | | | |
|  |  | **16b** (20 mol %), *i*-PrOH, 0°, 48 h |  (72) *syn*/*anti* = 50:1 er 88.5:11.5 | 258 |
| |  | **34** (20 mol %), 2-$HOC_6H_4CO_2H$ (20 mol %), *i*-PrOH, rt |  (50) er 88.5:11.5 | 273 |
| |  | **34** (5 mol %), **35** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h |  (90)[a] er 85.5:14.5 | 274 |
| |  | **64** (20 mol %), toluene, 20° |  (93) er 98.0:2.0 | 300 |
| |  | **79** (5 mol %), benzene, rt, 3.5 d |  (53) er 93.0:7.0 | 267 |
| |  | **98** (15 mol %), $PhCO_2H$ (5 mol %), $H_2O$ (200 mol %), toluene, rt |  (44) er 96.6:3.5 | 304 |

$C_{6-8}$





**17** (20 mol %),
$PhCO_2H$ (2 mol %),
toluene, rt

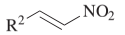


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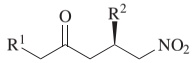
| R | | rr | dr | er |
|---|---|---|---|---|
| *n*-Pr | (51) | >30:1 | 11:1 | 99.5:0.5 |
| *n*-Bu | (53) | >30:1 | 15:1 | 99.5:0.5 |
| *n*-$C_5H_{11}$ | (50) | >30:1 | 20:1 | 99.0:1.0 |

$C_{6-7}$





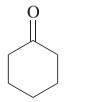
**17** (*x* mol %),
$PhCO_2H$ (*y* mol %),
toluene, rt

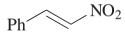


144

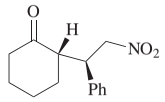
| $R^1$ | $R^2$ | *x* | *y* | | rr | er |
|---|---|---|---|---|---|---|
| *n*-Pr | *i*-Bu | 20 | 2 | (50) | 4:1 | 98.0:2.0 |
| *n*-Pr | Ph | 20 | 0 | (67) | 4:1 | 98.5:1.5 |
| *i*-Bu | *i*-Bu | 20 | 2 | (56) | >30:1 | 98.5:1.5 |
| *i*-Bu | Ph | 10 | 0 | (71) | >30:1 | 98.5:1.5 |

$C_6$

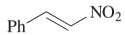




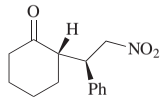
**1** (*x* mol %), solvent, rt



| *x* | Solvent | Time (h) | | *syn*/*anti* | er | |
|---|---|---|---|---|---|---|
| 15 | DMSO | 2–24 | (94) | >20:1 | 61.5:38.5 | 136 |
| 20 | MeOH | 96 | (79) | 97:3 | 78.5:21.5 | 137 |



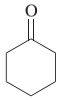
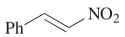
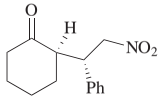
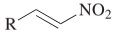
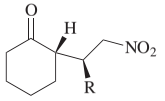
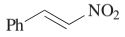
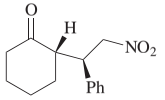
**1** (10 mol %),
**118** (10 mol %),
toluene, rt, 96 h



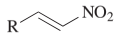
(56) *syn*/*anti* = 90:10
er (*syn*) 71.0:29.0
er (*anti*) 74.0:26.0

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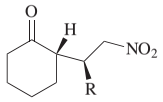
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_6$  |  | **3** (15 mol %), HCl (15 mol %), $CHCl_3$, rt, 15 h |  (74) *syn*/*anti* = 95:5, er 87.0:13.0 | 250, 251 |
| |  | **4** (15 mol %), EtOH/*i*-PrOH (1:1), 20°, 24 h |  | 306, 307 |
| |  | **5** (20 mol %), THF, rt, 22 h |  (92) *syn*/*anti* = 98:2, er 95.0:5.0 | 253 |

| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (59) | >15:1 | 82.5:17.5 |
| 2-$C_4H_3S$ | (74) | >15:1 | 78.5:21.5 |
| 2-$C_5H_4N$ | (47) | >15:1 | 80.0:20.0 |
| Ph | (80) | >15:1 | 81.0:19.0 |
| 4-$MeOC_6H_4$ | (83) | >15:1 | 79.0:21.0 |
| 3-$O_2NC_6H_4$ | (92) | >15:1 | 82.5:17.5 |
| 4-$CF_3C_6H_4$ | (58) | >15:1 | 77.5:22.5 |



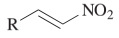
**5** (10 mol %),
TFA (10 mol %),
solvent, rt



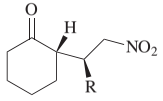
252

| R | Solvent | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | brine | 24 | (94) | 96:4 | 93.0:7.0 |
| Ph | seawater | 24 | (89) | 96:4 | 95.5:4.5 |
| Ph | brine | 12 | (93) | 95:5 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | brine | 20 | (98) | 96:4 | 91.5:8.5 |
| 3-$O_2NC_6H_4$ | brine | 96 | (57) | 74:26 | 91.5:8.5 |
| 2-Np | brine | 48 | (99) | 98:2 | 98.5:1.5 |





**6** (20 mol %),
THF/$H_2O$ (9:1), 4°



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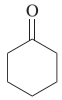
| R | | *syn*/*anti* | er |
|---|---|---|---|
| 4-$MeOC_6H_4$ | (84) | >98:2 | 85.0:15.0 |
| 2-$CF_3C_6H_4$ | (60) | >98:2 | 94.0:6.0 |

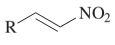
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

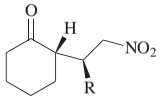
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



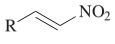


**7** (10 mol %),
co catalyst (10 mol %),
solvent, rt, 65 h

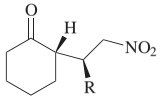


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| R | Co-catalyst | Solvent | | dr | er |
|---|---|---|---|---|---|
| Ph | none | $PhCF_3$ | (53) | 28:1 | 55.0:45.0 |
| Ph | **8** | $PhCF_3$ | (94) | >100:1 | 75.5:24.5 |
| Ph | **9** | $PhCF_3$ | (98) | 34:1 | 65.5:34.5 |
| Ph | **10** | $PhCF_3$ | (88) | >100:1 | 70.5:29.5 |
| Ph | **8** | $CH_2Cl_2$ | (99) | 65:1 | 84.0:16.0 |
| Ph | **9** | $CH_2Cl_2$ | (95) | 42:1 | 74.0:26.0 |
| Ph | **10** | $CH_2Cl_2$ | (99) | 84:1 | 82.0:18.0 |
| 4-$MeOC_6H_4$ | **8** | $CH_2Cl_2$ | (42) | 40:1 | 84.0:16.0 |
| 4-$MeOC_6H_4$ | **9** | $CH_2Cl_2$ | (53) | 45:1 | 78.5:21.5 |
| 4-$MeOC_6H_4$ | **10** | $CH_2Cl_2$ | (47) | 36:1 | 87.0:13.0 |
| 3-$O_2NC_6H_4$ | **10** | $CHCl_3$ | (82) | 27:1 | 92.5:7.5 |

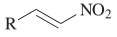


**7** (*x* mol %),
**99** (10 mol %), $CHCl_3$

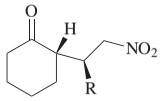


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| R | *x* | Temp | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| 2-$C_4H_3S$ | 10 | rt | 65 | (70) | 50:1 | 73.5:26.5 |
| Ph | 5 | rt | 65 | (—) | 46:1 | 81.5:18.5 |
| Ph | 10 | rt | 65 | (—) | 58:1 | 89.5:10.5 |
| Ph | 10 | 3° | 65 | (81) | 72:1 | 87.0:13.0 |
| 4-$MeOC_6H_4$ | 10 | rt | 65 | (70) | 26:1 | 80.5:19.5 |
| 3-$O_2NC_6H_4$ | 10 | rt | 22 | (71) | 19:1 | 87.5:12.5 |




Catalyst (15 mol %),
TFA (5 mol %), rt






Catalyst **13** Recycling (R = Ph)

| Run | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 8 | (100) | 99:1 | 99.5:0.5 |
| 2 | 8 | (97) | 97:3 | 97.0:3.0 |
| 3 | 24 | (99) | 96:4 | 95.5:4.5 |
| 4 | 48 | (96) | 97:3 | 96.5:3.5 |

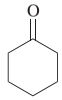
| R | Catalyst | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$ClC_6H_4$ | **12** | 12 | (99) | 99:1 | 98.0:2.0 |
| 2-$ClC_6H_4$ | **13** | 12 | (100) | 99:1 | 99.5:0.5 |
| 4-$ClC_6H_4$ | **12** | 12 | (92) | 98:2 | 97.5:2.5 |
| 4-$ClC_6H_4$ | **13** | 10 | (100) | 99:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | **12** | 20 | (94) | 99:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | **13** | 12 | (99) | 99:1 | 97.5:2.5 |
| 3-$O_2NC_6H_4$ | **12** | 15 | (76) | 98:2 | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | **13** | 10 | (94) | 98:2 | 98.0:2.0 |
| 3,4-$(OCHO)C_6H_3$ | **12** | 42 | (99) | 98:2 | 97.0:3.0 |
| 3,4-$(OCHO)C_6H_3$ | **13** | 24 | (99) | 99:1 | 98.5:1.5 |
| 4-$MeC_6H_4$ | **12** | 16 | (94) | 99:1 | 96.0:4.0 |
| 4-$MeC_6H_4$ | **13** | 12 | (99) | 99:1 | 97.5:2.5 |
| 2-Np | **12** | 12 | (99) | 99:1 | 97.5:2.5 |
| 2-Np | **13** | 10 | (99) | 99:1 | 98.5:1.5 |

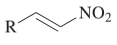
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

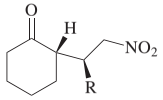
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



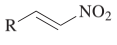


**15** (10 mol %), solvent, rt

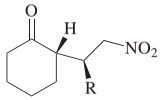


257

| R | Solvent | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | $CHCl_3$ | 15 | (91) | 10:1 | 94.0:6.0 |
| 2-$C_4H_3O$ | $H_2O$ | 7 | (90) | 11:1 | 99.0:1.0 |
| 5-Me-2-$C_4H_2O$ | $CHCl_3$ | 26 | (94) | 9:1 | 99.0:1.0 |
| 5-Me-2-$C_4H_2O$ | $H_2O$ | 12 | (94) | 9:1 | >99.5:0.5 |
| Ph | $CHCl_3$ | 36 | (75) | 14:1 | 99.5:0.5 |
| Ph | $H_2O$ | 17 | (94) | 29:1 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | $CHCl_3$ | 36 | (76) | 14:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | $H_2O$ | 13 | (96) | 38:1 | 99.5:0.5 |
| 3,4-$(OCH_2O)C_6H_3$ | $CHCl_3$ | 48 | (79) | 43:1 | 96.5:3.5 |
| 3,4-$(OCH_2O)C_6H_3$ | $H_2O$ | 20 | (97) | 54:1 | 99.5:0.5 |
| 1-Np | $CHCl_3$ | 48 | (77) | >99:1 | >99.5:0.5 |
| 1-Np | $H_2O$ | 17 | (99) | >99:1 | >99.5:0.5 |
| 2-Np | $CHCl_3$ | 48 | (71) | 11:1 | >99.5:0.5 |
| 2-Np | $H_2O$ | 24 | (94) | 23:1 | >99.5:0.5 |



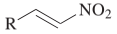
Catalyst (10 mol %),
TFA (2.5 mol %), rt



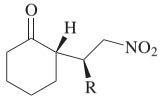
326

| R | Catalyst | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Ph | **15** | 18 | (99) | 49:1 | 96.0:4.0 |
| Ph | **104** | 17 | (95) | 24:1 | 96.5:3.5 |
| 2-$BrC_6H_4$ | **15** | 16 | (99) | 99:1 | 97.0:3.0 |
| 2-$ClC_6H_4$ | **15** | 16 | (98) | 49:1 | 97.5:2.5 |

| | | | | | |
|---|---|---|---|---|---|
| 2-$ClC_6H_4$ | **104** | 19 | (97) | 49:1 | 98.0:2.0 |
| 4-$ClC_6H_4$ | **15** | 18 | (93) | 49:1 | 96.5:3.5 |
| 4-$ClC_6H_4$ | **104** | 18 | (>99) | 99:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | **15** | 38 | (95) | 49:1 | 95.0:5.0 |
| 2,4-$(MeO)_2C_6H_3$ | **15** | 24 | (93) | 99:1 | 96.5:3.5 |
| 3,4-$(OCH_2O)C_6H_3$ | **15** | 24 | (98) | 49:1 | 97.0:3.0 |
| 4-$MeC_6H_4$ | **15** | 22 | (99) | 49:1 | 96.5:3.5 |
| 2-Np | **15** | 22 | (99) | 99:1 | 96.5:3.5 |




**16a** (20 mol %),
$PhCO_2H$ (20 mol %), 0–4°



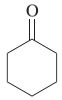

| R | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 3 | (90) | 90:10 | 96.5:3.5 |
| 3-$C_4H_3O$ | 6 | (89) | >99:1 | 91.0:9.0 |
| 2-$C_4H_3S$ | 3 | (92) | 90:10 | 97.0:3.0 |
| Ph | 3 | (92) | 98:2 | 97.5:2.5 |
| 4-$BrC_6H_4$ | 3 | (87) | 98:2 | 96.5:3.5 |
| 2-$ClC_6H_4$ | 11 | (80) | 98:2 | 95.0:5.0 |
| 4-$ClC_6H_4$ | 4 | (83) | 93:7 | 96.0:4.0 |
| 2-$MeOC_6H_4$ | 8 | (92) | 94:6 | 95.5:4.5 |
| 3-$MeOC_6H_4$ | 8 | (83) | >99:1 | 92.0:8.0 |
| 4-$MeOC_6H_4$ | 6 | (85) | 94:6 | 95.5:4.5 |
| 2-$MeC_6H_4$ | 11 | (82) | 97:3 | 96.0:4.0 |
| 3-$MeC_6H_4$ | 17 | (85) | 95:5 | 94.5:5.5 |
| 4-$MeC_6H_4$ | 7 | (83) | 96:4 | 96.0:4.0 |
| PhCH=CH | 12 | (82) | 97:3 | 98.0:2.0 |

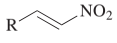
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

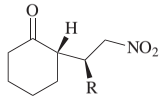
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$

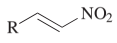




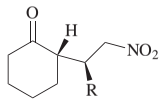
**16b** (20 mol %),
*i*-PrOH, 0°



| R | Time (h) | | *syn*/*anti* | er | Refs. |
|---|---|---|---|---|---|
| 2-$C_4H_3S$ | 36 | (79) | 30:1 | 93.0:7.0 | 258 |
| Ph | 10 | (96) | 50:1 | 98.5:1.5 | 258, 73 |
| 4-$ClC_6H_4$ | 24 | (83) | 50:1 | 99.5:0.5 | 258 |
| 4-$MeOC_6H_3$ | 16 | (92) | 50:1 | 99.0:1.0 | 258 |
| 3,4-$(OCH_2O)C_6H_3$ | 48 | (91) | 50:1 | 99.0:1.0 | 258 |
| 4-$MeC_6H_4$ | 24 | (84) | 50:1 | 98.0:2.0 | 258 |
| 2-$CF_3C_6H_4$ | 34 | (70) | 50:1 | 94.0:6.0 | 258 |

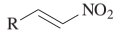


**18** (20 mol %),
*n*-$PrCO_2H$ (10 mol %),
neat, 0°

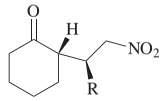


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Pr | 144 | (63) | >99:1 | 97.0:3.0 |
| 2-$C_4H_3O$ | 36 | (99) | 91:9 | 95.0:5.0 |
| Ph | 38 | (93) | 96:4 | 95.0:5.0 |
| 2-$BrC_6H_4$ | 29 | (88) | 99:1 | 98.0:2.0 |
| 4-$BrC_6H_4$ | 38 | (90) | 95:5 | 97.5:2.5 |
| 2,4-$Cl_2C_6H_3$ | 49 | (89) | 97:3 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 44 | (95) | 97:3 | 94.0:6.0 |
| 3.4-$(OCH_2O)C_6H_3$ | 38 | (87) | 94:6 | 99.0:1.0 |
| 2-$O_2NC_6H_4$ | 38 | (95) | 96:4 | 98.5:1.5 |
| 1-Np | 60 | (93) | 99:1 | 97.5:2.5 |



**19** (20 mol %), 3-xylene



260

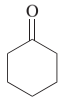
| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 0 | 12 | (87) | 61:39 | 80.5:19.5 |
| Ph | 0 | 12 | (98) | 76:24 | 92.0:8.0 |
| Ph | –20 | 36 | (80) | 82:18 | 93.5:6.5 |
| 4-$BrC_6H_4$ | 0 | 12 | (83) | 68:32 | 92.5:7.5 |
| 4-$BrC_6H_4$ | –20 | 36 | (65) | 70:30 | 94.0:6.0 |
| 3-$ClC_6H_4$ | 0 | 12 | (74) | 70:30 | 92.5:7.5 |
| 2,4-$Cl_2C_6H_3$ | –20 | 12 | (99) | 87:13 | 97.0:3.0 |
| 2,4-$Cl_2C_6H_3$ | 0 | 36 | (53) | 96:4 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 0 | 12 | (65) | 74:26 | 92.5:7.5 |
| 4-$MeOC_6H_4$ | –20 | 36 | (86) | 80:20 | 96.5:3.5 |
| 3-$NO_2C_6H_4$ | 0 | 12 | (40) | 58:42 | 89.0:11.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 0 | 12 | (89) | 73:27 | 95.0:5.0 |
| 3,4-$(OCH_2O)C_6H_3$ | –20 | 36 | (68) | 87:13 | 97.5:2.5 |
| 4-$MeC_6H_4$ | 0 | 12 | (69) | 83:17 | 92.5:7.5 |
| 1-Np | 0 | 12 | (82) | 88:12 | 96.0:4.0 |
| 1-Np | –20 | 36 | (62) | 96:4 | 97.0:3.0 |

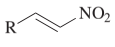
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

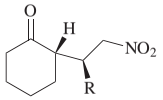
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



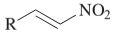


**20** (15 mol %), additive, 4-TsOH (15 mol %), rt, 10 h

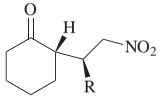


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| R | Additive | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | — | (99) | 91:9 | 97.0:3.0 |
| Ph | — | (91) | 93:7 | 96.5:3.5 |
| Ph | $H_2O$ | (91) | 94:6 | 96.0:4.0 |
| 4-$BrC_6H_4$ | — | (99) | 90:10 | 97.0:3.0 |
| 3-$ClC_6H_4$ | — | (99) | 91:9 | 97.5:2.5 |
| 2,4-$Cl_2C_6H_3$ | — | (99) | 94:6 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | — | (95) | 91:9 | 95.5:4.5 |
| 3-$O_2NC_6H_4$ | — | (99) | 90:10 | 98.0:2.0 |
| 3,4-$(OCH_2O)C_6H_3$ | — | (88) | 92:8 | 98.0:2.0 |
| 4-$MeC_6H_4$ | — | (99) | 92:8 | 97.5:2.5 |
| 1-Np | — | (88) | 94:6 | 97.5:2.5 |



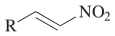
**21** (20 mol %), $(CF_3SO)_2NH$ (20 mol %), *i*-PrOH, 0°



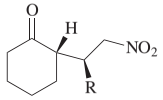
261

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 12 | (97) | 95:5 | 95.5:4.5 |
| Ph | 20 | (95) | 99:1 | 97.0:3.0 |
| 4-$BrC_6H_4$ | 24 | (95) | 97:3 | 96.5:3.5 |
| 2-$ClC_6H_4$ | 8 | (99) | 99:1 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 20 | (96) | 99:1 | 97.0:3.0 |
| 3,4-$Cl_2C_6H_3$ | 24 | (95) | 99:1 | 99.0:1.0 |

| | | | | |
|---|---|---|---|---|
| 4-$FC_6H_4$ | 24 | (96) | 98:2 | 97.0:3.0 |
| 3-$MeOC_6H_4$ | 12 | (92) | 99:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 8 | (94) | 99:1 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 49 | (89) | 85:15 | 90.5:9.5 |
| 4-$MeC_6H_4$ | 12 | (96) | 99:1 | 97.0:3.0 |
| 4-$NCC_6H_4$ | 20 | (97) | 99:1 | 92.0:8.0 |



**22** (15 mol %),
TFA (5 mol %), rt

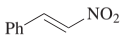


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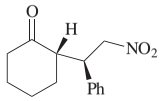
Catalyst Recycling (R = Ph)

| Run | | *syn*/*anti* | er |
|---|---|---|---|
| 1 | (96) | 97:3 | 97.0:3.0 |
| 2 | (94) | 96:4 | 97.5:2.5 |
| 3 | (97) | 95:5 | 96.5:3.5 |
| 4 | (95) | 97:3 | 97.0:3.0 |

| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (94) | 92:8 | 92.5:7.5 |
| Ph | (97) | 97:3 | 97.0:3.0 |
| 2-$BrC_6H_4$ | (96) | 98:2 | 97.5:2.5 |
| 4-$BrC_6H_4$ | (94) | 98:2 | 98.5:1.5 |
| 2-$ClC_6H_4$ | (97) | 98:2 | 96.5:3.5 |
| 4-$ClC_6H_4$ | (99) | 98:2 | 97.0:3.0 |
| 2,4-$Cl_2C_6H_3$ | (97) | 97:3 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (98) | 98:2 | 96.0:4.0 |
| 3.4-$(OCH_2O)C_6H_3$ | (95) | 97:3 | 97.0:3.0 |
| 3-$O_2NC_6H_4$ | (97) | 92:8 | 97.0:3.0 |
| 4-$MeC_6H_4$ | (99) | 97:3 | 97.0:3.0 |
| 2-Np | (96) | 98:2 | 97.0:3.0 |



**23** (15 mol %), $H_2O$ (2 eq),
AcOH (15 mol %),
toluene, rt, 72 h



(82) *syn*/*anti* = 80:20
er 98.0:2.0

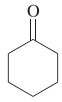
263

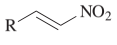
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

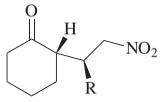
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



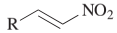


**24** (*x* mol %),
TFA (10 mol %)
brine, rt

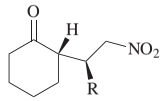


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| R | *x* | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 10 | 18 | (80) | 99:1 | 98.5:1.5 |
| 2-$C_4H_3S$ | 10 | 18 | (75) | 96:4 | 98.0:2.0 |
| *c*-$C_6H_{11}$ | 10 | 30 | (88) | 95:5 | 93.5:6.5 |
| Ph | 10 | 10 | (98) | 94:6 | 98.0:2.0 |
| 4-$BrC_6H_4$ | 10 | 18 | (70) | 94:6 | 95.0:5.0 |
| 2-$ClC_6H_4$ | 10 | 12 | (78) | 98:2 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 10 | 19 | (75) | 94:6 | 97.0:3.0 |
| 4-Cl-6-$FC_6H_3$ | 10 | 12 | (91) | 94:6 | 99.0:1.0 |
| 3-$FC_6H_4$ | 10 | 22 | (75) | 94:6 | 97.5:2.5 |
| 4-$FC_6H_4$ | 10 | 12 | (85) | 95:5 | 98.0:2.0 |
| 2,3-$F_2C_6H_3$ | 10 | 18 | (90) | 94:6 | 96.5:3.5 |
| 2-$MeOC_6H_4$ | 20 | 13 | (95) | 94:6 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 20 | 18 | (90) | 97:3 | 94.0:6.0 |
| 4-$(CF_3O)C_6H_4$ | 20 | 24 | (71) | 95:5 | 91.0:9.0 |
| 2-$O_2NC_6H_4$ | 10 | 7 | (75) | 95:5 | 95.0:5.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 10 | 7 | (92) | 99:1 | 99.5:0.5 |
| 3-$MeC_6H_4$ | 10 | 18 | (70) | 95:5 | 98.5:1.5 |
| 4-$NCC_6H_4$ | 10 | 8 | (78) | 98:2 | 97.5:2.5 |
| 4-*i*-$PrC_6H_4$ | 10 | 30 | (80) | 97:3 | 93.0:6.0 |
| 2-Np | 10 | 20 | (86) | 98:2 | 95.0:5.0 |

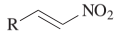


**25** (10 mol %),
$Me_2PEG$ (10 mol %),
$H_2O$, rt, 24 h

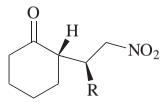


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| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (80) | 90:10 | 89.5:10.5 |
| Ph | (85) | 95:5 | 95.0:5.0 |
| 2-$BrC_6H_4$ | (76) | >99:1 | 97.5:2.5 |
| 3-$BrC_6H_4$ | (78) | 95:5 | 96.0:4.0 |
| 4-$BrC_6H_4$ | (84) | 96:4 | 95.0:5.0 |
| 2-$MeOC_6H_4$ | (83) | 95:5 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | (84) | 95:5 | >99.5:0.5 |
| 2-$O_2NC_6H_4$ | (81) | 98:2 | 96.5:3.5 |
| 3,4-$(OCH_2O)C_6H_3$ | (77) | 93:7 | 97.0:3.0 |



**26** (15 mol %),
$CHCl_3$, rt, 16 h



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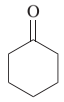
| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (60) | >97.5:2.5 | 91.0:9.0 |
| 2-$C_4H_3S$ | (45) | >97.5:2.5 | 82.5:17.5 |
| Ph | (96) | 97:3 | 95.0:5.0 |
| 4-$BrC_6H_4$ | (70) | >97.5:2.5 | 93.0:7.0 |
| 2-$MeOC_6H_4$ | (62) | >97.5:2.5 | 62.5:37.5 |
| 2-$O_2NC_6H_4$ | (46) | >97.5:2.5 | 90.5:9.5 |
| 2-$CF_3C_6H_4$ | (42) | >97.5:2.5 | 97.0:3.0 |

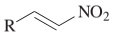
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

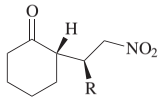
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



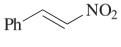



**27** (10 mol %), $PhCO_2H$ (10 mol %), *n*-hexane

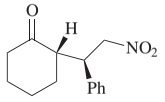



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| R | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3S$ | rt | 18 | (88) | 90:10 | 91.5:8.5 |
| 2-$C_4H_3S$ | 4° | 41 | (87) | 93:7 | 94.5:5.5 |
| Ph | rt | 11 | (93) | 96:4 | 96.0:4.0 |
| Ph | 4° | 48 | (87) | 99:1 | 98.0:2.0 |
| 3-$BrC_6H_4$ | rt | 31 | (78) | 96:4 | 96.5:3.5 |
| 4-$BrC_6H_4$ | rt | 10.5 | (92) | 97:3 | 99.0:1.0 |
| 2-$ClC_6H_4$ | rt | 12 | (90) | 98:2 | 96.5:3.5 |
| 4-$ClC_6H_4$ | rt | 12 | (84) | 95:5 | 95.5:4.5 |
| 4-$ClC_6H_4$ | 4° | 48 | (80) | 98:2 | 97.5:2.5 |
| 2,4-$Cl_2C_6H_3$ | rt | 10 | (93) | 98:2 | 99.0:1.0 |
| 4-$FC_6H_4$ | rt | 11 | (85) | 97:3 | 95.0:5.0 |
| 4-$FC_6H_4$ | 4° | 53 | (78) | 99:1 | 97.0:3.0 |
| 4-$HOC_6H_4$ | rt | 180 | (69) | 90:10 | 94.5:5.5 |
| 4-$MeC_6H_4$ | rt | 24 | (80) | 95:5 | 95.5:4.5 |
| 1-Np | rt | 47 | (97) | 97:3 | 97.0:3.0 |

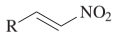



**27** (10 mol %), $PhCO_2H$ (10 mol %), brine, rt

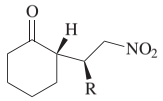



(82) *syn*/*anti* = 97:3, er 96.5:3.5

335




**27** (10 mol %),
$PhCO_2H$ (10 mol %),
$H_2O$, 35°



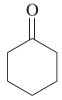

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 3.5 | (87) | 87:13 | 89.5:10.5 |
| 2-$C_4H_3S$ | 6 | (90) | 92:8 | 94.0:6.0 |
| Ph | 12 | (90) | 98:2 | 98.0:2.0 |
| 3-$BrC_6H_4$ | 23.5 | (72) | 95:5 | 96.5:3.5 |
| 4-$BrC_6H_4$ | 12.5 | (93) | 98:2 | >99.5:0.5 |
| 2-$ClC_6H_4$ | 12.5 | (91) | 99:1 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 12.5 | (83) | 97:3 | 99.5:0.5 |
| 2,4-$Cl_2C_6H_3$ | 2.5 | (86) | >99:1 | >99.5:0.5 |
| 2-$FC_6H_4$ | 12 | (84) | 99:1 | 97.0:3.0 |
| 4-$FC_6H_4$ | 11 | (89) | 95:5 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 12 | (98) | 95:5 | 95.5:4.5 |
| 3-$PhOC_6H_4$ | 34 | (73) | 94:6 | 94.0:6.0 |
| 4-$MeC_6H_4$ | 12.5 | (87) | 97:3 | 97.0:3.0 |
| 1-Np | 12.5 | (87) | 98:2 | 97.0:3.0 |

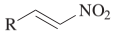
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

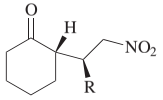
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



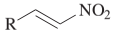


**29** (10 mol %), TBBP (10 mol %), $H_2O$, rt

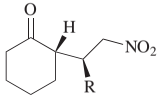


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 10 | (99) | 78:22 | 97.5:2.5 |
| Ph | 12 | (92) | 90:10 | 99.0:1.0 |
| 4-$BrC_6H_4$ | 3 | (95) | 93:7 | 98.5:1.5 |
| 3-$ClC_6H_4$ | 18 | (98) | 90:10 | 99.0:1.0 |
| 2,4-$Cl_2C_6H_3$ | 10 | (99) | 96:4 | 99.0:1.0 |
| 3-$MeOC_6H_4$ | 20 | (91) | 91:9 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 40 | (86) | 89:11 | 98.5:1.5 |
| 3,4-$(MeO)_2C_6H_3$ | 48 | (90) | 93:7 | 99.0:1.0 |
| 2-$O_2NC_6H_4$ | 12 | (99) | 98:2 | 99.0:1.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 60 | (70) | 88:12 | 98.0:2.0 |
| 4-$MeC_6H_4$ | 40 | (98) | 89:11 | 97.5:2.5 |
| 4-$NCC_6H_4$ | 120 | (82) | 90:10 | 98.0:2.0 |
| 1-Np | 48 | (94) | 95:5 | 99.0:1.0 |

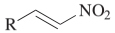


**30** (10 mol %), TFA (1.7 mol %), neat, 0°

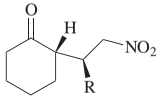


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 3-$C_4H_3O$ | 12 | (89) | 98:2 | 95.5:4.5 |
| Ph | 12 | (95) | 98:2 | 95.5:4.5 |
| 2-Cl-3-$O_2NC_6H_3$ | 15 | (97) | 99:1 | 93.5:6.5 |
| 4-$MeOC_6H_4$ | 19 | (92) | 99:1 | 96.0:4.0 |
| 2,5-$(MeO)_2C_6H_3$ | 16 | (96) | 99:1 | 97.0:3.0 |
| 3-$O_2NC_6H_4$ | 16 | (98) | 99:1 | 95.0:5.0 |
| 4-$MeC_6H_4$ | 13 | (90) | 99:1 | 97.0:3.0 |
| 2-Np | 18 | (92) | 99:1 | 96.0:4.0 |



**31** (10 mol %), rt



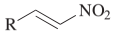
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Catalyst Recycling (R = Ph)

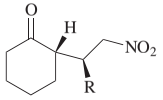
| Run | | *syn*/*anti* | er |
|---|---|---|---|
| 1 | (97) | 96:4 | 95.5:4.5 |
| 2 | (96) | 97:3 | 95.0:5.0 |
| 3 | (93) | 95:5 | 95.0:5.0 |
| 4 | (95) | 94:6 | 95.5:4.5 |

| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (97) | 94:6 | 94.0:6.0 |
| Ph | (97) | 96:4 | 95.5:4.5 |
| 2-$BrC_6H_4$ | (97) | >20:1 | 93.5:6.5 |
| 4-$BrC_6H_4$ | (96) | 96:4 | 94.5:5.5 |
| 2-$ClC_6H_4$ | (96) | >20:1 | 94.5:5.5 |
| 4-$ClC_6H_4$ | (97) | >20:1 | 96.5:3.5 |
| 2,4-$Cl_2C_6H_3$ | (97) | >20:1 | 94.0:6.0 |
| 4-$MeOC_6H_4$ | (98) | >20:1 | 92.0:8.0 |
| 3-$O_2NC_6H_4$ | (97) | 93:7 | 93.5:6.5 |
| 4-$MeC_6H_4$ | (98) | 96:4 | 92.5:7.5 |
| 2-Np | (94) | >20:1 | 88.5:11.5 |





**32** (10 mol %),
TFA (2.5 mol %), rt



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Catalyst Recycling (R = Ph)

| Run | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 18 | (98) | 45:1 | 97.0:3.0 |
| 2 | 18 | (95) | 45:1 | 96.5:3.5 |
| 3 | 18 | (95) | 45:1 | 96.0:4.0 |
| 4 | 24 | (93) | 42:1 | 95.5:4.5 |
| 5 | 30 | (88) | 40:1 | 96.0:4.0 |
| 6 | 36 | (80) | 40:1 | 95.0:5.0 |

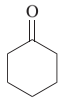
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 18 | (93) | 25:1 | 96.0:4.0 |
| 2-$C_4H_3S$ | 18 | (95) | 16:1 | 94.5:5.5 |
| Ph | 18 | (99) | 45:1 | 96.5:3.5 |
| 4-$BrC_6H_4$ | 18 | (94) | 45:1 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 18 | (93) | 40:1 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 18 | (94) | 35:1 | 94.0:6.0 |
| 2,4-$(MeO)_2C_6H_3$ | 18 | (92) | 35:1 | 95.5:4.5 |
| 3-$O_2NC_6H_4$ | 18 | (91) | 35:1 | 96.5:3.5 |
| 4-$MeC_6H_4$ | 18 | (96) | 45:1 | 96.0:4.0 |
| 2-Np | 18 | (99) | 25:1 | 96.0:4.0 |

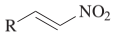
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

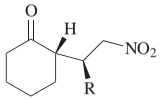
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$





**33** (10 mol %), toluene, rt

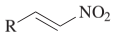


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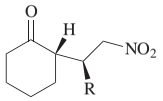
Catalyst Recycling (R = 2-$O_2NC_6H_4$)

| Run | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 6 | (95) | 95:5 | 92.0:8.0 |
| 2 | 6 | (98) | 95:5 | 91.5:8.5 |
| 3 | 6 | (91) | 96:4 | 92.0:8.0 |
| 4 | 10 | (93) | 95:5 | 92.0:8.0 |
| 5 | 13 | (89) | 95:5 | 90.5:9.5 |
| 6 | 21 | (77) | 94:6 | 90.0:10.0 |

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 24 | (94) | 94:6 | 93.5:6.5 |
| 2-$ClC_6H_4$ | 15 | (96) | 95:5 | 94.5:5.5 |
| 4-$ClC_6H_4$ | 20 | (56) | 94:6 | 94.0:6.0 |
| 4-$MeOC_6H_4$ | 24 | (97) | 94:6 | 91.0:9.0 |
| 2,4-$(MeO)_2C_6H_3$ | 24 | (78) | 94:6 | 93.5:6.5 |
| 2-$O_2NC_6H_4$ | 6 | (95) | 95:5 | 92.0:8.0 |
| 3-$O_2NC_6H_4$ | 12 | (77) | 95:5 | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | 8 | (80) | 96:4 | 94.0:6.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 30 | (70) | 93:7 | 84.0:16.0 |
| 4-$MeC_6H_4$ | 24 | (91) | 95:5 | 94.5:5.5 |
| 1-Np | 24 | (97) | 95:5 | 94.5:5.5 |
| 4-$PhC_6H_4$ | 30 | (88) | 96:4 | 90.0:10.0 |

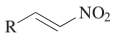


**34** (20 mol %),
2-$HOC_6H_4CO_2H$
(20 mol %), *i*-PrOH, rt

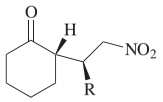


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| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (85) | 85:15 | 89.0:11.0 |
| 2-$C_4H_3S$ | (90) | 86:14 | 96.0:4.0 |
| Ph | (95) | 97:3 | 99.5:0.5 |
| 2-$BrC_6H_4$ | (95) | 92:8 | 98.0:2.0 |
| 3-$BrC_6H_4$ | (83) | 87:13 | 97.5:2.5 |
| 4-$ClC_6H_4$ | (86) | 92:8 | 98.5:1.5 |
| 2-$MeOC_6H_4$ | (92) | 91:9 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (94) | 94:6 | 99.5:0.5 |
| 2-$O_2NC_6H_4$ | (89) | 80:20 | 94.5:0.5 |
| 4-$MeC_6H_4$ | (92) | 93:7 | 99.5:0.5 |
| 4-$CF_3C_6H_4$ | (85) | 93:7 | 97.5:2.5 |
| 2-Np | (91) | 98:2 | 98.0:2.0 |



**34** (5 mol %), **35** (5 mol %),
cyclohexane/*n*-butanol (1:1),
rt, 12 h



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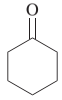
| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (95)[a] | 94:6 | 93.5:6.5 |
| 2-$C_4H_3S$ | (94)[a] | 93:7 | 97.5:2.5 |
| Ph | (94) | 97:3 | 99.0:1.0 |
| 2-$BrC_6H_4$ | (93)[a] | 94:6 | 96.0:4.0 |
| 3-$MeOC_6H_4$ | (92) | 95:5 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | (88) | 96:4 | 99.5:0.5 |
| 2-$O_2NC_6H_4$ | (92)[a] | 96:4 | 93.5:6.5 |
| 4-$MeC_6H_4$ | (90) | 98:2 | 95.0:5.0 |
| 4-$CF_3C_6H_4$ | (85)[a] | 94:6 | 98.5:1.5 |
| 2-Np | (92)[a] | 85:15 | 94.5:5.5 |

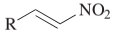
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

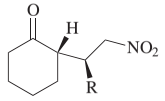
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$





**37** (10 mol %),
TFA (2 mol %), neat

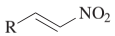


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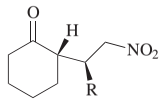
Catalyst Recycling (R = Ph)

| Run | Time (h) | | dr | er |
|---|---|---|---|---|
| 1 | 24 | (98) | 99:1 | 99.5:0.5 |
| 2 | 24 | (90) | 94:6 | 95.0:5.0 |
| 3 | 24 | (83) | 93:7 | 94.0:6.0 |
| 4 | 24 | (74) | 93:7 | 79:21 |

| R | Time (h) | | dr | er |
|---|---|---|---|---|
| 2-$MeOC_6H_4$ | 23 | (95) | 95:5 | 92.0:8.0 |
| 4-$MeOC_6H_4$ | 22 | (97) | 95:5 | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | 20 | (93) | 99:1 | 91.5:8.5 |

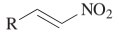


Catalyst (15 mol %),
TFA (5 mol %), neat

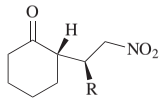


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| R | Catalyst | Temp | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|---|
| Ph | **38** | rt | 48 | (73) | 93:7 | 99.0:1.0 |
| Ph | **39** | 4° | 48 | (91) | >99:1 | 99.0:1.0 |
| 2-$ClC_6H_4$ | **38** | rt | 36 | (85) | 99:1 | 98.0:2.0 |
| 2-$ClC_6H_4$ | **39** | 4° | 21 | (98) | 99:1 | 98.0:2.0 |
| 2,4-$Cl_2C_6H_3$ | **38** | rt | 36 | (87) | >99:1 | 98.5:1.5 |
| 2,4-$Cl_2C_6H_3$ | **39** | 4° | 24 | (95) | >99:1 | 98.5:1.5 |
| 3-$MeOC_6H_4$ | **38** | rt | 48 | (75) | >99:1 | 98.0:2.0 |
| 3-$MeOC_6H_4$ | **39** | 4° | 48 | (98) | 99:1 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | **38** | rt | 48 | (73) | 93:7 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | **39** | 4° | 48 | (91) | >99:1 | 99.0:1.0 |
| 2-$O_2NC_6H_4$ | **38** | rt | 41 | (94) | 99:1 | 98.0:2.0 |
| 2-$O_2NC_6H_4$ | **39** | 4° | 24 | (100) | 99:1 | 97.0:3.0 |
| 4-$MeC_6H_4$ | **38** | rt | 48 | (77) | 96:4 | 99.5:0.5 |
| 4-$MeC_6H_4$ | **39** | 4° | 36 | (91) | 97:3 | 99.0:1.0 |
| 2-$CF_3C_6H_4$ | **38** | rt | 48 | (83) | 97:3 | 98.0:2.0 |
| 2-$CF_3C_6H_4$ | **39** | 4° | 36 | (92) | 99:1 | 98.5:1.5 |



**41** (10 mol %), neat, rt, 36 h

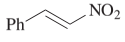


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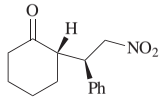
Catalyst Recycling (R = Ph)

| Run | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 24 | (91) | 98:2 | 99.0:1.0 |
| 2 | 24 | (89) | 98:2 | 99.0:1.0 |
| 3 | 24 | (90) | 98:2 | 98.5:1.5 |
| 4 | 24 | (88) | 98:2 | 99.0:1.0 |
| 5 | 24 | (81) | 98:2 | 99.0:1.0 |
| 6 | 24 | (85) | 97:3 | 99.0:1.0 |

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 36 | (85) | 99:1 | >99.5:0.5 |
| Ph | 36 | (91) | 99:1 | 99.0:1.0 |
| 2-$BrC_6H_4$ | 36 | (88) | 99:1 | 99.0:1.0 |
| 3-$BrC_6H_4$ | 36 | (89) | 98:2 | 98.0:2.0 |
| 4-$BrC_6H_4$ | 36 | (90) | 99:1 | 99.0:1.0 |
| 4-$ClC_6H_4$ | 36 | (92) | 99:1 | 99.5:0.5 |
| 4-$FC_6H_4$ | 36 | (94) | 98:2 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 36 | (88) | 99:1 | 99.5:0.5 |
| 3,4-$(OCH_2O)_2C_6H_3$ | 36 | (86) | 98:2 | 99.0:1.0 |
| 4-$MeC_6H_4$ | 36 | (93) | 99:1 | 99.5:0.5 |
| 1-Np | 36 | (84) | 98:2 | 99.0:1.0 |
| 2-Np | 36 | (87) | >99:1 | >99.5:0.5 |



**42** (30 mol %),
$PhCO_2H$ (20 mol %),
toluene, rt, 4 d



(52) *syn*/*anti* = 1.2:1
er (*syn*) 86.5:13.5
er (*anti*) 96.5:3.5

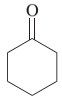
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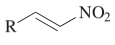
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

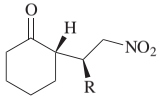
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



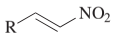


**44** (15 mol %),
2-NpOH (5 mol %),
THF, rt

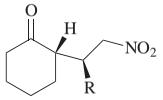


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 12 | (99) | 97:3 | 94.0:6.0 |
| 2-$C_4H_3S$ | 17 | (99) | 96:4 | 93.0:7.0 |
| Ph | 20 | (99) | 98:2 | 97.5:2.5 |
| 2-$ClC_6H_4$ | 12 | (99) | 99:1 | 97.5:2.5 |
| 3-$ClC_6H_4$ | 12 | (99) | 95:5 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 12 | (99) | 98:2 | 97.0:3.0 |
| 2,4-$(MeO)_2C_6H_3$ | 48 | (92) | 97:3 | 98.0:2.0 |
| 4-$O_2NC_6H_4$ | 14 | (96) | 94:6 | 96.0:4.0 |
| 4-$MeC_6H_4$ | 17 | (96) | 99:1 | 96.0:4.0 |
| 1-Np | 20 | (96) | 97:3 | 98.5:1.5 |



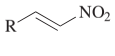
**45** (20 mol %),
$Et_3N$ (20 mol %),
*n*-$PrCO_2H$ (10 mol %)



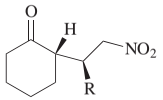
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| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | –15 | 52 | (81) | 92:8 | 96.0:4.0 |
| Ph | –15 | 60 | (98) | 99:1 | 97.5:2.5 |
| 4-$ClC_6H_4$ | –15 | 49 | (86) | 98:2 | 97.0:3.0 |
| 2,4-$Cl_2C_6H_4$ | –15 | 96 | (87) | >99:1 | 97.0:3.0 |
| 4-$FC_6H_4$ | –15 | 49 | (78) | >99:1 | 97.5:2.5 |
| 2-$MeOC_6H_4$ | –15 | 47 | (82) | 98:2 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | –15 | 72 | (96) | 98:2 | 96.0:4.0 |
| 2,4-$(MeO)_2C_6H_3$ | –15 | 120 | (90) | 97:3 | 96.5:3.5 |
| 4-$BnOC_6H_4$ | –15 | 61 | (>99) | 97:3 | 96.0:4.0 |

| | | | | | |
|---|---|---|---|---|---|
| 2-$O_2N$-5-$ClC_6H_3$ | –15 | 120 | (98) | 98:2 | 98.5:1.5 |
| 3,4-$(OCH_2O)C_6H_3$ | –15 | 52 | (>99) | >99:1 | 98.0:2.0 |
| 4-$MeC_6H_4$ | –15 | 49 | (81) | 98:2 | 96.5:3.5 |
| 2-$CF_3C_6H_4$ | –15 | 49 | (76) | 97:3 | 98.5:1.5 |
| 3-$CF_3C_6H_4$ | –15 | 80 | (95) | 98:2 | 96.5:3.5 |
| 4-$CF_3C_6H_4$ | –15 | 80 | (71) | 97:3 | 97.5:2.5 |
| $BnCH_2$ | rt | 35 | (73) | 76:24 | 96.5:3.5 |
| PhCH=CH | –15 | 48 | (87) | 95:5 | 97.0:3.0 |
| 1-Np | –15 | 49 | (88) | 99:1 | 97.0:3.0 |

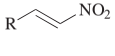


**46** (30 mol %),
NaOH (30 mol %),
$H_2O$, rt

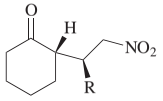


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| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 26 | (92) | 97:3 | 70.5:29.5 |
| Ph | 17 | (99) | 95:5 | 84.0:16.0 |
| 4-$ClC_6H_4$ | 28 | (89) | 92:8 | 83.0:17.0 |
| 4-$MeOC_6H_4$ | 48 | (75) | 95:5 | 79.0:21.0 |
| 4-$O_2NC_6H_4$ | 17 | (78) | 92:8 | 85.0:15.0 |
| 2-Np | 16 | (96) | 99:1 | 82.0:18.0 |



**47** (10 mol %),
*i*-PrOH, rt



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Catalyst Recycling (R = Ph)

| Run | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 1 | 12 | (92) | 95:5 | 95.0:5.0 |
| 2 | 16 | (90) | 95:5 | 95.0:5.0 |
| 3 | 18 | (93) | 94:6 | 95.0:5.0 |
| 4 | 24 | (86) | 95:5 | 94.5:5.5 |
| 5 | 40 | (80) | 93:7 | 94.0:6.0 |

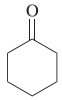
| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 24 | (97) | 92:8 | 90.0:10.0 |
| Ph | 16 | (91) | 95:5 | 95.0:5.0 |
| 4-$BrC_6H_4$ | 17 | (87) | 93:7 | 97.0:3.0 |
| 2,4-$Cl_2C_6H_3$ | 24 | (96) | 99:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 24 | (83) | 99:1 | 99.0:1.0 |
| 2-$O_2NC_6H_4$ | 24 | (96) | 97:3 | 95.0:5.0 |
| 4-$MeC_6H_4$ | 17 | (90) | 99:1 | 99.5:0.5 |
| 2-$CF_3C_6H_4$ | 20 | (90) | 98:2 | 97.5:2.5 |

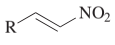
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

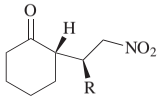
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



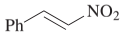


**48** (10 mol %), neat, rt

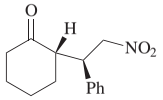


| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (98) | 98:2 | 97.0:3.0 |
| 3-$C_4H_3O$ | (99) | 99:1 | 98.0:2.0 |
| 2-$C_4H_3S$ | (93) | 95:5 | 96.5:3.5 |
| Ph | (97) | 98:2 | 98.5:1.5 |
| 2-$ClC_6H_4$ | (99) | 98:2 | 99.5:0.5 |
| 4-$ClC_6H_4$ | (97) | 96:4 | 97.0:3.0 |
| 2-$MeOC_6H_4$ | (96) | 98:2 | 97.0:3.0 |
| 3-$MeOC_6H_4$ | (95) | 97:3 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (99) | >99:1 | 97.0:3.0 |
| 3,4-$(OCH_2O)C_6H_3$ | (93) | 98:2 | 97.5:2.5 |
| 2-$MeC_6H_4$ | (93) | 98:2 | 97.5:2.5 |
| 3-$MeC_6H_4$ | (97) | 99:1 | 96.5:3.5 |
| 4-$MeC_6H_4$ | (99) | 95:5 | 97.0:3.0 |
| PhCH=CH | (98) | 98:2 | 95.5:4.5 |
| 2-Np | (96) | 98:2 | 96.0:4.0 |

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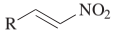


**49** (10 mol %),
$Et_3N$ (10 mol %),
*i*-PrOH/EtOH (1:1), rt, 18 h

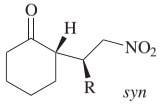


(64) dr 19:1
er 95.0:5.0

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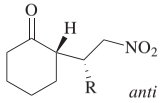


**51** (10 mol %),
4-$O_2NC_6H_4CO_2H$
(10 mol %), $H_2O$, rt



*syn*

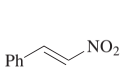
+



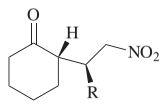
*anti*

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| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| *n*-Bu | 86 | (42) | 5:95 | 94.5:5.5 |
| 2-$C_4H_3O$ | 48 | (91) | 89:11 | 94.0:6.0 |
| 2-$C_4H_3S$ | 72 | (98) | 89:11 | 93:7 |
| Ph | 48 | (94) | 93.7 | 95.5:4.5 |
| 2-$BrC_6H_4$ | 47 | (96) | 95:5 | 96.5:3.5 |
| 3-$BrC_6H_4$ | 57 | (93) | 94:6 | 96.0:4.0 |
| 4-$BrC_6H_4$ | 71 | (98) | 95:5 | 95.5:4.5 |
| 2-$ClC_6H_4$ | 24 | (95) | 95:5 | 95.0:5.0 |
| 4-$ClC_6H_4$ | 48 | (94) | 94:6 | 92.5:7.5 |
| 2,4-$Cl_2C_6H_3$ | 29 | (90) | 96:4 | 96.5:3.5 |
| 2-$FC_6H_4$ | 28 | (97) | 97:3 | 96.5:3.5 |
| 4-$FC_6H_4$ | 71 | (92) | 93:7 | 95.5:4.5 |
| 2-$MeOC_6H_4$ | 71 | (97) | 95:5 | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 72 | (87) | 88:12 | 93.5:6.5 |
| 2-$O_2NC_6H_4$ | 42 | (100) | 96:4 | 95.0:5.0 |
| 3-$O_2NC_6H_4$ | 72 | (95) | 93:7 | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | 48 | (100) | 94:6 | 95.0:5.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 72 | (84) | 93:7 | 95.5:4.5 |
| 4-$MeC_6H_4$ | 55 | (95) | 94:6 | 96.0:4.0 |
| 1-Np | 72 | (96) | 95:5 | 95.5:4.5 |
| 2-Np | 72 | (86) | 94:6 | 96.5:3.5 |




**51** (20 mol %),
4-$O_2NC_6H_4CO_2H$
(20 mol %), $H_2O$, rt




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Catalyst Recycling

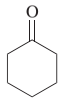
| Run | Time (d) | | *syn/anti* | er |
|---|---|---|---|---|
| 1 | 1.4 | (92) | 93:7 | 96.0:4.0 |
| 2 | 2.5 | (94) | 93:7 | 96.0:4.0 |
| 3 | 2 | (91) | 93:7 | 96.0:4.0 |
| 4 | 3 | (92) | 93:7 | 95.5:4.5 |
| 5 | 3 | (89) | 92:8 | 96.0:4.0 |
| 6 | 4 | (82) | 92:8 | 95.5:4.5 |

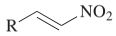
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

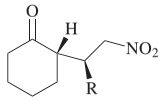
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



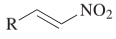


**53** (10 mol %), neat, rt, 24 h

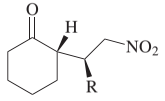


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| R | | *syn*/*anti* | er |
|---|---|---|---|
| *i*-Pr | (75) | 94:6 | 96.5:3.5 |
| Ph | (98) | 99:1 | 99.5:0.5 |
| 2-$BrC_6H_4$ | (93) | 99:1 | 99.0:1.0 |
| 3-$BrC_6H_4$ | (90) | 98:2 | 96.5:3.5 |
| 4-$BrC_6H_4$ | (95) | 99:1 | 99.5:0.5 |
| 2-$ClC_6H_4$ | (90) | 99:1 | 95.5:4.5 |
| 4-$ClC_6H_4$ | (94) | 98:2 | 96.0:4.0 |
| 4-$FC_6H_4$ | (97) | 99:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | (97) | 99:1 | 99.5:0.5 |
| 3,4-$(MeO)_2C_6H_3$ | (90) | >99:1 | >99.5:0.5 |
| 3,4-$(OCH_2O)C_6H_3$ | (84) | 99:1 | 99.5:0.5 |
| 4-$MeC_6H_4$ | (96) | >99:1 | >99.5:0.5 |
| 4-$CF_3C_6H_4$ | (98) | >99:1 | >99.5:0.5 |
| 1-Np | (86) | 99:1 | 99.5:0.5 |
| 2-Np | (91) | >99:1 | 99.5:0.5 |

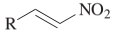


**54** (20 mol %), [bmim][$BF_4$], rt

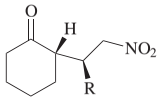


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 28 | (97) | 93:7 | 95.0:5.0 |
| 2-$C_4H_3S$ | 60 | (93) | 96:4 | 95.0:5.0 |
| Ph | 22 | (100) | 96:4 | 95.5:4.5 |
| 2-$ClC_6H_4$ | 20 | (100) | 99:1 | 98.5:1.5 |
| 3-$ClC_6H_4$ | 36 | (98) | 97:3 | 93.5:6.5 |
| 4-$ClC_6H_4$ | 20 | (87) | 98:2 | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | 20 | (95) | 94:6 | 95.5:4.5 |
| 2,4-$(MeO)_2C_6H_3$ | 96 | (92) | 97:3 | 96.0:4.0 |
| 4-$MeC_6H_4$ | 68 | (94) | 99:1 | 96.5:3.5 |
| 1-Np | 72 | (91) | 98:2 | 98.5:1.5 |



**55** (10 mol %), solvent, rt







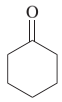
| R | Solvent | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | — | 12 | (97) | 98:2 | 95.5:4.5 |
| 2-$C_4H_3S$ | — | 12 | (>99) | 92:8 | 94.5:5.5 |
| Ph | — | 12 | (99) | 98:2 | 98.5:1.5 |
| 2-$BrC_6H_4$ | — | 12 | (90) | >99:1 | 96.0:4.0 |
| 4-$BrC_6H_4$ | — | 12 | (90) | 98:2 | 96.0:4.0 |
| 2-$ClC_6H_4$ | — | 12 | (>99) | >99:1 | 95.0:5.0 |
| 4-$ClC_6H_4$ | — | 12 | (92) | >99:1 | 99.5:0.5 |
| 2,4-$Cl_2C_6H_3$ | — | 10 | (93) | >99:1 | >99.5:0.5 |
| 4-$FC_6H_4$ | — | 12 | (92) | 98:2 | 95.0:5.0 |
| 2-$MeOC_6H_4$ | — | 10 | (>99) | 97:3 | >99.5:0.5 |
| 4-$MeOC_6H_4$ | — | 10 | (93) | 97:3 | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | $CHCl_3$ | 12 | (96) | 88:12 | 92.0:8.0 |
| 4-$MeC_6H_4$ | — | 10 | (>99) | 99:1 | 95.5:4.5 |
| PhCH=CH | — | 16 | (94) | >99:1 | 94.0:6.0 |
| 2-Np | — | 12 | (88) | 99:1 | 95.0:5.0 |

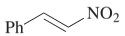
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

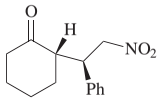
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$

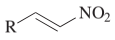




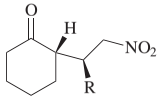
**56** (5 mol %), 4-$O_2NC_6H_4CO_2H$ (15 mol %), THF, rt, 72 h



(85) *syn/anti* = 69:31, er 98.5:1.5 — 293

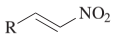


**60** (10 mol %), $NaHCO_3$ (50 mol %), [bmim][$BF_4$], rt

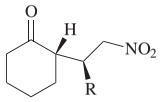


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| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 88 | (99) | 89:11 | 89.0:11.0 |
| 2-$C_4H_3S$ | 88 | (99) | 85:15 | 85.0:15.0 |
| Ph | 45 | (99) | 99:1 | 92.0:8.0 |
| 2-$ClC_6H_4$ | 64 | (99) | 99:1 | 93.5:6.5 |
| 3-$ClC_6H_4$ | 64 | (99) | 94:6 | 85.0:15.0 |
| 4-$ClC_6H_4$ | 64 | (99) | 95:5 | 92.0:8.0 |
| 2,4-$(MeO)_2C_6H_3$ | 112 | (92) | 98:2 | 94.0:6.0 |
| 4-$Me_2NC_6H_4$ | 40 | (99) | 94:6 | 89.0:11.0 |
| 4-$MeC_6H_4$ | 85 | (99) | 98:2 | 92.0:8.0 |
| 1-Np | 112 | (95) | 99:1 | 92.0:8.0 |



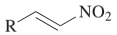
**61** (10 mol %), $PhCO_2H$ (10 mol %), brine, rt



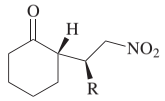
297

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| Ph | 14 | (94) | 94:6 | 97.0:3.0 |
| 4-$BrC_6H_4$ | 12 | (96) | 96:4 | 96.5:3.5 |
| 4-$FC_6H_4$ | 14 | (97) | 96:4 | 96.0:4.0 |
| 2-$MeOC_6H_4$ | 12 | (96) | 95:5 | 96.5:3.5 |

| | | | | |
|---|---|---|---|---|
| 4-$MeOC_6H_4$ | 14 | (95) | 97:3 | 97.5:2.5 |
| 2,3-$(MeO)_2C_6H_3$ | 12 | (96) | 96:4 | 97.0:3.0 |
| 3,4-$(MeO)_2C_6H_3$ | 12 | (97) | 94:6 | 97.5:2.5 |
| 4-$BnOC_6H_4$ | 12 | (90) | 94:6 | 97.0:3.0 |
| 4-$Me_2NC_6H_4$ | 18 | (84) | 95:5 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 12 | (94) | 97:3 | 96.0:4.0 |
| 4-$MeC_6H_4$ | 12 | (92) | 94:6 | 97.0:3.0 |
| 4-$CF_3C_6H_4$ | 12 | (96) | 94:6 | 96.5:3.5 |
| 2-Np | 16 | (16) | 97:3 | 96.0:4.0 |



**62** (*x* mol %),
TFA (2 mol %), neat, rt



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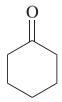
| R | *x* | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 3-$C_4H_3O$ | 10 | 18 | (94) | 95:5 | 95.0:5.0 |
| 3-$C_4H_3S$ | 10 | 18 | (93) | 94:6 | 93.0:7.0 |
| 2-pyridyl | 10 | 20 | (90) | 92:8 | 94.5:5.5 |
| Ph | 2 | 72 | (92) | 94:6 | 97.0:3.0 |
| Ph | 5 | 50 | (95) | 97:3 | 96.5:3.5 |
| Ph | 10 | 15 | (98) | 98:2 | 97.5:2.5 |
| Ph | 20 | 15 | (98) | 98:2 | 97.5:2.5 |
| 2-Cl-5-$O_2NC_6H_3$ | 10 | 18 | (98) | 96:4 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 10 | 15 | (97) | 96:4 | 99.0:1.0 |
| 2,4-$(MeO)_2C_6H_3$ | 10 | 15 | (95) | 98:2 | 97.5:2.5 |
| 3-$O_2NC_6H_4$ | 10 | 15 | (96) | 96:4 | 96.0:4.0 |
| 4-$MeC_6H_4$ | 10 | 15 | (93) | 97:3 | 99.5:0.5 |
| 2-Np | 10 | 18 | (92) | 94:6 | 96.0:4.0 |

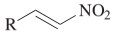
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

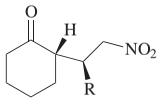
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



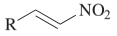


**63** (10 mol %), 2,4-$(O_2N)_2C_6H_3CO_2H$ (10 mol %), toluene

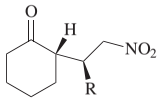


299

| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *i*-Pr | rt | 72 | (80) | 75:25 | 96.0:4.0 |
| 2-$C_4H_3O$ | 0 | 72 | (86) | 98:2 | 96.5:3.5 |
| 2-$C_4H_3S$ | 0 | 108 | (50) | 97:3 | 97.0:3.0 |
| Ph | 0 | 24 | (98) | >99:1 | 99.0:1.0 |
| 4-$BrC_6H_4$ | 0 | 48 | (95) | 99:1 | 99.0:1.0 |
| 2-$ClC_6H_4$ | 0 | 48 | (99) | >99:1 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 0 | 48 | (99) | 98:2 | 98.0:2.0 |
| 2,4-$Cl_2C_6H_3$ | 0 | 48 | (92) | >99:1 | 99.5:0.5 |
| 4-$FC_6H_4$ | 0 | 72 | (99) | 98:2 | 98.5:1.5 |
| 3,4-$(MeO)_2C_6H_3$ | 0 | 120 | (52) | 93:7 | 96.5:3.5 |
| 3-$O_2NC_6H_4$ | 0 | 48 | (99) | 97:3 | 98.5:1.5 |
| 4-$MeC_6H_4$ | 0 | 36 | (99) | 98:2 | 98.0:2.0 |
| $BnCH_2$ | rt | 72 | (50) | 98:2 | 99.0:1.0 |



**65** (5 mol %), MeOH, rt



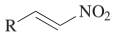
301

Catalyst Recycling (R = Ph)

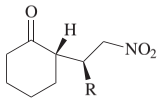
| Run | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 12 | (93) | 99:1 | 99.0:1.0 |
| 2 | 12 | (91) | 99:1 | 98.5:1.5 |
| 3 | 16 | (88) | 99:1 | 98.0:2.0 |
| 4 | 20 | (84) | 98:2 | 98.5:1.5 |
| 5 | 24 | (80) | 99:1 | 98.5:1.5 |
| 6 | 24 | (75) | 97:3 | 99.0:1.0 |

| R | | *syn*/*anti* | er |
|---|---|---|---|
| Ph | (91) | 99:1 | 99.0:1.0 |
| 2-$ClC_6H_4$ | (87) | 96:4 | 98.5:1.5 |
| 4-$ClC_6H_4$ | (91) | 97:3 | 98.0:2.0 |
| 2,4-$Cl_2C_6H_3$ | (92) | 99:1 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | (80) | 99:1 | 98.5:1.5 |
| 2-$O_2NC_6H_4$ | (90) | 98:2 | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | (93) | 99:1 | 97.5:2.5 |
| 4-$MeC_6H_4$ | (90) | 98:2 | 99.0:1.0 |





**67** (10 mol %), $CCl_3CO_2H$ (10 mol %), brine, rt



303

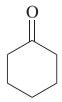
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 12 | (88) | 86:14 | 89.0:11.0 |
| *c*-$C_6H_{11}$ | 14 | (80) | 57:43 | 88.0:12.0 |
| Ph | 12 | (90) | 96:4 | 95.0:5.0 |
| 2-$ClC_6H_4$ | 14 | (88) | 95:5 | 92.0:8.0 |
| 4-$ClC_6H_4$ | 9 | (93) | 91:9 | >99.5:0.5 |
| 4-$FC_6H_4$ | 10 | (90) | 91:9 | 88.0:12.0 |
| 4-$MeOC_6H_4$ | 10 | (89) | 93:7 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 8 | (91) | 75:25 | 87.5:12.5 |
| 3,4-$(MeO)_2C_6H_3$ | 10 | (89) | 93:7 | 93.5:6.5 |
| 4-$MeC_6H_4$ | 10 | (86) | 95:5 | 94.0:6.0 |
| PhCH=CH | 8 | (94) | 96:4 | 92.0:8.0 |
| 1-Np | 12 | (89) | 86:14 | 89.0:11.0 |
| 2-Np | 10 | (87) | 97:3 | 98.5:1.5 |

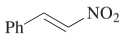
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

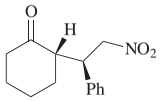
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$

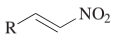




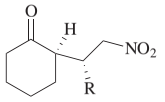
**68** (30 mol %), $PhCO_2H$ (20 mol %), toluene, rt, 4 d



(82) *syn/anti* = 2.6:1; er (*syn*) 93.0:7.0; er (*anti*) 96.0:4.0 — 279

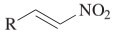


Catalyst (*x* mol %), $H_2O$ (10 eq), NMP/DMSO (1:1)

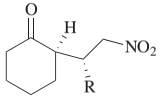


312

| R | Catalyst | *x* | Temp (°) | Time (d) | | *syn/anti* | er |
|---|---|---|---|---|---|---|---|
| Ph | **71** | 30 | 4 | 3 | (67) | 22:1 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | **77** | 40 | –20 | 3 | (76) | 20:1 | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | **77** | 40 | –20 | 2 | (68) | 25:1 | 97.0:3.0 |
| 2-Np | **77** | 40 | –20 | 3 | (79) | 22:1 | 99.0:1.0 |

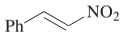


**72** (30 mol %), $H_2O$ (10 eq), 4-TsOH (*x* mol %), solvent

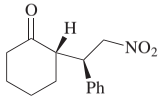


313

| R | *x* | Solvent | Temp | | *syn/anti* | er |
|---|---|---|---|---|---|---|
| Ph | 15 | NMP | rt | (92) | 27:1 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 15 | NMP | rt | (82) | 19:1 | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | 15 | NMP | 4° | (82) | 34:1 | 98.0:2.0 |
| 2-Np | 0 | NMP/DMSO (9:1) | rt | (75) | 23:1 | 99.0:1.0 |

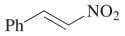


**73** (20 mol %),
4-$O_2NC_6H_4CO_2H$
(20 mol %), MeCN, rt, 1 d

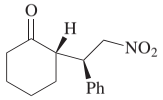


(80) *syn*/*anti* = 90:10
er 82.5:17.5

314

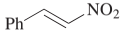


Catalyst (20 mol %),
$PhCO_2H$ (20 mol %),
neat, rt, 1 d

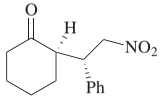


315

| Catalyst | | dr | er |
|---|---|---|---|
| **74** | (87) | 98:2 | 93.5:6.5 |
| **75** | (95) | 89:11 | 86.5:13.5 |

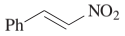


**79** (5 mol %),
benzene, rt, 3 d

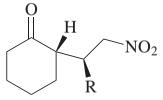


(92) *syn*/*anti* = 93:7
er 92.0:8.0

267



**80a** (10 mol %),
$PhCO_2H$ (10 mol %),
neat, rt, 3 d

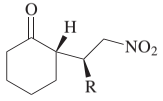


(91) *syn*/*anti* = 7.1:1
er 92.0:8.0

318



**81** (5 mol %),
2-$MeC_6H_4CO_2H$ (5 mol %),
*n*-hexane, rt, 40 h



(83) *syn*/*anti* = 99:1
er 97.0:3.0

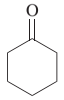
319

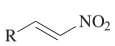
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

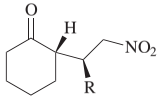
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$





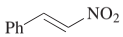
**81** (*x* mol %),
2-$MeC_6H_4CO_2H$ (5 mol %),
*n*-hexane, rt



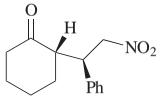
319

| R | *x* | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 5 | 24 | (97) | 88:12 | 95.5:4.5 |
| 2-$C_4H_3S$ | 5 | 72 | (72) | 90:10 | 97.0:3.0 |
| Ph | 2 | 36 | (86) | 96:4 | 98.0:2.0 |
| Ph | 5 | 24 | (99) | 97:3 | 98.0:2.0 |
| Ph | 10 | 11 | (99) | 97:3 | 98.0:2.0 |
| 2-$BrC_6H_4$ | 5 | 12 | (98) | 97:3 | 98.0:2.0 |
| 3-$BrC_6H_4$ | 5 | 48 | (72) | 95:5 | 97.5:2.5 |
| 4-$BrC_6H_4$ | 5 | 12 | (96) | 97:3 | 98.5:1.5 |
| 2-$ClC_6H_4$ | 5 | 12 | (99) | 96:4 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 5 | 12 | (99) | 97:3 | 96.5:3.5 |
| 2,4-$Cl_2C_6H_3$ | 5 | 12 | (99) | 96:4 | 97.0:3.0 |
| 2-$FC_6H_4$ | 5 | 36 | (97) | 98:2 | 99.0:1.0 |

| R | *x* | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|
| 4-$FC_6H_4$ | 5 | 24 | (98) | 94:6 | 97.5:2.5 |
| 2-$MeOC_6H_4$ | 5 | 24 | (99) | 96:4 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 5 | 64 | (99) | 95:5 | 97.5:2.5 |
| 2-$O_2NC_6H_4$ | 5 | 12 | (99) | 96:4 | 97.5:2.5 |
| 3-$O_2NC_6H_4$ | 5 | 12 | (93) | 90:10 | 97.5:2.5 |
| 4-$O_2NC_6H_4$ | 5 | 12 | (96) | 92:8 | 97.5:2.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 5 | 62 | (68) | 99:1 | 95.5:4.5 |
| 2-$MeC_6H_4$ | 5 | 48 | (95) | 94:6 | 99.0:1.0 |
| 3-$MeC_6H_4$ | 5 | 24 | (84) | 96:4 | 97.5:2.5 |
| 4-$MeC_6H_4$ | 5 | 48 | (99) | 97:3 | 98.5:1.5 |
| 1-Np | 5 | 36 | (91) | 99:1 | 96.5:3.5 |
| 2-Np | 5 | 48 | (83) | 99:1 | 99.0:1.0 |

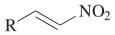


**82** (10 mol %),
$PhCO_2H$ (10 mol %),
EtOH, rt, 36 h

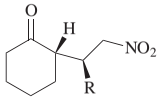


(95) *syn/anti* = 99:1
er >99.5:0.5

320



**84** (5 mol %),
$CHCl_3$/MeOH (1:1),
rt, 48 h

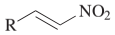


*syn*/*anti* > 98:2

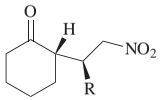
Catalyst Recycling (R = Ph)

| Run | | *syn*/*anti* | er |
|---|---|---|---|
| 1 | (94) | >98:2 | 80.0:20.0 |
| 2 | (65) | >98:2 | 80.0:20.0 |
| 3 | (27) | 95:5 | 72.5:27.5 |
| 4 | (24) | 91:9 | <55.0:45.0 |

| R | | er | |
|---|---|---|---|
| *i*-Pr | (60) | 79.0:21.0 | 323 |
| Ph | (94) | 80.0:20.0 | |
| 4-$BrC_6H_4$ | (80) | 82.5:17.5 | |
| 4-$ClC_6H_4$ | (89) | 82.0:18.0 | |
| 4-$FC_6H_4$ | (83) | 80.5:19.5 | |
| 4-$MeOC_6H_4$ | (72) | 78.5:21.5 | |
| 1-Np | (88) | 78.0:22.0 | |



**86** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt



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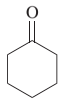
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 28 | (88) | 99:1 | >99.5:0.5 |
| 2-$BrC_6H_4$ | 25 | (81) | 99:1 | 98.5:1.5 |
| 4-$BrC_6H_4$ | 20 | (90) | 99:1 | 99.0:0.5 |
| 4-$ClC_6H_4$ | 20 | (86) | 99:1 | 99.0:0.5 |
| 2-$MeOC_6H_4$ | 38 | (77) | >99:1 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 36 | (79) | >99:1 | 98.5:1.5 |
| 2-$O_2NC_6H_4$ | 30 | (85) | 97:3 | 97.5:2.5 |
| 4-$MeC_6H_4$ | 33 | (90) | 99:1 | 99.0:0.5 |

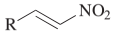
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

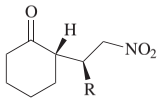
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



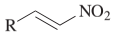


**87** (15 mol %), $H_2O$, 10°

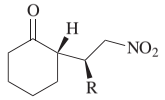


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 3-$C_4H_3O$ | 18 | (99) | >99:1 | 95.0:5.0 |
| 3-$C_4H_3S$ | 17 | (92) | 95:5 | 92.5:7.5 |
| Ph | 14 | (98) | >99:1 | 99.0:1.0 |
| 2-$BrC_6H_4$ | 20 | (95) | 95:5 | 95.5:4.5 |
| 4-$BrC_6H_4$ | 19 | (95) | 98:2 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 17 | (95) | >99:1 | 97.0:3.0 |
| 2-$FC_6H_4$ | 17 | (96) | >99:1 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 24 | (89) | >99:1 | 97.5:2.5 |
| 2-$O_2NC_6H_4$ | 14 | (95) | >99:1 | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | 12 | (95) | 97:3 | 96.0:4.0 |
| 2-$MeC_6H_4$ | 20 | (90) | >99:1 | 97.5:2.5 |
| 4-$MeC_6H_4$ | 18 | (96) | >99:1 | 99.0:1.0 |
| 1-Np | 18 | (85) | >99:1 | 97.0:3.0 |



Catalyst (20 mol %),
additive (20 mol %), DMF



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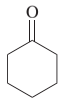
| R | Catalyst | Additive | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|---|
| 2-$C_4H_3O$ | **88a** | $MeSO_3H$ | 0° | 45 | (82) | 15:1 | 94.0:6.0 |
| 2-$C_4H_3S$ | **88a** | HCl | rt | 24 | (75) | 12:1 | 91.5:8.5 |
| 2-$C_4H_3S$ | **88b** | HCl | rt | 24 | (99) | 19:1 | 92.0:8.0 |
| 2-$C_4H_3S$ | **88a** | $MeSO_3H$ | 0° | 45 | (74) | 19:1 | 92.5:7.5 |
| 2-$C_4H_3S$ | **88b** | $MeSO_3H$ | 0° | 45 | (88) | 20:1 | 96.0:4.0 |
| 2-$C_4H_3S$ | **88b** | TsOH | rt | 24 | (91) | 50:1 | 90.5:9.5 |
| Ph | **88a** | TsOH | rt | 24 | (83) | 19:1 | 99.5:0.5 |
| 2-$MeOC_6H_4$ | **88a** | $MeSO_3H$ | 0° | 45 | (95) | 50:1 | 99.5:0.5 |
| 2-$MeOC_6H_4$ | **88a** | TsOH | rt | 24 | (99) | 5:1 | 93.0:7.0 |
| 4-$MeOC_6H_4$ | **88a** | TsOH | rt | 24 | (83) | 19:1 | 99.5:0.5 |
| 3-$O_2NC_6H_4$ | **88a** | TsOH | rt | 24 | (80) | 19:1 | 93.0:7.0 |
| 3-$O_2NC_6H_4$ | **88b** | TsOH | rt | 24 | (90) | 19:1 | 95.0:5.0 |
| 2-$CF_3C_6H_4$ | **88a** | TsOH | rt | 24 | (89) | 19:1 | 95.0:5.0 |
| 2-$CF_3C_6H_4$ | **88b** | TsOH | rt | 24 | (90) | 19:1 | 95.5.:4.5 |
| 4-$CF_3C_6H_4$ | **88a** | TsOH | rt | 24 | (81) | 15:1 | 96.0:4.0 |
| 4-$CF_3C_6H_4$ | **88b** | TsOH | rt | 24 | (95) | 20:1 | 98.0:2.0 |
| 1-Np | **88a** | TsOH | rt | 24 | (90) | 19:1 | 99.5:0.5 |
| 2-Np | **88a** | TsOH | rt | 24 | (86) | 12:1 | 93.5:6.5 |

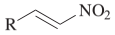
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

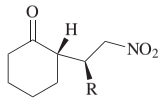
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$





**89** (10 mol %), neat

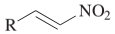


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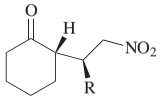
Catalyst Recycling (R = Ph)

| Run | | *syn*/*anti* | er |
|---|---|---|---|
| 1 | (97) | 98:2 | 99.5:0.5 |
| 2 | (94) | 98:2 | 99.5:0.5 |
| 3 | (95) | 98:2 | 99.5:0.5 |
| 4 | (89) | 98:2 | 99.5:0.5 |
| 5 | (91) | 98:2 | 99.5:0.5 |
| 6 | (88) | 98:2 | 99.5:0.5 |
| 7 | (89) | 97:3 | 99.5:0.5 |
| 8 | (87) | 98:2 | 99.5:0.5 |

| R | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *i*-Pr | rt | 24 | (69) | 93:7 | 95:5:4.5 |
| $C_4H_3S$ | rt | 24 | (90) | 99:1 | >99.5:0.5 |
| Ph | rt | 24 | (97) | 99:1 | 99.5:0.5 |
| 2-$BrC_6H_4$ | rt | 24 | (96) | 99:1 | 99.0:1.0 |
| 3-$BrC_6H_4$ | rt | 24 | (93) | 98:2 | 98.0:2.0 |
| 4-$BrC_6H_4$ | rt | 24 | (96) | 99:1 | 99.5:0.5 |
| 2-$ClC_6H_4$ | rt | 24 | (94) | 95:5 | 96.5:3.5 |
| 2-$ClC_6H_4$ | 0° | 48 | (82) | 97:3 | 98.0:2.0 |
| 4-$ClC_6H_4$ | rt | 24 | (97) | 99:1 | 99.5:0.5 |
| 4-$FC_6H_4$ | rt | 24 | (97) | 98:2 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | rt | 24 | (96) | 99:1 | 99.5:0.5 |
| 3,4-$(MeO)_2C_6H_3$ | rt | 24 | (92) | >99:1 | >99.5:0.5 |
| 3,4-$(OCH_2O)C_6H_3$ | rt | 24 | (94) | 98:2 | 99.0:1.0 |
| 4-$MeC_6H_4$ | rt | 24 | (96) | >99:1 | >99.5:0.5 |
| 4-$CF_3C_6H_4$ | rt | 24 | (98) | >99:1 | >99.5:0.5 |
| 4-$NCC_6H_4$ | rt | 24 | (97) | 95:5 | 98.0:2.0 |
| 1-Np | rt | 24 | (86) | 98:2 | 99.0:1.0 |
| 2-Np | rt | 24 | (90) | >99:1 | >99.5:0.5 |



**90** (20 mol %),
$Et_3N$ (20 mol %),
$PhCO_2H$ (10 mol %),
neat



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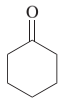
| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_3H_4O$ | –30 | 16 | (>99) | 98:2 | 97.5:2.5 |
| Ph | –30 | 22 | (>99) | >99:1 | 98.0:2.0 |
| 2-$BrC_6H_4$ | –30 | 21 | (98) | >99:1 | 98.5:1.5 |
| 4-$BrC_6H_4$ | –30 | 21 | (83) | >99:1 | 99.0:1.0 |
| 4-$ClC_6H_4$ | –30 | 21 | (85) | 98:2 | 99.0:1.0 |
| 4-$FC_6H_4$ | –30 | 19 | (95) | 99:1 | 98.5:1.5 |
| 2-$MeOC_6H_4$ | –30 | 19 | (77) | 99:1 | 98.0:2.0 |
| 3,4-$(OCH_2O)C_6H_3$ | –30 | 40 | (82) | >99:1 | 99.0:1.0 |
| 4-$MeC_6H_4$ | –30 | 19 | (>99) | 99:1 | 98.5:1.5 |
| 3-$CF_3C_6H_4$ | –30 | 21 | (85) | 98:2 | 98.0:2.0 |
| 4-$CF_3C_6H_4$ | –30 | 23 | (87) | >99:1 | 99.5:0.5 |
| $BnCH_2$ | rt | 4 | (89) | 73:27 | 95.5:4.5 |
| PhCH=CH | rt | 17 | (92) | 93:7 | 94.5:5.5 |
| 1-Np | –30 | 19 | (97) | >99:1 | 98.5:1.5 |

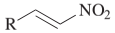
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

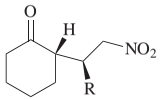
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



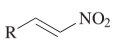


**91** (10 mol %), $H_2O$, rt

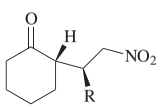


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 48 | (68) | 98:2 | 97.5:2.5 |
| 2-$C_4H_3S$ | 48 | (65) | >99:1 | 97.0:3.0 |
| Ph | 12 | (96) | 99:1 | 98.0:2.0 |
| 3-$BrC_6H_4$ | 24 | (85) | 97:3 | 98.0:2.0 |
| 4-$BrC_6H_4$ | 24 | (90) | 99:1 | 97.5:2.5 |
| 2-$ClC_6H_4$ | 24 | (91) | >99:1 | 98.5:1.5 |
| 4-$ClC_6H_4$ | 24 | (88) | >99:1 | 98.0:2.0 |
| 4-$FC_6H_4$ | 24 | (80) | 98:2 | 98.5:1.5 |
| 2-$MeOC_6H_4$ | 24 | (94) | 96:4 | 97.5:2.5 |
| 3,4-$(MeO)_2C_6H_3$ | 48 | (60) | 98:2 | 96.5:3.5 |
| 3-$O_2NC_6H_4$ | 24 | (85) | 98:2 | 98.5:1.5 |
| 4-$MeC_6H_4$ | 48 | (85) | >99:1 | 98.5:1.5 |



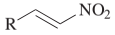
**91** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, Temp (°)



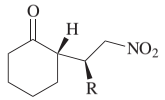
331

| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 0 | 48 | (50) | 99:1 | 97.0:3.0 |
| 2-$C_4H_3S$ | 0 | 70 | (63) | 98:2 | 96.5:3.5 |
| Ph | 0 | 24 | (97) | 99:1 | 97.5:2.5 |

| | | | | | |
|---|---|---|---|---|---|
| 2-$ClC_6H_4$ | 0 | 24 | (81) | >99:1 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 0 | 36 | (57) | 99:1 | 98.0:2.0 |
| 4-$FC_6H_4$ | 0 | 70 | (78) | 99:1 | 98.0:2.0 |
| 2-$MeOC_6H_4$ | 0 | 24 | (87) | >99:1 | 98.0:2.0 |
| 3,4-$(MeO)_2C_6H_3$ | rt | 96 | (42) | 99:1 | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | rt | 48 | (88) | 98:2 | 98.0:2.0 |
| 4-$MeC_6H_4$ | 0 | 48 | (47) | >99:1 | 97.5:2.5 |
| $BnCH_2$ | 0 | 70 | (30) | 67:33 | 85.5:14.5 |




**92** (10 mol %),
4-$MeOC_6H_4CO_2H$
(10 mol %), brine, rt



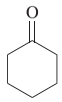

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 8 | (89) | 88:12 | 94.5:5.5 |
| *c*-$C_6H_{11}$ | 26 | (85) | 90:10 | 93.5:6.5 |
| Ph | 9 | (93) | 99:1 | 99.0:1.0 |
| 4-$BrC_6H_4$ | 8 | (80) | 99:1 | 97.0:3.0 |
| 2-$ClC_6H_4$ | 8 | (86) | 98:2 | 97.0:3.0 |
| 4-$ClC_6H_4$ | 7 | (92) | 99:1 | 99.5:0.5 |
| 2,4-$Cl_2C_6H_3$ | 8 | (85) | 99:1 | 98.0:2.0 |
| 4-$FC_6H_4$ | 8 | (85) | 98:2 | 96.0:4.0 |
| 2-$MeOC_6H_4$ | 10 | (91) | 99:1 | 95.5:4.5 |
| 3-$MeOC_6H_4$ | 10 | (80) | 98:2 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 10 | (82) | 98:2 | 95.0:5.0 |
| 3,4-$(MeO)_2C_6H_3$ | 10 | (80) | 97:3 | 94.0:6.0 |
| 4-$MeC_6H_4$ | 9 | (81) | 99:1 | 98.0:2.0 |

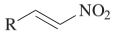
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

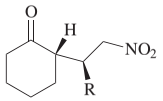
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



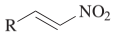


Catalyst (20 mol %),
toluene, rt, 48 h

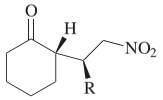


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| R | Catalyst | | *syn/anti* | er (*syn*) |
|---|---|---|---|---|
| 2-$C_4H_3O$ | **95a** | (80) | 11:1 | 92.0:8.0 |
| 2-$C_4H_3O$ | **95b** | (93) | 11:1 | 91.5:8.5 |
| 2-$C_4H_3O$ | **95c** | (89) | 10:1 | 94.5:5.5 |
| 2-$C_4H_3S$ | **95a** | (97) | 6:1 | 85.5:14.5 |
| 2-$C_4H_3S$ | **95b** | (20) | 16:1 | 89.5:10.5 |
| 2-$C_4H_3S$ | **95c** | (77) | 12:1 | 91.0:9.0 |
| Ph | **95a** | (69) | 15:1 | 93.5:6.5 |
| Ph | **95b** | (99) | 15:1 | 82.5:17.5 |
| Ph | **95c** | (80) | 17:1 | 88.5:11.5 |
| Ph | **95d** | (67) | 10:1 | 93.5:6.5 |
| 4-$MeOC_6H_4$ | **95a** | (97) | 25:1 | 75.0:25.0 |
| 4-$MeOC_6H_4$ | **95c** | (99) | 20:1 | 84.0:16.0 |
| 4-$MeOC_6H_4$ | **95d** | (87) | 25:1 | 86.5:13.5 |
| 4-$O_2NC_6H_4$ | **95b** | (76) | 20:1 | 94.5:5.5 |
| 4-$O_2NC_6H_4$ | **95c** | (88) | 9:1 | 93.5:6.5 |
| 2-$MeC_6H_4$ | **95b** | (74) | >20:1 | 95.0:5.0 |
| 2-$MeC_6H_4$ | **95c** | (99) | 15:1 | 93.5:6.5 |
| 2-$CF_3C_6H_4$ | **95d** | (82) | 20:1 | 88.0:12.0 |



**95e** (10 mol %), $H_2O$, rt

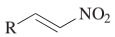


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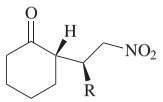
Catalyst Recycling (R = Ph)

| Run | Time (h) | | dr | er |
|---|---|---|---|---|
| 1 | 6 | (92) | 34:1 | 95.0:5.0 |
| 2 | 9 | (95) | 33:1 | 95.0:5.0 |
| 3 | 10 | (90) | 33:1 | 95.0:5.0 |
| 4 | 14 | (95) | 36:1 | 94.5:5.5 |
| 5 | 24 | (85) | 22:1 | 94.5:5.5 |
| 6 | 50 | (70) | 11:1 | 94.5:5.5 |

| R | Time (h) | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 9 | (91) | 17:1 | 92.5:7.5 |
| Ph | 9 | (95) | 27:1 | 95.0:5.0 |
| 4-$ClC_6H_4$ | 7 | (95) | 17:1 | 95.0:5.0 |
| 2-$MeOC_6H_4$ | 12 | (92) | 50:1 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | 12 | (95) | 16:1 | 94.5:5.5 |
| 2-$CF_3C_6H_4$ | 11 | (90) | 50:1 | 96.5:3.5 |



**95f** (15 mol %),
*i*-PrOH, rt, 4 d



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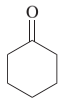
| R | | *syn*/*anti* | er |
|---|---|---|---|
| Ph | (83) | 98:2 | 97.0:3.0 |
| 4-$BrC_6H_4$ | (83) | 94:6 | 97.0:3.0 |
| 2-$ClC_6H_4$ | (92) | 99:1 | 97.5:2.5 |
| 2,4-$Cl_2C_6H_3$ | (93) | 98:2 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | (65) | 99:1 | 99.5:0.5 |
| 2-$O_2NC_6H_4$ | (91) | 99:1 | 96.5:3.5 |
| 4-$MeC_6H_4$ | (77) | 96:4 | 99.5:0.5 |
| 2-$CF_3C_6H_4$ | (87) | 99:1 | 97.5:2.5 |

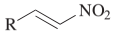
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

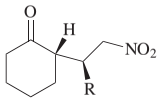
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$





**96** (20 mol %), PEG-800, rt

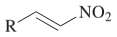


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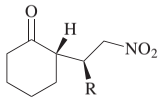
Catalyst Recycling (R = Ph)

| Run | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 12 | (95) | 97:3 | 98.5:1.5 |
| 2 | 12 | (95) | 96:4 | 98.5:1.5 |
| 3 | 12 | (93) | 96:4 | 98.5:1.5 |
| 4 | 18 | (90) | 93:7 | 98.0:2.0 |
| 5 | 18 | (88) | 94:6 | 98.5:1.5 |
| 6 | 24 | (83) | 96:4 | 97.0:3.0 |
| 7 | 24 | (76) | 98:2 | 98.0:2.0 |
| 8 | 24 | (75) | 96:4 | 98.0:2.0 |

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 12 | (96) | 90:10 | 97.0:3.0 |
| 2-$C_4H_3S$ | 12 | (75) | 94:6 | 96.0:4.0 |
| Ph | 12 | (95) | 97:3 | 98.5:1.5 |
| 4-$ClC_6H_4$ | 12 | (94) | 93:7 | 99.0:1.0 |
| 2-$MeOC_6H_4$ | 12 | (97) | 93:7 | 97.0:3.0 |
| 3-$MeOC_6H_4$ | 12 | (90) | 96:4 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 12 | (79) | 97:3 | 99.5:0.5 |
| 2-$O_2NC_6H_4$ | 48 | (78) | 96:4 | 94.0:6.0 |
| 4-$MeC_6H_4$ | 24 | (87) | 93:7 | 99.5:0.5 |
| 4-$CF_3C_6H_4$ | 48 | (90) | 94:6 | 99.5:0.5 |
| 2-Np | 12 | (88) | 90:10 | 98.0:2.0 |

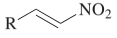


**97** (5 mol %),
$PhCO_2H$ (5 mol %),
$H_2O$, rt

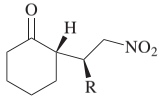


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 6 | (81) | 90:10 | 90.0:10.0 |
| Ph | 8 | (83) | 99:1 | 98.0:2.0 |
| 4-$BrC_6H_4$ | 11 | (82) | 98:2 | 95.0:5.0 |
| 2-$ClC_6H_4$ | 6 | (89) | 98:2 | 96.5:3.5 |
| 4-$ClC_6H_4$ | 13 | (69) | 88:12 | 94.0:6.0 |
| 2,4-$Cl_2C_6H_3$ | 5 | (80) | 99:1 | 96.0:4.0 |
| 2-$FC_6H_4$ | 11 | (83) | 94:6 | 96.0:4.0 |
| 4-$FC_6H_4$ | 10 | (80) | 94:6 | 96.0:4.0 |
| 3-$PhOC_6H_4$ | 5 | (74) | 95:5 | 93.0:7.0 |
| 4-$MeC_6H_4$ | 5 | (93) | 97:3 | 97.0:3.0 |



**100** (15 mol %), neat, rt



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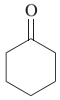
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 14 | (97) | >99:1 | >99.5:0.5 |
| 3-$C_4H_3O$ | 13 | (98) | 99:1 | 99.0:1.0 |
| Ph | 16 | (99) | >99:1 | >99.5:0.5 |
| 4-$BrC_6H_4$ | 13 | (97) | >99:1 | 99.5:0.5 |
| 2-$ClC_6H_4$ | 24 | (93) | 99:1 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 17 | (96) | 98:2 | 99.0:1.0 |
| 2-$MeOC_6H_4$ | 24 | (96) | >99:1 | 98.5:1.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 18 | (92) | >99:1 | >99.5:0.5 |
| 2-$MeC_6H_4$ | 26 | (95) | >99:1 | 99.0:1.0 |
| 3-$MeC_6H_4$ | 24 | (98) | >99:1 | 99.0:1.0 |

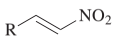
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

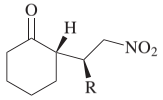
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



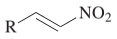


**101** (5 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
1 M KOH (50 μL), neat, rt

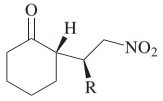


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| R | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 20 | (93) | 82:18 | 95.5:4.5 |
| Ph | 7 | (82) | 92:8 | 98.0:2.0 |
| 2-$BrC_6H_4$ | 7 | (91) | 99:1 | 98.0:2.0 |
| 2-$ClC_6H_4$ | 7 | (94) | 99:1 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 7 | (87) | 92:8 | 95.5:4.5 |
| 4-$FC_6H_4$ | 17 | (99) | 90:10 | 97.0:3.0 |
| 2-$MeC_6H_4$ | 20 | (87) | 93:7 | 97.5:2.5 |
| 3-$MeC_6H_4$ | 17 | (91) | 92:8 | 98.0:2.0 |
| 4-$MeC_6H_4$ | 17 | (88) | 92:8 | 96.0:4.0 |



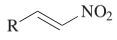
Catalyst (10 mol %),
2,4-$(O_2N)_2C_6H_3SO_3H$
(5 mol %), $CHCl_3$, 0°



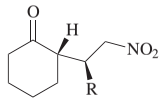
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| R | Catalyst | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3S$ | **102a** | 29 | (92) | 94:6 | 94.0:6.0 |
| 2-$C_4H_3S$ | **102b** | 48 | (98) | 93:7 | 95.0:5.0 |
| Ph | **102a** | 20 | (98) | 98:2 | 97.5:2.5 |
| Ph | **102b** | 24 | (95) | 98:2 | 99.5:0.5 |
| 2-$MeOC_6H_4$ | **102a** | 21 | (100) | 98:2 | 96.0:4.0 |
| 2-$MeOC_6H_4$ | **102b** | 24 | (99) | 98:2 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | **102a** | 46 | (97) | 97:3 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | **102b** | 24 | (100) | 97:3 | 98.0:2.0 |

| | | | | | |
|---|---|---|---|---|---|
| 1-Np | **102a** | 50 | (92) | 97:3 | 99.0:1.0 |
| 1-Np | **102b** | 36 | (100) | 97:3 | 96.5:3.5 |
| 2-Np | **102a** | 24 | (99) | 99:1 | 97.0:3.0 |
| 2-Np | **102b** | 8 | (99) | 98:2 | 96.5:3.5 |




**103** (20 mol %), $H_2O$, rt




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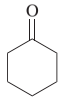
| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| Ph | 12 | (93) | 97:3 | 98.5:1.5 |
| 2-$BrC_6H_4$ | 12 | (99) | 99:1 | 99.0:1.0 |
| 2-$ClC_6H_4$ | 12 | (>99) | 99:1 | 99.0:1.0 |
| 4-$ClC_6H_4$ | 12 | (64) | 97:3 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 15 | (84) | 99:1 | 97.0:3.0 |
| 2,4-$(MeO)_2C_6H_3$ | 23 | (98) | 94:6 | 95.5:4.5 |
| 3-$O_2NC_6H_4$ | 36 | (83) | 97:3 | 98.5:1.5 |
| 4-$MeC_6H_4$ | 12 | (90) | 97:3 | 97.5:2.5 |
| 2-Np | 15 | (84) | 97:3 | 98.0:2.0 |

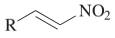
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

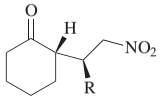
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$





Catalyst (10 mol %),
[bmim][$BF_4$], rt, 20 h

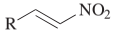


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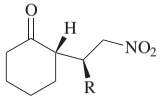
Catalyst **105a** Recycling (R = Ph)

| Run | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 20 | (94) | 94:6 | 99.5:0.5 |
| 2 | 24 | (94) | 94:6 | 99.5:0.5 |
| 3 | 24 | (92) | 94:6 | 99.5:0.5 |
| 4 | 24 | (90) | 94:6 | 98.5:1.5 |
| 5 | 24 | (90) | 94:6 | 98.0:2.0 |

| R | catalyst | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | **105a** | (95) | 90:10 | 93.5:6.5 |
| 2-$C_4H_3O$ | **105b** | (95) | 91:9 | 95.5:4.5 |
| 2-$C_4H_3S$ | **105a** | (95) | 92:8 | 87.5:12.5 |
| Ph | **105a** | (94) | 94:6 | 99.5:0.5 |
| Ph | **105b** | (95) | 96:4 | 96.5:3.5 |
| 2-$BrC_6H_4$ | **105a** | (95) | 96:4 | 90.5:9.5 |
| 3-$BrC_6H_4$ | **105a** | (94) | 92:8 | 91.0:9.0 |
| 4-$ClC_6H_4$ | **105a** | (95) | 95:5 | 91.5:8.5 |
| 2-$MeOC_6H_4$ | **105a** | (95) | 95:5 | 91.0:9.0 |
| 2-$MeOC_6H_4$ | **105b** | (95) | 96:4 | 98.5:1.5 |
| 3-$MeOC_6H_4$ | **105a** | (93) | 95:5 | 96.0:4.0 |
| 3-$MeOC_6H_4$ | **105b** | (95) | 93:7 | 96.5:3.5 |
| 4-$MeOC_6H_3$ | **105a** | (95) | 92:8 | 100.0:0.0 |
| 4-$MeOC_6H_3$ | **105b** | (95) | 94:6 | 96.5:3.5 |
| 2-$O_2NC_6H_4$ | **105a** | (93) | 95:5 | 88.5:11.5 |
| 4-$MeC_6H_4$ | **105a** | (94) | 94:6 | 93.5:6.5 |
| 4-$MeC_6H_4$ | **105b** | (94) | 95:5 | 99.0:1.0 |
| 4-$CF_3C_6H_4$ | **105a** | (93) | 95:5 | 92.0:8.0 |
| 2-Np | **105a** | (95) | 93:7 | 91.0:9.0 |

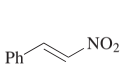


Catalyst (20 mol %),
toluene, rt, 48 h

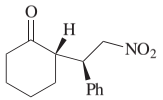


350

| R | Catalyst | | *syn/anti* | er |
|---|---|---|---|---|
| Ph | **106b** | (53) | 99:1 | 99.5:0.5 |
| 4-$BrC_6H_4$ | **106a** | (50) | 93:7 | 93.0:7.0 |
| 4-$BrC_6H_4$ | **106b** | (30) | 93:7 | 97.0:3.0 |
| 2-$ClC_6H_4$ | **106b** | (71) | 93:7 | 96.5:3.5 |
| 3-$ClC_6H_4$ | **106b** | (80) | 89:11 | 99.5:0.5 |
| 4-$ClC_6H_4$ | **106b** | (65) | 93:7 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | **106a** | (68) | 90:10 | 88.0:12.0 |
| 4-$MeOC_6H_4$ | **106b** | (54) | 87:13 | 75.5:24.5 |
| 4-$(Me_2N)C_6H_4$ | **106b** | (41) | 84:16 | 53.5:46.5 |
| 4-$MeC_6H_4$ | **106b** | (69) | 99:1 | 84.5:15.5 |
| 9-$C_{14}H_9$ | **106b** | (80) | 95:5 | 75.0:25.0 |



**107** (20 mol %), $Et_2O$, 4°, 6 d



(38) *syn/anti* = 95:5
er 91.0:9.0

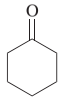
351

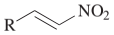
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

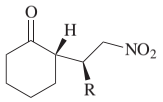
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



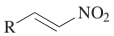


**108** (15 mol %),
**109** (15 mol %), $H_2O$, rt

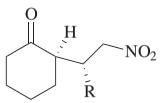


352

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 36 | (95) | 95:5 | 92.5:7.5 |
| 2-$ClC_6H_4$ | 72 | (94) | 95:5 | 94.0:6.0 |
| 4-$ClC_6H_4$ | 48 | (81) | 98:2 | 92.5:7.5 |
| 4-$MeOC_6H_4$ | 72 | (99) | 96:4 | 93.5:6.5 |
| 3-$O_2NC_6H_4$ | 24 | (67) | 94:6 | 90.5:9.5 |
| 2-Np | 48 | (99) | 95:5 | 93.5:6.5 |

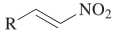


**110** (10 mol %),
toluene, 0°, 72 h

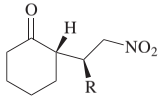


353

| R | Conv. (%) | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 68 | 80.5:19.5 | 91.0:9.0 |
| 4-$BrC_6H_4$ | 65 | 81:19 | 90.0:10.0 |
| 4-$MeOC_6H_4$ | 55 | 99:1 | 77.5:22.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 26 | 99:1 | 97.5:2.5 |
| 2-$O_2NC_6H_4$ | 59 | 99:1 | 74.5:25.5 |
| 4-$O_2NC_6H_4$ | 64 | 99:1 | 96.5:3.5 |
| 4-$MeC_6H_4$ | 66 | 85:15 | 89.5:10.5 |
| 2-Np | 65 | 85.5:14.5 | 87.5:12.5 |

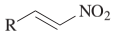


**111** (10 mol %), $H_2O$, rt, 16 h

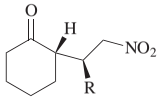


920

| R | | *syn/anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (66) | 86:14 | 90.0:10.0 |
| Ph | (70) | 97:3 | 99.5:0.5 |
| 4-$ClC_6H_4$ | (53) | 95:5 | 97.0:3.0 |
| 2-$MeOC_6H_4$ | (95) | 94:3 | 93.0:7.0 |
| 3-$MeOC_6H_4$ | (74) | 94:6 | 96.5:3.5 |
| 2-$O_2NC_6H_4$ | (90) | 92:8 | 96.5:3.5 |
| 3-$O_2NC_6H_4$ | (60) | 90:10 | 95.0:5.0 |
| 4-$MeC_6H_4$ | (83) | 94:3 | 96.5:3.5 |



**112** (10 mol %), TFA (2.5 mol %), 10°, 72 h

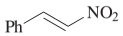


354

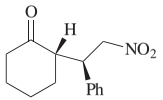
Catalyst Recycling (R = Ph)

| Run | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 1 | 72 | (97) | 99:1 | >99.5:0.5 |
| 2 | 72 | (95) | 99:1 | >99.5:0.5 |
| 3 | 72 | (96) | 99:1 | >99.5:0.5 |
| 4 | 72 | (93) | 99:1 | >99.5:0.5 |
| 5 | 72 | (95) | 99:1 | >99.5:0.5 |
| 6 | 72 | (94) | 99:1 | >99.5:0.5 |
| 7 | 72 | (93) | 99:1 | >99.5:0.5 |
| 8 | 72 | (90) | 99:1 | >99.5:0.5 |
| 9 | 96 | (88) | 99:1 | >99.5:0.5 |
| 10 | 96 | (89) | 99:1 | >99.5:0.5 |

| R | | *syn/anti* | er |
|---|---|---|---|
| Ph | (97) | >99:1 | >99.5:0.5 |
| 4-$BrC_6H_4$ | (90) | 98:2 | >99.5:0.5 |
| 2-$ClC_6H_4$ | (92) | 98:2 | 95.0:5.0 |
| 4-$ClC_6H_4$ | (92) | >99:1 | 99.5:0.5 |
| 4-$FC_6H_4$ | (94) | >99:1 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | (85) | >99:1 | >99.5:0.5 |
| 3-$O_2NC_6H_4$ | (95) | 97:3 | 94.0:6.0 |
| 4-$MeC_6H_4$ | (88) | 99:1 | >99.5:0.5 |
| 4-$CF_3C_6H_4$ | (91) | 99:1 | 98.0:2.0 |
| 3,4-$(CH_2OCH_2)C_6H_3$ | (89) | 99:1 | 98.0:2.0 |



Catalyst (10 mol %), $PhCO_2H$ (10 mol %), $CHCl_3$, rt



355

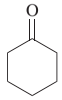
| Catalyst | Time (d) | Conv. (%) | | *syn/anti* | er |
|---|---|---|---|---|---|
| **113** | 4 | 60 | — | 95:5 | 80.5:19.5 |
| **114** | 3 | 100 | (81) | 92:8 | 93.5:6.5 |

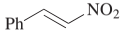
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

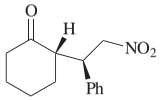
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



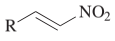


Catalyst (20 mol %), additive (5 mol %), solvent, 6 d

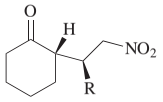


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| Catalyst | Additive | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| **115a** | none | MeCN | (38) | 95:5 | 94.0:6.0 |
| **115b** | TFA | MeOH | (40) | 94:6 | 95.0:5.0 |

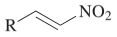


**116** (5 mol %), solvent, rt

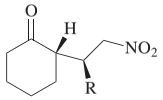


357

| R | Solvent | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Ph | neat | 40 | (94) | 94:6 | 97.5:2.5 |
| Ph | $H_2O$ | 48 | (96) | 95:5 | 93.5:6.5 |
| 2-$ClC_6H_4$ | neat | 40 | (83) | 93:7 | 94.5:5.5 |
| 2-$ClC_6H_4$ | $H_2O$ | 30 | (98) | 94:6 | 93.5:6.5 |
| 4-$MeOC_6H_4$ | neat | 40 | (97) | 95:5 | 93.0:7.0 |
| 2-$O_2NC_6H_4$ | neat | 24 | (96) | 95:5 | 93.0:7.0 |
| 3-$O_2NC_6H_4$ | neat | 28 | (91) | 94:6 | 94.5:5.5 |
| 4-$O_2NC_6H_4$ | neat | 28 | (95) | 92:8 | 93.5:6.5 |
| 4-$O_2NC_6H_4$ | $H_2O$ | 24 | (89) | 96:4 | 93.0:7.0 |
| 4-$MeC_6H_4$ | neat | 40 | (86) | 93:7 | 93.0:7.0 |
| 4-$MeC_6H_4$ | $H_2O$ | 48 | (99) | 95:5 | 94.0:6.0 |
| 1-Np | neat | 40 | (95) | 94:6 | 90.0:10.0 |
| 1-Np | $H_2O$ | 48 | (79) | 93:7 | 93.0:7.0 |

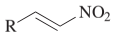


**117** (15 mol %),
$PhCO_2H$ (15 mol %),
toluene, 21°, 21 h

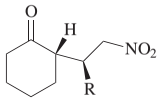


358

| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (95) | 93:7 | 92.0:8.0 |
| 2-$C_4H_3S$ | (96) | 90.5:9.5 | 96.5:3.5 |
| Ph | (62) | 95:5 | 88.0:12.0 |
| 4-$BrC_6H_4$ | (99) | 93.5:6.5 | 93.0:7.0 |
| 2-$MeOC_6H_4$ | (93) | >97.5:2.5 | 96.5:3.5 |
| 2-$O_2NC_6H_4$ | (90) | 96.5:3.5 | 89.0:11.0 |



Catalyst (5 mol %),
solvent, rt, 72 h



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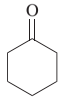
| R | Catalyst | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | **119a** | neat | (39) | 98:2 | 90.5:9.5 |
| 2-$C_4H_3O$ | **119b** | toluene | (92) | 96:4 | 89.0:11.0 |
| Ph | **119a** | neat | (70) | 96:4 | 98.5:1.5 |
| Ph | **119b** | toluene | (91) | 95:5 | 99.0:1.0 |
| 2-$BrC_6H_4$ | **119b** | toluene | (89) | 99:1 | 99.0:1.0 |
| 3-$BrC_6H_4$ | **119b** | toluene | (73) | 97:3 | 91.0:9.0 |
| 2-$ClC_6H_4$ | **119b** | neat | (57) | 99:1 | 95.0:5.0 |
| 2-$ClC_6H_4$ | **119a** | toluene | (87) | 97:3 | 93.0:7.0 |
| 4-$ClC_6H_4$ | **119b** | toluene | (86) | 97:3 | 99.0:1.0 |
| 4-$FC_6H_4$ | **119b** | neat | (73) | 98:2 | 97.0:3.0 |
| 4-$FC_6H_4$ | **119a** | toluene | (84) | 96:4 | 90.5:9.5 |
| 4-$MeOC_6H_4$ | **119b** | toluene | (86) | 99:1 | 97.0:3.0 |
| 3,4-$(MeO)_2C_6H_3$ | **119b** | toluene | (80) | 92:8 | 91.5:8.5 |
| 3,4-$(OCH_2O)C_6H_3$ | **119b** | toluene | (75) | 98:2 | 96.0:4.0 |
| 4-$MeC_6H_4$ | **119a** | neat | (62) | 98:2 | 93.0:7.0 |
| 4-$MeC_6H_4$ | **119b** | toluene | (90) | 95:5 | 90.0:10.0 |
| 4-$CF_3C_6H_4$ | **119b** | toluene | (85) | 93:7 | 94.0:6.0 |

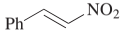
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

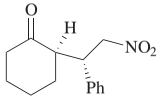
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



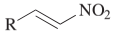


**120** (10 mol %), AcOH (15 mol %), $H_2O$ (1 eq), toluene, rt, 5 h

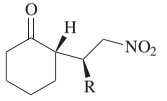


(91) *syn/anti* = 91:9, er 96.0:4.0

360



**121** (15 mol %), TFA (5 mol %), neat, rt

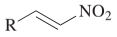


361

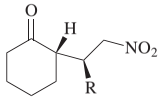
Catalyst Recycling (R = Ph)

| Run | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 1 | 72 | (80) | 99:1 | 99.5:0.5 |
| 2 | 72 | (76) | 99:1 | 99.0:1.0 |
| 3 | 480 | (70) | 96:4 | 98.0:2.0 |

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$ClC_6H_4$ | 168 | (88) | 99:1 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 168 | (85) | 97:3 | 97.0:3.0 |
| 2,4-$Cl_2C_6H_3$ | 168 | (68) | 99:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 144 | (76) | 99:1 | 89.0:11.0 |
| 2-$O_2NC_6H_4$ | 144 | (55) | 97:3 | 98.0:2.0 |
| 4-$MeC_6H_4$ | 72 | (73) | 99:1 | 97.0:3.0 |

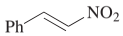


**122** (10 mol %),
$PhCO_2H$ (10 mol %),
*n*-hexane/$CH_2Cl_2$ (2:1)

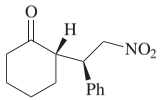


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| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | –10 | 25 | (94) | 92:8 | 91.5:8.5 |
| Ph | –10 | 25 | (89) | 97:3 | 96.0:4.0 |
| 2-$BrC_6H_4$ | –10 | 15 | (85) | 99:1 | 96.5:3.5 |
| 4-$BrC_6H_4$ | –10 | 27 | (93) | 97:3 | 96.5:3.5 |
| 2-$ClC_6H_4$ | –10 | 11 | (94) | 97:3 | 96.5:3.5 |
| 4-$ClC_6H_4$ | –10 | 30 | (95) | 97:3 | 96.5:3.5 |
| 2,4-$Cl_2C_6H_3$ | –10 | 22 | (89) | 99:1 | 97.5:2.5 |
| 4-$FC_6H_4$ | –10 | 45 | (89) | 98:2 | 96.5:3.5 |
| 2-$MeOC_6H_4$ | –10 | 15 | (96) | 97:3 | 94.5:5.5 |
| 4-$MeOC_6H_4$ | –10 | 58 | (95) | 92:8 | 89.5:10.5 |
| 3,4-$(MeO)_2C_6H_3$ | rt | 27 | (96) | 93:7 | 92.5:7.5 |
| 4-$O_2NC_6H_4$ | –10 | 41 | (90) | 98:2 | 97.0:3.0 |
| 4-$MeC_6H_4$ | –10 | 48 | (91) | 96:4 | 94.0:6.0 |
| 1-Np | –10 | 44 | (94) | 98:2 | 95.5:4.5 |



Catalyst (5 mol %),
$CH_2Cl_2$, rt, 48 h



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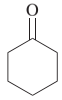
| Catalyst | | *syn*/*anti* | er (*syn*) |
|---|---|---|---|
| **123** | (60) | 59:41 | 68:0:32.0 |
| **124** | (55) | 62:38 | 62.0:38.0 |

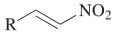
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

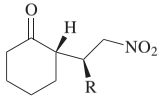
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



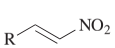


**126** (10 mol %),
$PhCO_2H$ (10 mol %),
THF, rt, 48 h

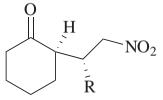


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| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (70) | 80:20 | 90.5:9.5 |
| 2-$C_4H_3S$ | (71) | 83:17 | 87.5:12.5 |
| Ph | (60) | 88:12 | 96.5:3.5 |
| 2-$BrC_6H_4$ | (84) | 97:3 | 92.0:8.0 |
| 4-$BrC_6H_4$ | (80) | 87:13 | 91.5:8.5 |
| 2-$ClC_6H_4$ | (60) | 98:2 | 96.5:3.5 |
| 2,4-$Cl_2C_6H_3$ | (80) | 80:20 | 92.0:8.0 |
| 4-$FC_6H_4$ | (81) | 86:14 | 91.0:9.0 |
| 2-$MeOC_6H_4$ | (74) | 97:3 | 90.5:9.5 |
| 3-$O_2NC_6H_4$ | (50) | 86:14 | 93.0:7.0 |
| 4-$MeC_6H_4$ | (72) | 83:17 | 90.0:10.0 |
| 4-$CF_3C_6H_4$ | (41) | 88:12 | 90.0:10.0 |

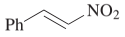
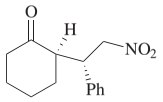
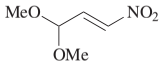
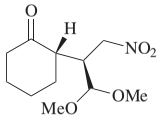
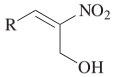
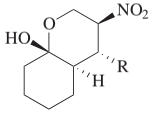


**127** (10 mol %),
$PhCO_2H$ (10 mol %),
THF, rt, 48 h



364

| R | | *syn*/*anti* | er |
|---|---|---|---|
| Ph | (60) | 90:10 | 93.0:7.0 |
| 2-$ClC_6H_4$ | (55) | 96:4 | 96.0:4.0 |

| | | | | |
|---|---|---|---|---|
|  | **128** (20 mol %), rt, 48 h |  | (85)[b] *syn*/*anti* = 79:21<br>er (*syn*) 99.5:0.5<br>er (*anti*) 97.5:2.5 | 365 |
|  | **16a** (10 mol %), THF, rt |  | (51) *syn*/*anti* > 20:1<br>er 98.5:1.5 | 116 |
|  | **15** (20 mol %),<br>TFA (10 mol %),<br>neat, rt |  | | 366 |

| R | Time (d) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 10 | (45) | 99.0:1.0 |
| Ph | 7 | (62) | 98.5:1.5 |
| 4-$BrC_6H_4$ | 10 | (60) | 95.5:4.5 |
| 3-$FC_6H_4$ | 8 | (57) | 94.5:5.5 |
| 4-$MeOC_6H_4$ | 12 | (53) | 99.5:0.5 |
| 3-$O_2NC_6H_4$ | 8 | (59) | 96.0:4.0 |
| 4-$MeC_6H_4$ | 12 | (41) | 97.0:3.0 |
| 4-$NCC_6H_4$ | 8 | (45) | 94.0:6.0 |

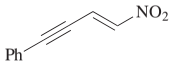
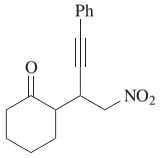
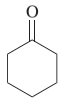
| | | | | |
|---|---|---|---|---|
|  | **59** (15 mol %),<br>$PhCO_2H$ (5 mol %),<br>$H_2O$ (200 mol %),<br>toluene, rt, 6 d |  | (89) *syn*/*anti* = 71:29<br>er 95.5:4.5 | 304 |

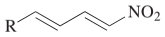
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

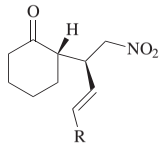
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



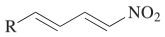


**34** (5 mol %), **85** (5 mol %), $CH_2Cl_2$, rt

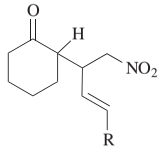


| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 24 | (92) | 98:2 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 18 | (93) | 99:1 | 93.5:6.5 |
| 4-$MeOC_6H_4$ | 36 | (90) | 99:1 | 92.5:7.5 |

325

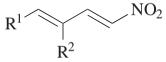


**59** (15 mol %), $PhCO_2H$ (5 mol %), $H_2O$ (200 mol %), toluene, rt

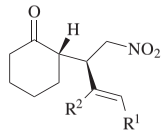


| R | Time (d) | | *syn*/*anti* | er (*syn*) |
|---|---|---|---|---|
| Ph | — | (94) | 70:30 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 6 | (98) | 66:34 | 95.5:4.5 |
| 2-$O_2NC_6H_4$ | 6 | (85) | 99:1 | 98.0:2.0 |

304

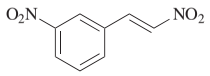


**94** (10 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), $H_2O$ (2 eq), toluene, rt, 48 h

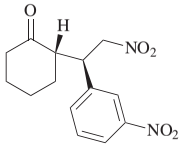


| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | H | (93) | 98:2 | 98.5:1.5 |
| Ph | Me | (80) | 95:5 | 98.0:2.0 |
| 4-$ClC_6H_4$ | H | (92) | 96:4 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | H | (73) | >98:2 | 97.5:2.5 |
| 2-$O_2NC_6H_4$ | H | (91) | >98:2 | 99.0:1.0 |

334

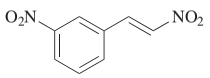


**4** (15 mol %),
EtOH/*i*-PrOH (1:1),
20°, 24 h

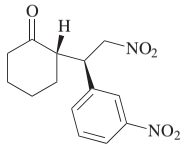


(62) *syn*/*anti* = 10:1
er 85.0:15.0

306, 307

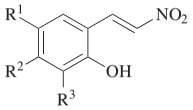


**7** (10 mol %),
**99** (10 mol %),
$CHCl_3$, rt, 65 h

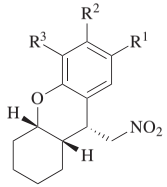


(60) dr 35:1
er 97.0:3.0

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1. *ent*-**1** (5 mol %),
**69b** (5 mol %),
0.5 M in $CH_2Cl_2$, rt, 5 h
2. $Et_3SiH$, $BF_3{\bullet}OEt_2$,
0.1 M in $CH_2Cl_2$, –10° to rt, 2 h



309

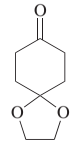
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| H | H | H | (90) | 97.0:3.0 | >99.5:0.5 |
| H | H | MeO | (74) | 97.5:2.5 | 95.0:5.0 |
| H | H | HO | (74) | >99.5:0.5 | 98.5:1.5 |
| H | MeO | H | (69) | 95.5:4.5 | 99.5:0.5 |
| Br | H | H | (78) | 97.0:3.0 | 99.5:0.5 |
| Cl | H | H | (75) | 93.5:6.5 | 99.0:1.0 |
| F | H | H | (78) | 96.0:4.0 | 99.5:0.5 |
| MeO | H | H | (73) | 96.5:3.5 | 99.5:0.5 |
| Me | H | H | (94) | 95.0:5.0 | 98.5:1.5 |

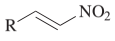
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

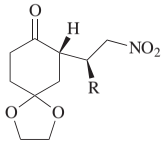
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



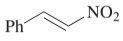


**16b** (20 mol %), *i*-PrOH, 0°

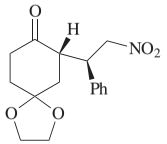


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 18 | (81) | 50:1 | 97.5:2.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 48 | (93) | 50:1 | 99.5:0.5 |

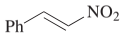


**21** (20 mol %), $(CF_3SO_2)_2NH$ (20 mol %), *i*-PrOH, 0°, 20 h

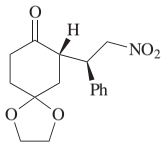


(51) *syn*/*anti* = 94:6 er 88.5:11.5

261

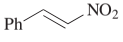


**24** (10 mol %), TFA (10 mol %), brine, THF, rt, 20 h

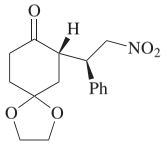


(90) *syn*/*anti* = 96:4 er 94.5:5.5

119



**51** (10 mol %), $4\text{-}O_2NC_6H_4CO_2H$ (10 mol %), $H_2O$, rt, 72 h



(57) *syn*/*anti* = 90:10 er 95.5:4.5

288

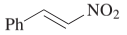
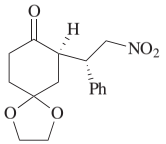
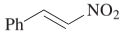
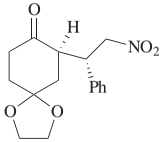
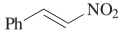
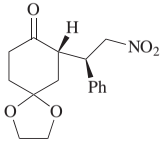
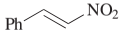
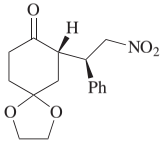
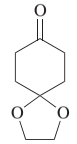
| | | | | |
|---|---|---|---|---|
|  | **71** (30 mol %), $H_2O$ (10 eq), NMP/DMSO (1:1), 4°, 3 d |  | (58) *syn*/*anti* = 22:1<br>er 97.0:3.0 | 312 |
|  | **72** (30 mol %), $H_2O$ (10 eq), NMP/DMSO (9:1), rt |  | (68) *syn*/*anti* > 28:1<br>er 97.5:2.5 | 313 |
|  | **81** (5 mol %), 2-$MeC_6H_4CO_2H$ (5 mol %), *n*-hexane, rt, 24 h |  | (86) *syn*/*anti* = 79:21<br>er (*syn*) 98.5:1.5<br>er (*anti*) 94.5:5.5 | 319 |
|  | **90** (20 mol %), $Et_3N$ (20 mol %), $PhCO_2H$ (10 mol%), –30°, 68 h |  | (>99) *syn*/*anti* = 98:2<br>er (*syn*) 97.5:2.5<br>er (*anti*) 81.5:18.5 | 330 |

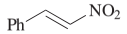
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

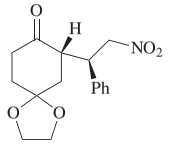
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



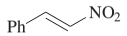


Catalyst (20 mol %),
toluene, rt, 48 h

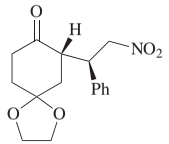


| Catalyst | | *syn*/*anti* | er (*syn*) |
|---|---|---|---|
| **95a** | (79) | 20:1 | 96.0:4.0 |
| **95b** | (97) | 3:1 | 88.0:12.0 |

336

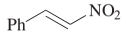


**97** (10 mol %),
$PhCO_2H$ (10 mol %),
0.5 M in $CH_2Cl_2$, rt, 34 h

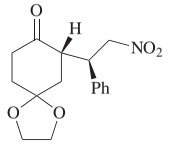


(67) *syn*/*anti* = 90:10
er 89.0:11.0

340

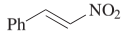


**100** (15 mol %),
toluene, rt, 36 h

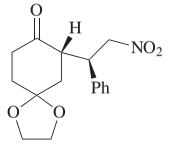


(88) *syn*/*anti* = 99:1
er 96.0:4.0

341

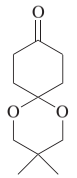


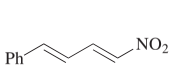
**100** (5 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
1 M KOH (50 μL), neat, rt



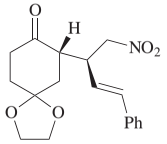
(90) *syn*/*anti* = 90:10
er 92.5:7.5

342



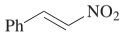


**94** (10 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
$H_2O$ (2 eq), toluene, rt, 48 h

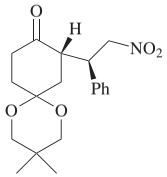


(73) *syn*/*anti* = 70:30
er 98.0:2.0

334

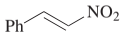


**24** (10 mol %),
TFA (10 mol %)
brine, THF, rt, 20 h

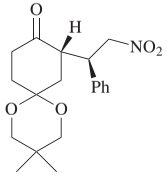


(88) *syn*/*anti* = 95:5
er 94.0:6.0

119



**31** (10 mol %), rt



(68) *syn*/*anti* = 95:5
er 82.5:17.5

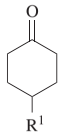
270

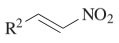
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

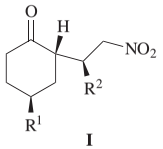
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{6-12}$



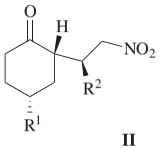


**130** (10 mol %), 2-$HOC_6H_4CO_2H$ (5 mol %), solvent, rt



**I**

+



**II**

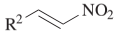
367

Catalyst Recycling ($R^1$ = Me; $R^2$ = 2-$O_2NC_6H_4$)

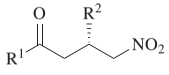
| Run | Time (h) | | **I/II** | er |
|---|---|---|---|---|
| 1 | 3 | (93) | 4.4:1 | 98.5:1.5 |
| 2 | 4 | (99) | 4.8:1 | 98.5:1.5 |
| 3 | 12 | (94) | 5.1:1 | 96.5:3.5 |
| 4 | 24 | (78) | 6.3:1 | 98.0:2.0 |

| $R^1$ | $R^2$ | Solvent | Time (h) | | **I/II** | er |
|---|---|---|---|---|---|---|
| $N_3$ | Ph | dioxane | 20 | (61) | >5:1 | 96.5:3.5 |
| AcS | Ph | dioxane | 24 | (65) | >5:1 | 96.5:3.5 |
| Me | Ph | neat | 10 | (89) | 6.2:1 | 93.5:6.5 |
| Me | 2-$ClC_6H_4$ | neat | 10 | (99) | >10:1 | 98.5:1.5 |
| Me | 4-$ClC_6H_4$ | neat | 10 | (89) | 6.1:1 | 99.5:0.5 |
| Me | 4-$MeOC_6H_4$ | neat | 21 | (94) | 7.6:1 | 98.5:1.5 |
| Me | 2-$O_2NC_6H_4$ | neat | 3 | (93) | 4.4:1 | 98.5:1.5 |
| Me | 3-$O_2NC_6H_4$ | neat | 12 | (80) | 4.0:1 | 99.0:1.0 |
| Me | 4-$O_2NC_6H_4$ | neat | 3 | (88) | 5.0:1 | 99.0:1.0 |
| Me | 3,4-$(OCH_2O)C_6H_3$ | neat | 24 | (95) | 6.8:1 | 98.0:2.0 |
| Me | 4-$MeC_6H_4$ | neat | 16 | (89) | 7.0:1 | 99.0:1.0 |
| Me | 1-Np | neat | 24 | (99) | 8.1:1 | 98.5:1.5 |
| Me | 4-$PhC_6H_4$ | neat | 12 | (92) | 6.0:1 | 97.0:3.0 |
| Et | Ph | neat | 10 | (81) | 6.5:1 | 98.5:1.5 |
| *t*-Bu | Ph | dioxane | 12 | (88) | 7.9:1 | 99.0:1.0 |
| Ph | Ph | dioxane | 10 | (63) | 12:1 | 98.0:2.0 |





**129** (15 mol %),
**148** (15 mol %),
$H_2O$, 35°, 3–4 d





| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | Ph | (40) | 89.5:10.5 |
| Ph | 2-$C_4H_3O$ | (58) | 96.5:3.5 |
| Ph | Ph | (85) | 96.5:3.5 |
| Ph | 2-$ClC_6H_4$ | (52) | 94.0:6.0 |
| Ph | 2,4-$Cl_2C_6H_3$ | (78) | 97.0:3.0 |
| Ph | 3-$MeOC_6H_4$ | (70) | 95.5:4.5 |
| Ph | 4-$MeOC_6H_4$ | (81) | 90.0:10.0 |
| Ph | 2-$O_2NC_6H_4$ | (43) | 96.0:4.0 |
| Ph | 3-$O_2NC_6H_4$ | (80) | 93.5:6.5 |
| Ph | 4-$O_2NC_6H_4$ | (81) | 93.5:6.5 |
| Ph | 3,4-$(OCH_2O)C_6H_3$ | (77) | 96.0:4.0 |
| Ph | 4-$MeC_6H_4$ | (83) | 95.5:4.5 |
| Ph | 1-Np | (85) | 98.0:2.0 |
| Ph | 2-Np | (80) | 95.0:5.0 |
| 2-$FC_6H_4$ | Ph | (62) | 97.0:3.0 |
| 4-$FC_6H_4$ | Ph | (70) | 95.0:5.0 |
| 3-$MeOC_6H_4$ | Ph | (85) | 95.5:4.5 |
| 2-$MeC_6H_4$ | Ph | (42) | 96.0:4.0 |
| 2-Np | Ph | (88) | 95.0:5.0 |

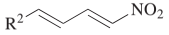
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

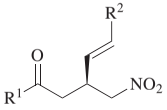
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{6-12}$





**59** (15 mol %), $PhCO_2H$ (5 mol %), $CH_2Cl_2$, rt, 6 d

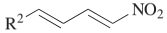


304

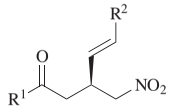
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | Ph | (56) | 92.5:7.5 |
| 2-$C_4H_3S$ | Ph | (90) | 92.0:8.0 |
| 2-pyridyl | Ph | (79) | 97.0:3.0 |
| 3-pyridyl | Ph | (70) | 98.5:1.5 |
| Ph | Ph | (78) | 98.0:2.0 |
| Ph | 4-$MeOC_6H_4$ | (48) | 99.5:0.5 |
| Ph | 2-$O_2NC_6H_4$ | (94) | 98.0:2.0 |
| 4-$BrC_6H_4$ | Ph | (80) | 98.0:2.0 |
| 4-$ClC_6H_4$ | Ph | (72) | 97.0:3.0 |
| 4-$FC_6H_4$ | Ph | (83) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Ph | (77) | 98.5:1.5 |
| 3,4-$(OCH_2O)C_6H_3$ | Ph | (89) | 99.0:1.0 |
| 4-$MeC_6H_4$ | Ph | (90) | 98.0:2.0 |
| 2-Np | Ph | (58) | 97.5:2.5 |

$C_{6-14}$





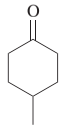
**70** (15 mol %), $CHCl_3$, 80°

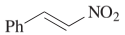


305

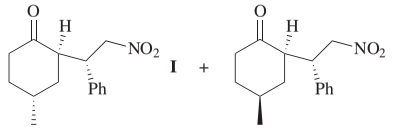
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Ph | 72 | (100) | 93.0:7.0 |
| Ph | Ph | 72 | (100) | 99.5:0.5 |
| Ph | 4-$ClC_6H_4$ | 120 | (79) | 96.0:4.0 |
| Ph | 4-$MeOC_6H_4$ | 96 | (72) | 99.5:0.5 |
| Ph | 2-$O_2NC_6H_4$ | 120 | (71) | 97.0:3.0 |
| Ph | 4-$O_2NC_6H_4$ | 72 | (77) | 97.0:3.0 |
| 4-$FC_6H_4$ | Ph | 72 | (82) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | Ph | 72 | (84) | 98.0:2.0 |
| 4-$AcOC_6H_4$ | Ph | 72 | (97) | 98.0:2.0 |
| 4-$O_2NC_6H_4$ | Ph | 72 | (100) | 97.5:2.5 |
| 4-$MeC_6H_4$ | Ph | 72 | (75) | 98.0:2.0 |
| 4-$NCC_6H_4$ | Ph | 72 | (94) | 99.5:0.5 |
| 2-Np | Ph | 72 | (87) | 97.0:3.0 |
| 4-$PhC_6H_4$ | Ph | 72 | (72) | 91.0:9.0 |

$C_7$





**70** (30 mol %),
$H_2O$ (10 eq),
NMP/DMSO (1:1), 4°, 3 d



**I** + **II** 312

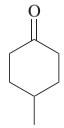
**I** + **II** (69), **I**/**II** = 2:1
*syn*/*anti* = 22:1, er **II** 97.0:3.0

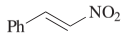
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

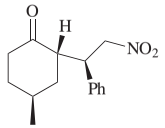
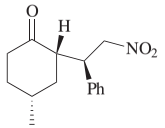
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_7$



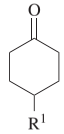


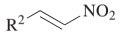
**90** (20 mol %),
$Et_3N$ (20 mol %),
$PhCO_2H$ (10 mol %),
–30°, 68 h


**I** +

**II** 330

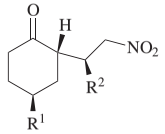
**I** + **II** (90), **I**/**II** = 79:21
er **I** 98.0:2.0, er **II** 91.0:9.0

$C_{7–10}$



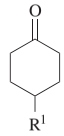


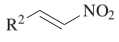
**67** (10 mol %),
$CCl_3CO_2H$ (10 mol %),
brine, rt


303

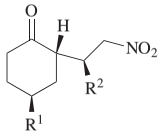
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | 2-$ClC_6H_4$ | 14 | (82) | 94.5:5.5 |
| Me | 4-$ClC_6H_4$ | 14 | (77) | 90.5:9.5 |
| Me | 4-$MeOC_6H_4$ | 16 | (89) | 89.5:10.5 |
| Me | 4-$O_2NC_6H_4$ | 18 | (71) | 91.0:9.0 |
| Me | 4-$MeC_6H_4$ | 17 | (82) | 88.5:11.5 |
| *t*-Bu | Ph | 14 | (94) | 89.0:11.0 |

$C_{7-12}$

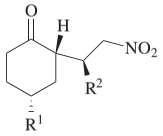




**97** (10 mol %),
$PhCO_2H$ (10 mol %),
0.5 M in $CH_2Cl_2$, rt



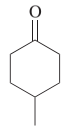
**I** +

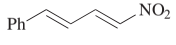


**II** 340

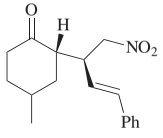
| $R^1$ | $R^2$ | Time (h) | | **I/II** | er |
|---|---|---|---|---|---|
| Me | Ph | 12 | (78) | >99:1 | 96.5:3.5 |
| Me | 4-$BrC_6H_4$ | 10 | (76) | 90:10 | 94.0:6.0 |
| Me | 4-$ClC_6H_4$ | 10 | (77) | 98:2 | 94.0:6.0 |
| Me | 4-$FC_6H_4$ | 10 | (95) | 91:9 | 95.0:5.0 |
| Me | 4-$MeOC_6H_4$ | 10 | (63) | 99:1 | 91.5:8.5 |
| Me | 4-$MeC_6H_4$ | 10 | (90) | 90:10 | 87.0:13.0 |
| Et | Ph | 17 | (59) | 97:3 | 91.5:8.5 |
| Et | 4-$FC_6H_4$ | 10 | (67) | 94:6 | 95.0:5.0 |
| Et | 4-$MeOC_6H_4$ | 32 | (90) | 99:1 | 90.0:10.0 |
| Ph | Ph | 23 | (56) | 97:3 | 91.5:8.5 |
| Ph | 4-$FC_6H_4$ | 9 | (67) | 94:6 | 95.0:5.0 |
| Ph | 4-$MeOC_6H_4$ | 23 | (90) | 99:1 | 90.0:10.0 |

$C_7$





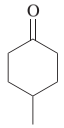
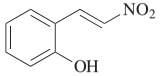
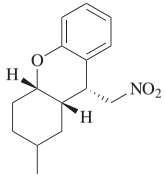
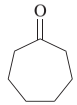
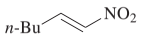
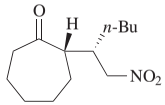
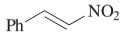
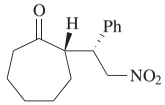
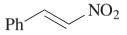
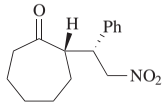
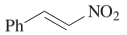
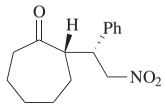
**94** (10 mol %),
4-$O_2NC_6H_4CO_2H$
(10 mol %), $H_2O$ (2 eq),
toluene, rt, 48 h



(82) dr = 58:42
er 98.0:2.0

334

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_7$ | | | | |
|  |  | 1. *ent*-**1** (5 mol %), **69b** (5 mol %), 0.5 M in $CH_2Cl_2$, rt, 24 h<br>2. $Et_3SiH$, $BF_3{\bullet}OEt_2$, 0.1 M in $CH_2Cl_2$, –10° to rt, 2 h |  | (79) dr 1.8:1, er 98.0:2.0 | 309 |
|  |  | **81** (20 mol %), 2-$MeC_6H_4CO_2H$ (20 mol %), *n*-hexane, rt, 42 h |  | (97) *syn*/*anti* = 63:37<br>er (*syn*) 98.5:1.5<br>er (*anti*) 99.0:1.0 | 319 |
| |  | **5** (20 mol %), THF, rt, 5 d |  | (32) *syn*/*anti* = 88:12<br>er (*syn*) 76.5:23.5 | 253 |
| |  | **16b** (20 mol %), *i*-PrOH, 0°, 72 h |  | (7) | 258 |
| |  | **34** (5 mol %), **45** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h |  | (40)[a] er 70.0:30.0 | 274 |

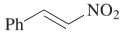
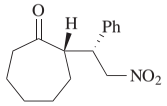
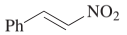
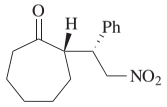
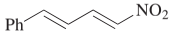
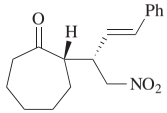
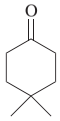
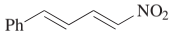
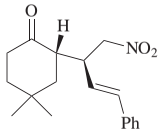
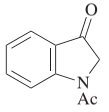
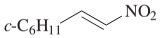
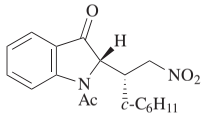
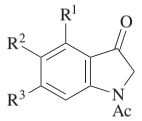
| | | | | | |
|---|---|---|---|---|---|
| |  | **44** (15 mol %), 2-$HOC_{10}H_7$ (5 mol %), THF, rt, 72 h |  | (65) *syn/anti* = 99:1 er 99.5:0.5 | 281 |
| |  | **84** (5 mol %), $CHCl_3$/MeOH (1:1), rt, 48 h |  | (39) *syn/anti* = >98:2 er 71.5:21.5 | 323 |
| |  | **94** (10 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), $H_2O$ (2 eq), toluene, rt, 48 h |  | (80) *syn/anti* = 90:10 er 86.5:13.5 | 334 |
| $C_8$ | | | | | |
|  |  | **94** (10 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), $H_2O$ (2 eq), toluene, rt, 48 h |  | (57) *syn/anti* = 90:10 er 90.0:10.0 | 334 |
|  |  | **69b** (20 mol %), $CH_2Cl_2$, 16°, 36 h |  | (96) dr 1.3:1 er 88.5:11.5 | 369 |

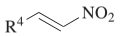
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

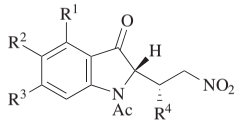
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{8-9}$





**69b** (5 mol %), $CH_2Cl_2$, –40°, 12–24 h

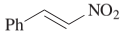


369

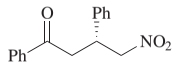
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | | dr | er |
|---|---|---|---|---|---|---|
| H | H | H | Ph | (99) | 12:1 | 95.5:4.5 |
| H | H | H | 2-$BrC_6H_4$ | (92) | 4:1 | 93.5:6.5 |
| H | H | H | 3-$BrC_6H_4$ | (75) | 10:1 | 90.0:10.0 |
| H | H | H | 4-$BrC_6H_4$ | (97) | 28:1 | 93.0:7.0 |
| H | H | H | 2-$ClC_6H_4$ | (98) | 18:1 | 95.0:5.0 |
| H | H | H | 3-$ClC_6H_4$ | (95) | 15:1 | 94.5:5.5 |
| H | H | H | 4-$ClC_6H_4$ | (91) | 18:1 | 95.0:5.0 |
| H | H | H | 4-$MeC_6H_4$ | (90) | 13:1 | 94.0:6.0 |
| H | Br | H | Ph | (91) | 13:1 | 96.0:4.0 |
| Br | H | H | Ph | (89) | 12:1 | 96.0:4.0 |
| H | H | $MeO_2C$ | Ph | (80) | 11:1 | 92.5:7.5 |
| H | Me | H | Ph | (93) | 8:1 | 95.5:4.5 |

$C_8$



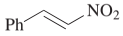


**1** (20 mol %), MeOH, rt, 8 d

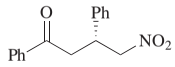


(30) er 71.0:29.0

137

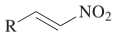


**5** (20 mol %), THF, rt, 5 d

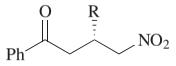


(21) er 86.0:14.0

253

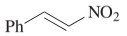


**43** (15 mol %),
$CH_2Cl_2$, rt, 48 h

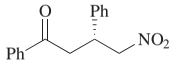


280

| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (70) | 99.0:1.0 |
| Ph | (68) | 97.5:2.5 |
| 4-$FC_6H_4$ | (71) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | (43) | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | (61) | 98.0:2.0 |



**44** (15 mol %),
2-$HOC_{10}H_7$ (5 mol %),
THF, rt, 20 h

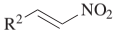


(53) er 92.5:7.5

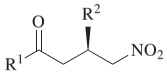
281

$C_{8-12}$





**50** (15 mol %),
$CH_2Cl_2$, rt, 96 h



370

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Et | (20) | 97.0:3.0 |
| Ph | 2-$C_4H_3O$ | (99) | 99.0:1.0 |
| Ph | Ph | (72) | 98.5:1.5 |
| Ph | 2-$BrC_6H_4$ | (83) | 98.5:1.5 |
| Ph | 2-$ClC_6H_4$ | (99) | 99.0:1.0 |
| Ph | 4-$ClC_6H_4$ | (65) | 97.5:2.5 |
| Ph | 4-$MeOC_6H_4$ | (78) | 98.0:2.0 |
| Ph | 4-$MeC_6H_4$ | (89) | 98.5:1.5 |
| Ph | 2-Np | (74) | 97.0:3.0 |
| 4-$ClC_6H_4$ | Ph | (92) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Ph | (64) | 98.5:1.5 |
| 4-$MeC_6H_4$ | Ph | (84) | 98.0:2.0 |
| 2-Np | Ph | (46) | 97.5:2.5 |

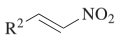
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

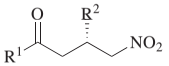
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{8-9}$





**56** (5 mol %), 4-$O_2NC_6H_4CO_2H$ (15 mol %), THF, rt, 72 h

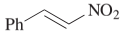


293

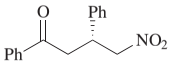
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | 2-$C_3H_4O$ | (98) | 98.0:2.0 |
| Ph | 2-$C_3H_4S$ | (82) | 99.5:0.5 |
| Ph | Ph | (95) | 99.5:0.5 |
| Ph | 2-$BrC_6H_4$ | (95) | 99.5:0.5 |
| Ph | 4-$BrC_6H_4$ | (82) | 99.0:1.0 |
| Ph | 4-$ClC_6H_4$ | (70) | 97.5:2.5 |
| Ph | 4-$MeOC_6H_4$ | (90) | 98.5:1.5 |
| Ph | 4-$MeC_6H_4$ | (85) | 99.5:0.5 |
| 4-$BrC_6H_4$ | Ph | (75) | 99.0:1.0 |
| 3-$ClC_6H_4$ | Ph | (98) | 99.5:0.5 |
| 4-$ClC_6H_4$ | Ph | (82) | 97.5:2.5 |
| 3-$MeOC_6H_4$ | Ph | (90) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | Ph | (87) | 99.5:0.5 |
| 4-$MeC_6H_4$ | Ph | (90) | 94.5:5.5 |

$C_8$



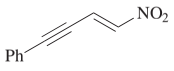


**62** (10 mol %), TFA (2 mol %), neat, rt, 24 h

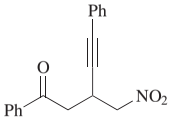


(72) er 57.5:42.5

298

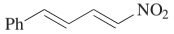


**59** (15 mol %), $PhCO_2H$ (5 mol %), $CH_2Cl_2$, rt, 6 d

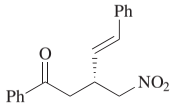


(85) er 98.0:2.0

304



**56** (5 mol %),
4-$O_2NC_6H_4CO_2H$ (15 mol %),
THF, rt, 72 h

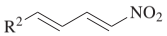


(98) er 99.5:0.5

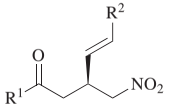
293

$C_{8-12}$





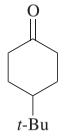
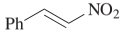
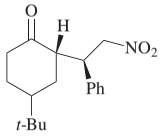
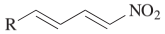
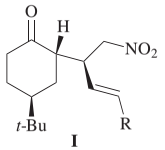
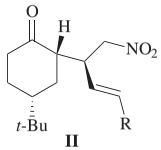
**131** (30 mol %),
toluene, rt, 4 d



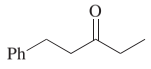
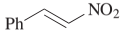
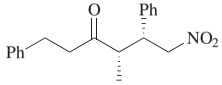
371

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Ph | (63) | 98.5:1.5 |
| 3-$BrC_6H_4$ | Ph | (74) | 98.0:2.0 |
| 4-$BrC_6H_4$ | Ph | (78) | 98.0:2.0 |
| 4-$ClC_6H_4$ | Ph | (75) | 97.5:2.5 |
| 4-$FC_6H_4$ | Ph | (70) | 99.0:1.0 |
| 4-$O_2NC_6H_4$ | Ph | (65) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | Ph | (55) | 97.5:2.5 |
| 4-$MeC_6H_4$ | Ph | (60) | 98.0:2.0 |
| 2-Np | Ph | (83) | 98.5:1.5 |
| 2-Np | 2,4-$Cl_2C_6H_3$ | (62) | 97.0:3.0 |
| 2-Np | 2-$O_2NC_6H_4$ | (65) | 97.5:2.5 |
| 2-Np | 4-$MeC_6H_4$ | (60) | 97.5:2.5 |
| 2-Np | 4-$NCC_6H_4$ | (78) | 97.5:2.5 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

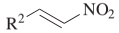
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_{10}$ | | | | |
|  |  | **34** (5 mol %), **35** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h |  (90) *syn*/*anti* = 90:10, er 98.5:1.5 | 274 |
| |  | **34** (5 mol %), **85** (5 mol %), $CH_2Cl_2$, rt |  **I** +  **II** | 325 |

| R | Time (h) | | **I/II** | er |
|---|---|---|---|---|
| Ph | 24 | (92) | 83:17 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 18 | (93) | 88:12 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 36 | (89) | 89:11 | 96.5:3.5 |

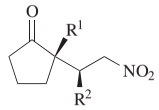
| | | | | |
|---|---|---|---|---|
| $C_{11}$ | | | | |
|  |  | **1** (20 mol %), MeOH, rt, 8 d |  (44) *syn*/*anti* = 90:10, er 86.0:14.0 | 137 |

$C_{11–12}$




**132** (10 mol %),
$CH_2Cl_2$, 4 Å MS, 12–48 h



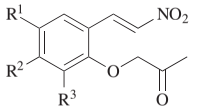

| $R^1$ | $R^2$ | Temp | | dr | er |
|---|---|---|---|---|---|
| Ph | *n*-Pr | rt | (50) | >99:1 | 90.0:10.0 |
| Ph | 2-$C_4H_3O$ | –20° | (93) | 98:2 | 97.0:3.0 |
| Ph | Ph | rt | (90) | >99:1 | 96.0:4.0 |
| Ph | 4-$BrC_6H_4$ | rt | (94) | >99:1 | 97.0:3.0 |
| Ph | 2-$ClC_6H_4$ | rt | (92) | >99:1 | 97.0:3.0 |
| Ph | 4-$ClC_6H_4$ | rt | (88) | >99:1 | 97.0:3.0 |
| Ph | 4-$FC_6H_4$ | rt | (83) | >99:1 | 97.5:2.5 |
| Ph | 2-$MeOC_6H_4$ | –20° | (85) | >99:1 | 97.0:3.0 |
| Ph | 3-$MeOC_6H_4$ | –20° | (93) | >99:1 | 97.0:3.0 |
| Ph | 4-$MeOC_6H_4$ | –20° | (87) | >99:1 | 97.5:2.5 |
| Ph | 4-$MeC_6H_4$ | –20° | (90) | >99:1 | 97.5:2.5 |
| Ph | PhCH=CH | rt | (89) | >99:1 | 98.0:2.0 |
| Ph | 1-Np | –20° | (89) | >99:1 | 98.0:2.0 |
| Ph | 2-Np | rt | (95) | >99:1 | 97.0:3.0 |
| 3-$ClC_6H_4$ | Ph | –20° | (95) | >99:1 | 97.0:3.0 |
| 4-$ClC_6H_4$ | Ph | rt | (89) | >99:1 | 95.5:4.5 |
| 3-$MeOC_6H_4$ | Ph | rt | (90) | >99:1 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | Ph | rt | (93) | >99:1 | 95.0:5.0 |
| 3-$MeC_6H_4$ | Ph | rt | (91) | >99:1 | 95.0:5.0 |
| 4-$MeC_6H_4$ | Ph | rt | (88) | >99:1 | 95.5:4.5 |
| 4-$CF_3C_6H_4$ | Ph | –20° | (90) | >99:1 | 97.5:2.5 |

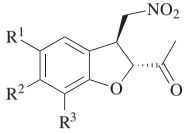
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{11–12}$



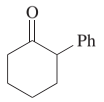


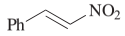
**98** (*x* mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
THF, 20°; then reflux, 8 h

373

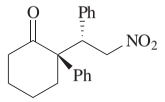
| $R^1$ | $R^2$ | $R^3$ | *x* | Time (h) | | *trans*/*cis* | er |
|---|---|---|---|---|---|---|---|
| H | H | H | 20 | 6 | (95) | 96:4 | 98.0:2.0 |
| H | H | H | 10 | 8 | (91) | 98:2 | >99.5:0.5 |
| H | H | MeO | 20 | 10 | (99) | 92:8 | 98.5:1.5 |
| Br | H | H | 20 | 12 | (97) | 94:6 | 98.5:1.5 |
| Cl | H | H | 20 | 10 | (99) | 94:6 | 98.5:1.5 |
| F | H | H | 20 | 8 | (>99) | 90:10 | 98.5:1.5 |
| MeO | H | H | 20 | 11 | (97) | 88:12 | 99.0:1.0 |
| $O_2N$ | H | H | 20 | 18 | (>99) | 95:5 | 97.0:3.0 |
| H | H | Me | 20 | 10 | (95) | 86:14 | 98.5:1.5 |
| H | Me | H | 20 | 10 | (92) | 96:4 | 99.0:1.0 |
| Me | H | H | 20 | 10 | (97) | 87:13 | 98.5:1.5 |

$C_{12}$





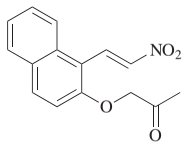
**132** (10 mol %),
4 Å MS, 50°, 30 h



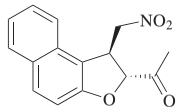
(20) dr >99:1, er 92.0:8.0

372

$C_{15}$



**98** (10–20 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
THF, 20°, 14 h; then reflux, 8 h



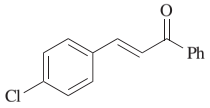
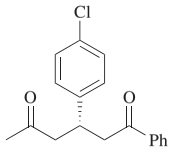
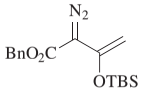
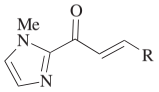
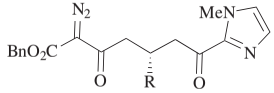
(96) *trans*/*cis* = 96:4
er 97.5:2.5

373

[a] The yield was determined by GC with an internal standard.

[b] The nitroalkene was generated in situ.

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **133** (30 mol %), $PhCO_2H$ (10 mol %), neat, 20°, 7 d |  (40) er 78.0:22.0 | 374 |
| $C_4$ | | | | |
|  |  | **143** (10 mol %), $CuCl_2$ (10 mol %), $AgSbF_6$ (20 mol %), $(CF_3)_2CHOH$, $CH_2Cl_2$, 4 Å MS, –78°, 3 d |  | 375 |

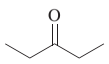
| R | | er |
|---|---|---|
| *t*-Bu | (62) | 97.5:2.5 |
| 2-$C_4H_3O$ | (80) | 90.0:10.0 |
| *c*-$C_6H_{11}$ | (79) | 90.5:9.5 |
| Ph | (75) | 95.5:4.5 |
| 4-$BrC_6H_4$ | (83) | 95.5:4.5 |
| 4-$FC_6H_4$ | (76) | 96.5:3.5 |
| 2-$ClC_6H_4$ | (75) | 97.5:2.5 |
| 4-$ClC_6H_4$ | (81) | 97.0:3.0 |
| 2,6-$Cl_2C_6H_3$ | (65) | 95.5:4.5 |
| 3-$O_2NC_6H_4$ | (68) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | (62) | 93.0:7.0 |
| 4-$MeC_6H_4$ | (77) | 95.5:4.5 |
| 2-Np | (72) | 95.5:4.5 |

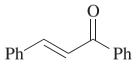
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

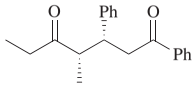
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_5$



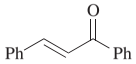


**134** (20 mol %), 4-$MeOC_6H_4CO_2H$ (20 mol %), neat, rt, 1.5 d

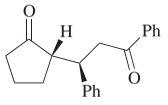


(90) *syn*/*anti* = 80:20, er 80.0:20.0 — 376

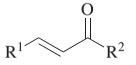




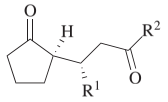
**44** (20 mol %), *t*-BuOH, rt, 48 h



(55) dr 82:18, er 85.5:14.5 — 377



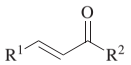
**125** (20 mol %), $HO_2C(CH_2)_4CO_2H$ (20 mol %), $MeOH/CHCl_3$ (1:1), rt



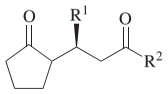
378

| $R^1$ | $R^2$ | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 4-$MeOC_6H_4$ | (56) | 1:3 | 99.0:1.0 | 98.5:1.5 |
| 2-$C_4H_3O$ | 4-$MeOC_6H_4$ | (54) | 1:>2 | 99.5:0.5[a] | 98.5:1.5[a] |
| 2-$C_4H_3S$ | Ph | (61) | 1:1 | 99.0:1.0 | 97.5:2.5 |
| 2-$C_4H_3S$ | 4-$MeOC_6H_4$ | (51) | 2:3 | 99.5:0.5 | 99.0:1.0 |
| 2-$C_4H_3S$ | 4-$O_2NC_6H_4$ | (29) | 1:1 | 99.0:1.0 | >99.5:0.5 |
| Ph | Ph | (69) | 2:3 | 99.5:0.5 | 98.5:1.5 |
| 3-$ClC_6H_4$ | Ph | (87) | 2:3 | 99.0:1.0 | 99.5:0.5 |
| 3-$ClC_6H_4$ | Ph | (85) | 2:3 | 99.5:0.5[a] | 99.0:1.0[a] |
| 4-$FC_6H_4$ | Ph | (83) | 2:3 | >99.5:0.5 | 99.0:1.0 |
| 4-$FC_6H_4$ | Ph | (81) | 2:3 | 99.0:1.0[a] | 99.0:1.0[a] |
| 4-$MeOC_6H_4$ | Ph | (43) | 1:2 | 99.0:1.0 | 98.0:2.0 |
| 4-$O_2NC_6H_4$ | Ph | (76) | 2:3 | 99.5:0.5[a] | 98.0:2.0[a] |
| Ph | 4-$MeC_6H_4$ | (85) | 1:3 | >99.5:0.5 | 98.5:1.5 |
| Ph | 4-$MeC_6H_4$ | (86) | 2:3 | 99.0:1.0[a] | 99.0:1.0[a] |

| | | | | | |
|---|---|---|---|---|---|
| 4-$MeC_6H_4$ | Ph | (73) | 1:2 | 99.0:1.0 | 98.5:1.5 |
| 3-$CF_3C_6H_4$ | Ph | (73) | 1:2 | >99.5:0.5 | >99.5:0.5 |
| 3-$CF_3C_6H_4$ | Ph | (71) | 2:3 | >99.5:0.5[a] | >99.5:0.5[a] |
| 4-$NCC_6H_4$ | Ph | (92) | 1:3 | >99.5:0.5 | >99.5:0.5 |

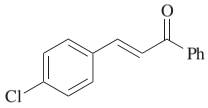


**135** (20 mol %),
$Et_3N$ (20 mol %),
$PhCO_2H$ (10 mol %),
toluene, rt

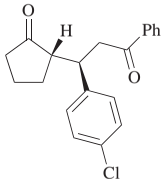


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| $R^1$ | $R^2$ | Time (d) | | *syn*/*anti* | er (*major*) | er (*minor*) |
|---|---|---|---|---|---|---|
| Ph | Ph | 7 | (98) | 90:10 | 96.0:4.0 | 88.5:11.5 |
| Ph | 4-$BrC_6H_4$ | 2 | (89) | 80:20 | 79.5:20.5 | 77.5:22.5 |
| 4-$BrC_6H_4$ | Ph | 6 | (93) | 71:29 | 80.5:19.5 | 79.0:21.0 |
| 2-$MeOC_6H_4$ | 4-$O_2NC_6H_4$ | 2 | (83) | 60:40 | 82.0:18.0 | 63.5:36.5 |
| 4-$MeOC_6H_4$ | Ph | 7 | (54) | 85:15 | 82.5:17.5 | 81.5:18.5 |
| 4-$MeOC_6H_4$ | 4-$O_2NC_6H_4$ | 6 | (59) | 64:36 | 80.0:20.0 | 75.5:24.5 |
| 2-$O_2NC_6H_4$ | Ph | 10 | (42) | 60:40 | 85.5:14.5 | 85.5:14.5 |
| Ph | 4-$MeC_6H_4$ | 10 | (74) | 72:28 | 79.0:21.0 | 76.5:23.5 |
| 4-$MeC_6H_4$ | Ph | 6 | (77) | 90:10 | 81.0:19.0 | 73.0:27.0 |
| 4-$CF_3C_6H_4$ | Ph | 3 | (90) | 65:35 | 83.0:17.0 | 80.5:19.5 |

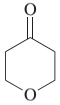


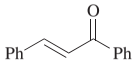
**133** (30 mol %),
$PhCO_2H$ (10 mol %),
neat, 20°, 7 d



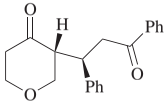
(95) dr 61:39
er 86.5:13.5

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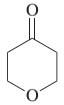
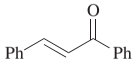
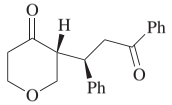
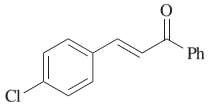
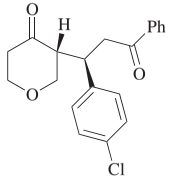
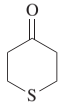
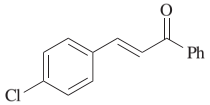
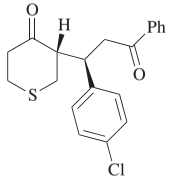
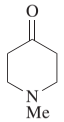
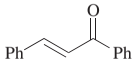
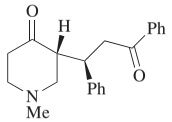
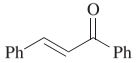
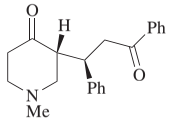
**44** (20 mol %),
*t*-BuOH, rt, 48 h



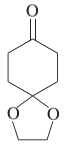
(57) dr 93:7
er 92.0:8.0

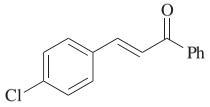
377

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

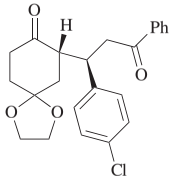
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **134** (20 mol %), 4-$MeOC_6H_4CO_2H$ (20 mol %), neat, rt, 3 d |  (81) *syn*/*anti* = 97:3 er 94.0:6.0 | 376 |
| |  | **133** (30 mol %), $PhCO_2H$ (10 mol %), neat, 20°, 7 d |  (63) dr 93:7 er 95.0:5.0 | 374 |
|  |  | **134** (20 mol %), 4-$MeOC_6H_4CO_2H$ (20 mol %), MeCN, rt, 3 d |  (71) *syn*/*anti* = 98:2 er 95.0:5.0 | 376 |
|  |  | **44** (20 mol %), *t*-BuOH, rt, 48 h |  (65) dr 84:16 er 92.0:8.0 | 377 |
| |  | **134** (20 mol %), 4-$MeOC_6H_4CO_2H$ (20 mol %), neat, rt, 3 d |  (84) *syn*/*anti* = 95:5 er 83.5:16.5 | 376 |

$C_6$



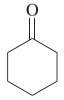


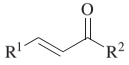
**134** (20 mol %),
4-$MeOC_6H_4CO_2H$
(20 mol %), MeCN, rt, 3 d



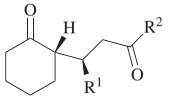
(76) *syn*/*anti* = 90:10
er 96.0:4.0

376





**16b** (10 mol %),
*i*-PrOH, rt



dr >50:1

380

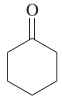
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 2-$C_4H_3S$ | 6 | (65) | 95.0:5.0 |
| Ph | Ph | 5 | (79) | 96.0:4.0 |
| Ph | 4-$ClC_6H_4$ | 3.5 | (82) | 97.0:3.0 |
| Ph | 4-$MeOC_6H_4$ | 6 | (63) | 95.0:5.0 |
| 2-$ClC_6H_4$ | Ph | 4 | (78) | 95.5:4.5 |
| 4-$ClC_6H_4$ | Ph | 4 | (80) | 95.0:5.0 |
| 4-$FC_6H_4$ | 4-$FC_6H_4$ | 4 | (84) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | Ph | 4 | (87) | 96.0:4.0 |

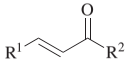
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

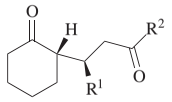
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



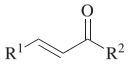


**44** (20 mol %),
*t*-BuOH, rt

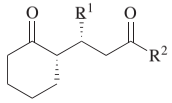


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| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Ph | Ph | 58 | (73) | 99:1 | 100.0:0.0 |
| Ph | 4-$BrC_6H_4$ | 48 | (63) | >99:1 | 93.0:7.0 |
| Ph | 4-$MeOC_6H_4$ | 96 | (45) | >99:1 | 92.5:7.5 |
| Ph | 4-$O_2NC_6H_4$ | 48 | (90) | 99:1 | 90.0:10.0 |
| 2-$ClC_6H_4$ | Ph | 72 | (54) | >99:1 | 94.5:5.5 |
| 2-$ClC_6H_4$ | 4-$MeOC_6H_4$ | 96 | (62) | >99:1 | 94.5:5.5 |
| 3-$ClC_6H_4$ | Ph | 72 | (65) | >99:1 | 93.0:7.0 |
| 4-$ClC_6H_4$ | Ph | 90 | (59) | 99:1 | 95.5:4.5 |
| 4-$FC_6H_4$ | Ph | 48 | (70) | >99:1 | 92.0:8.0 |
| 4-$O_2NC_6H_4$ | Ph | 48 | (93) | >99:1 | 94.0:6.0 |
| 4-$MeC_6H_4$ | Ph | 57 | (58) | >99:1 | 93.0:7.0 |
| Ph | 2-Np | 48 | (56) | >99:1 | 93.0:7.0 |
| 1-Np | Ph | 72 | (48) | >99:1 | 94.0:6.0 |



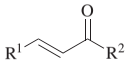
**133** (30 mol %),
$PhCO_2H$ (10 mol %),
neat, 20°, 7 d



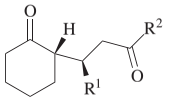
374

| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 2-$C_4H_3S$ | (67) | 83:17 | 95.5:4.5 |
| Ph | Ph | (98) | 96:4 | 96.0:4.0 |
| Ph | 4-$BrC_6H_4$ | (99) | 90:10 | 95.5:4.5 |
| Ph | 4-$ClC_6H_4$ | (99) | 93:7 | 94.0:6.0 |

| | | | | |
|---|---|---|---|---|
| Ph | 4-$FC_6H_4$ | (78) | 95:5 | 95.5:4.5 |
| Ph | 4-$O_2NC_6H_4$ | (91) | 92:8 | 94.0:6.0 |
| 4-$BrC_6H_4$ | Ph | (95) | 88:12 | 97.5:2.5 |
| 4-$ClC_6H_4$ | Me | (43) | 81:19 | 95.0:5.0 |
| 4-$ClC_6H_4$ | Ph | (91) | 92:8 | 97.0:3.0 |
| 2,4-$Cl_2C_6H_3$ | Ph | (82) | 98:2 | 98.0:2.0 |
| 4-$FC_6H_4$ | Ph | (99) | 93:7 | 96.5:3.5 |
| 2-$O_2NC_6H_4$ | Ph | (77) | 99:1 | 97.5:2.5 |
| 3-$O_2NC_6H_4$ | Ph | (93) | 84:16 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | Ph | (99) | 77:23 | 95.5:4.5 |
| Ph | 4-$MeC_6H_4$ | (66) | 99:1 | 90.5:9.5 |
| 4-$MeC_6H_4$ | Ph | (78) | 96:4 | 96.0:4.0 |




**134** (20 mol %),
4-$MeOC_6H_4CO_2H$
(20 mol %), neat, rt



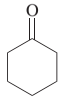

| $R^1$ | $R^2$ | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Ph | Ph | 3 | (77) | >99:1 | 94.5:5.5 |
| Ph | 4-$ClC_6H_4$ | 3 | (91) | 99:1 | 95.0:5.0 |
| Ph | 4-$MeOC_6H_4$ | 5 | (61) | 95:5 | 92.5:7.5 |
| Ph | 4-$H_2NC_6H_4$ | 5 | (67) | 98:2 | 93.5:6.5 |
| 4-$BrC_6H_4$ | Ph | 3 | (90) | 91:9 | 95.5:5.0 |
| 2-$ClC_6H_4$ | Ph | 3 | (86) | 83:17 | 92.5:7.5 |
| 2-$ClC_6H_4$ | 4-$MeOC_6H_4$ | 3 | (64) | >99:1 | 96.0:4.0 |
| 3-$ClC_6H_4$ | Ph | 3 | (84) | >99:1 | 95.0:5.0 |
| 4-$ClC_6H_4$ | Ph | 3 | (81) | 98:2 | 94.5:5.5 |
| 4-$FC_6H_4$ | Ph | 3 | (88) | >99:1 | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | Ph | 1.5 | (96) | 98:2 | 96.0:4.0 |
| 4-$MeC_6H_4$ | Ph | 4 | (76) | 99:1 | 91.0:9.0 |
| 1-Np | Ph | 3 | (73) | >99:1 | 93.0:7.0 |

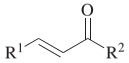
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

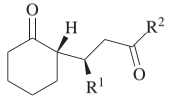
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$





**136** (20 mol %),
MeOH, rt

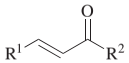


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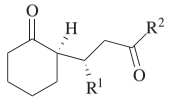
Catalyst Recycling ($R^1 = R^2 = Ph$)

| Run | Time (h) | | dr | er |
|---|---|---|---|---|
| 1 | 4 | (98) | 80:20 | 93.0:7.0 |
| 2 | 4 | (98) | 79:21 | 93.0:7.0 |
| 3 | 4 | (95) | 80:20 | 91.5:8.5 |
| 4 | 4 | (97) | 82:18 | 91.0:9.0 |
| 5 | 4 | (97) | 82:18 | 90.0:10.0 |
| 6 | 4 | (98) | 80:20 | 90.5:9.5 |

| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Ph | Ph | 4 | (98) | 80:20 | 93.0:7.0 |
| Ph | 4-$ClC_6H_4$ | 4 | (97) | 85:15 | 61.5:38.5 |
| Ph | 4-$H_2NC_6H_4$ | 8 | (87) | 96:4 | 97.0:3.0 |
| 4-$BrC_6H_4$ | Ph | 4 | (80) | 77:23 | 72.0:28.0 |
| 4-$ClC_6H_4$ | Ph | 4 | (98) | 96:4 | 80.0:20.0 |
| 2-$ClC_6H_4$ | 4-$MeC_6H_4$ | 4 | (99) | 99:1 | 64.5:35.5 |
| 4-$MeC_6H_4$ | Ph | 4 | (90) | 95:5 | 68.5:31.5 |



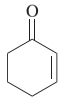
**136** (20 mol %),
DMSO, rt

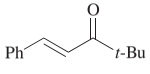


381

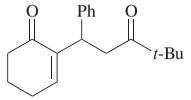
| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Ph | Ph | 4 | (95) | 88:12 | 89.0:11.0 |
| Ph | 4-$ClC_6H_4$ | 4 | (88) | 92:8 | 86.0:14.0 |
| Ph | 4-$H_2NC_6H_4$ | 8 | (85) | 96:4 | 95.5:4.5 |
| 4-$BrC_6H_4$ | Ph | 4 | (90) | 90:10 | 69.5:30.5 |
| 2-$ClC_6H_4$ | 4-$MeOC_6H_4$ | 4 | (99) | 96:4 | 58.0:42.0 |
| 4-$ClC_6H_4$ | Ph | 4 | (94) | 90.10 | 82.5:17.5 |
| 4-$MeC_6H_4$ | Ph | 4 | (98) | 84:16 | 86.0:14.0 |

$C_7$



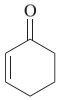


Catalyst (25 mol %),
KOH (50 %),
toluene, 24 h, rt

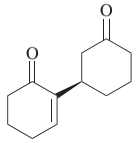


| Catalyst | | er |
|---|---|---|
| **144a** | (—) | 82.5:17.5 |
| **144b** | (—) | 73.5:26.5 |

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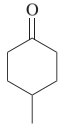


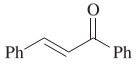
**144b** (25 mol %),
KOH (50 %),
toluene, 24 h, rt



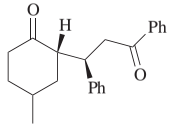
(90) er 94.0:6.0

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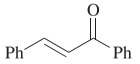


**44** (20 mol %),
*t*-BuOH, rt, 72 h

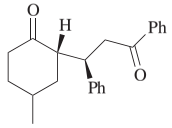


(69) dr >99:1
er 93.0:7.0

377

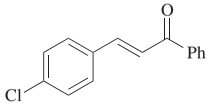


**134** (20 mol %),
4-$MeOC_6H_4CO_2H$
(20 mol %), neat, rt, 5 d

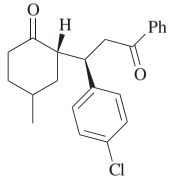


(46) *syn*/*anti* > 99:1
er 87.5:12.5

382



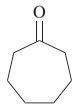
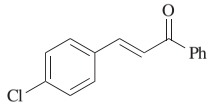
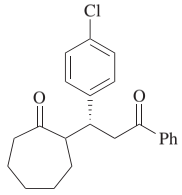
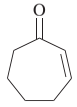
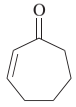
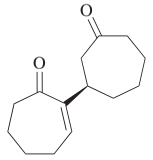
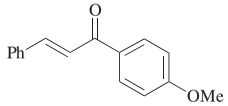
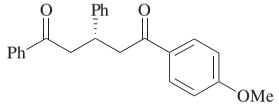
**133** (30 mol %),
$PhCO_2H$ (10 mol %),
neat, 20°, 7 d



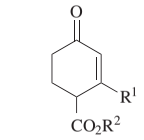
(95) dr 96:4
er 96.0:4.0

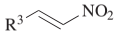
374

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

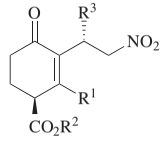
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_7$ | | | | |
|  |  | **133** (30 mol %), $PhCO_2H$ (10 mol %), neat, 20°, 7 d |  (39) dr 97:3 er 75.5:24.5 | 374 |
|  |  | **144b** (25 mol %), 50% of KOH, toluene, 2 d, rt |  (80) er 93.5:6.5 | 382 |
| $C_8$ | | | | |
|  |  | **137** (10 mol %), 50% of KOH, toluene, –10°, 36 h |  (72) er 90.0:10.0 | 94 |

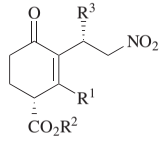
$C_{8-10}$





**162b** (30 mol %),
$H_2NCSNH_2$ (30 mol %),
0.1 M in toluene,
rt, 72–96 h



**I** +  **II**

383

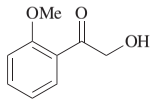
| $R^1$ | $R^2$ | $R^3$ | | dr **I/II** | er **I** | er **II** |
|---|---|---|---|---|---|---|
| Me | Me | Ph | (60) | 1:1.6 | 80.5:19.5 | 55.5:44.5 |
| Me | Et | 2-$C_4H_3O$ | (60) | 1.1:1 | 73.5:26.5 | 53.0:47.0 |
| Me | Et | 2-$C_4H_3S$ | (60) | 1.5:1 | 70.5:29.5 | 56.0:44.0 |
| Me | Et | Ph | (70) | 1.3:1 | 85.0:15.0 | 53.5:46.5 |
| Me | Et | 2-$ClC_6H_4$ | (63) | 1.1:1 | 80.0:20.0 | 52.0:48.0 |
| Me | Et | 2-$HOC_6H_4$ | (61) | 1.2:1 | 63.0:37.0 | 68.5:31.5 |
| Me | Et | 2-$MeOC_6H_4$ | (45) | 1.2:1 | 89.0:11.0 | 58.5:41.5 |
| Me | Et | 4-$MeOC_6H_4$ | (50) | 1:1.7 | 64.5:35.5 | 63.5:36.5 |
| Me | Et | 4-$O_2NC_6H_4$ | (74) | 1:1.7 | 71.0:29.0 | 63.5:36.5 |
| Me | Et | 2-$CF_3C_6H_4$ | (60) | 1:1.4 | 72.0:28.0 | 57.5:42.5 |
| Me | *t*-Bu | 2-$C_4H_3S$ | (66) | 5.2:1 | 84.5:15.5 | 55.5:44.5 |
| Me | *t*-Bu | Ph | (61) | 2.1:1 | 92.0:8.0 | 70.0:30.0 |
| Me | *t*-Bu | 2-$ClC_6H_4$ | (35) | 1.5:1 | 91.5:8.5 | 66.5:33.5 |
| *n*-Pr | Et | Ph | (36) | 2.0:1 | 88.5:11.5 | 51.5:48.5 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

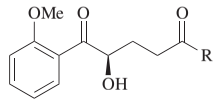
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_8$



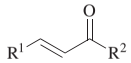


**139** (1 mol %),
$Et_2Zn$ (2 mol %),
THF, 4°

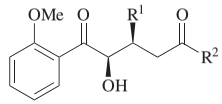


110, 48

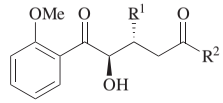
| R | Time (h) | | er |
|---|---|---|---|
| Me | 4 | (86) | 96.5:3.5 |
| Et | 4 | (82) | 95.5:4.5 |
| Ph | 4 | (86) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 12 | (84) | 96.0:4.0 |
| 2-$MeOC_6H_4$ | 12 | (90) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 8 | (83) | 97.5:2.5 |



**139** (*x* mol %),
$Et_2Zn$ (20–40 mol %),
THF, 3 Å MS, –20°



+



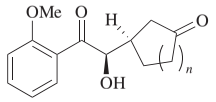
48

| $R^1$ | $R^2$ | *x* | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|---|
| *n*-$C_5H_{11}$ | Me | 10 | 24 | (39) | 68:32 | 96.5:3.5 | 93.0:7.0 |
| Ph | Me | 10 | 16 | (82) | 86:14 | 99.5:0.5 | 53.5:46.5 |
| $TBDPSOCH_2$ | Ph | 10 | 24 | (93) | 61:39 | 90.5:9.5 | 76.0:24.0 |
| Et | Ph | 10 | 7 | (85) | 81:19 | 98.5:1.5 | 89.5:10.5 |
| $BOMO(CH_2)_2$ | Ph | 10 | 24 | (72) | 77:23 | 90.0:10.0 | — |
| Ph | *i*-Pr | 10 | 17 | (73) | 86:14 | 93.5:6.5 | — |
| *i*-Bu | Ph | 5 | 7 | (95) | 69:31 | 98.5:1.5 | 82.5:17.5 |
| Ph | *t*-Bu | 10 | 24 | (58) | 93:7 | 87.0:13.0 | — |
| Ph | Ph | 5 | 3 | (93) | 78:22 | 97.5:2.5 | 96.5:3.5 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ph | 4-$ClC_6H_4$ | 5 | 3 | (95) | 79:21 | 98.5:1.5 | 91.5:8.5 |
| Ph | 4-$FC_6H_4$ | 5 | 3 | (96) | 81:19 | 98.5:1.5 | 90.0:10.0 |
| Ph | 4-$MeOC_6H_4$ | 5 | 6 | (99) | 85:15 | 98.5:1.5 | 76.0:24.0 |
| 4-$ClC_6H_4$ | Ph | 5 | 5 | (96) | 76:24 | 97.5:2.5 | 85.5:14.5 |



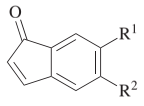
**139** (10 mol %),
$Et_2Zn$ (40 mol %),
THF, 3 Å MS



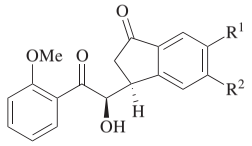
dr >98:2

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| *n* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|
| 1 | –20 | 19 | (81) | 92.5:7.5 |
| 2 | 0 | 26 | (61) | 99.5:0.5 |
| 3 | –20 | 26 | (45) | 99.0:1.0 |

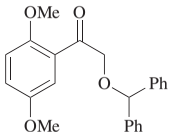


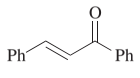
**139** (*x* mol %),
$Et_2Zn$ (2 mol %), THF



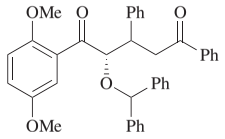
110, 48

| $R^1$ | $R^2$ | *x* | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|
| H | H | 1 | 4 | 1.5 | (68) | 95:5 | 98.5:1.5 |
| H | H | 1 | –20 | 4 | (74) | 98:2 | 99.5:0.5 |
| H | H | 3 | –20 | 3 | (80) | 98:2 | 99.5:0.5 |
| H | Br | 1 | 4 | 2 | (76) | 86:14 | 99.5:0.5 |
| H | Br | 1 | –20 | 4 | (74) | 98:2 | 99.5:0.5 |
| MeO | H | 1 | –20 | 4 | (65) | 97:3 | 98.5:1.5 |





**138** (20 mol %),
50% of KOH,
THF, –40°, 19 h



(63) *syn*/*anti* = 2:3
er (*syn*) 86.5:13.5
er (*anti*) 63.5:36.5

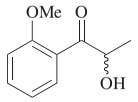
384

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

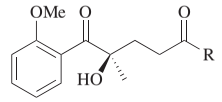
$C_9$





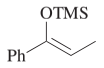


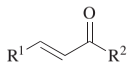
**139** (5 mol %), $Et_2Zn$ (20 mol %), THF, 3 Å MS, –20°



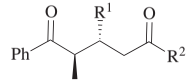

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| R | Time (h) | | er |
|---|---|---|---|
| Me | 16 | (88) | 98.0:2.0 |
| Et | 24 | (86) | 95.0:5.0 |
| Ph | 24 | (82) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 24 | (82) | 96.5:3.5 |
| 2-$MeOC_6H_4$ | 24 | (78) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | 12 | (95) | 95.0:5.0 |



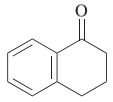

**137** (11 mol %), 50% of KOH, toluene, –20°

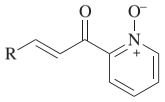



210

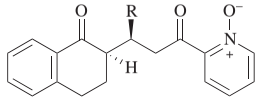
| $R^1$ | $R^2$ | Time (h) | | *anti*/*syn* | er (*anti*) | er (*syn*) |
|---|---|---|---|---|---|---|
| Ph | Ph | 10 | (90) | 9:1 | 99.5:0.5 | 95.0:5.0 |
| Ph | 4-$BrC_6H_4$ | 10 | (88) | 10:1 | 94.5:5.5 | 92.0:8.0 |
| Ph | 4-$FC_6H_4$ | 10 | (95) | 10:1 | 99.5:0.5 | 97.0:3.0 |
| Ph | 4-$MeOC_6H_4$ | 40 | (93) | 4:1 | 99.0:1.0 | 95.0:5.0 |
| 4-$BrC_6H_4$ | Ph | 10 | (94) | 7:1 | 96.0:4.0 | 97.5:2.5 |
| 4-$O_2NC_6H_4$ | Ph | 40 | (87) | 3:1 | 98.5:1.5 | 97.5:2.5 |
| 4-$MeC_6H_4$ | Ph | 15 | (85) | 10:1 | 99.5:0.5 | 90.5:9.5 |
| 1-Np | Ph | 15 | (82) | 20:1 | 96.0:4.0 | — |

$C_{10}$

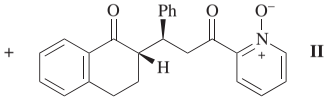




Ligand (10 mol %), $Cu(OTf)_2$ (10 mol %), $CH_2Cl_2$, rt



**I**

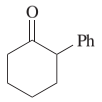


**II**

385

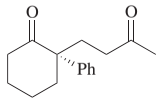
| R | Ligand | Time (d) | | dr **I/II** | er **I** | er **II** |
|---|---|---|---|---|---|---|
| Ph | **140** | 24 | (56) | 73:27 | 62.5:37.5 | 74.0:26.0 |
| Ph | **141** | 4 | (99) | 92:8 | 97.0:3.0 | 54.0:46.0 |
| 4-$BrC_6H_4$ | **141** | 3 | (99) | 82:18 | 96.0:4.0 | — |

$C_{12}$



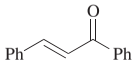


**144a** (5.6 mol %), 50% of NaOH, toluene, 20°

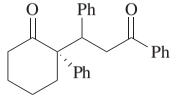


(95) er 73.0:27.0

386

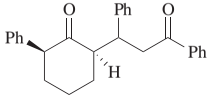


**144a** (5.6 mol %), 50% of NaOH, toluene, 20°



**I**

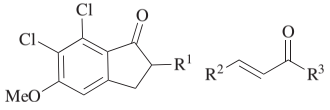
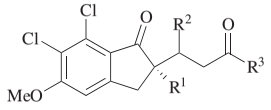
**I + II** (31)



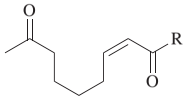
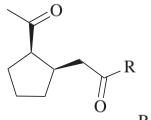
**II**

386

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_{12–15}$  |  | **144a** (5.6 mol %), 50% of NaOH, toluene, 20° |  | 386 |

| $R^1$ | $R^2$ | $R^3$ | | er |
|---|---|---|---|---|
| *n*-Pr | H | Me | (97) | 85.0:15.0 |
| *n*-Pr | Ph | Ph | (43) | 50.0:50.0 |
| Ph | H | Me | (50) | 76.0:24.0 |
| Ph | Ph | Ph | (10) | 55.0:45.0 |

| $C_{15–16}$  | 0.05–1 mg/mL **142**, pH 7.4 phosphate buffer, saline, 5% of MeCN, rt |  | 387 |
|---|---|---|---|

| R | | *cis*/*trans* | er |
|---|---|---|---|
| Ph | (—) | 90:1 | 98.5:1.5 |
| 4-$BrC_6H_4$ | (—) | 90:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (—) | 90:1 | 99.0:1.0 |
| 4-$MeC_6H_4$ | (—) | 30:1 | 99.0:1.0 |

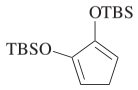
[a] The catalyst with the opposite configuration was also used and the opposite enantiomer obtained.

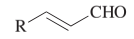
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS *(Continued)*
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

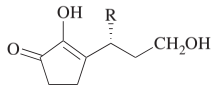
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_5$





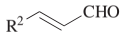
1. **145d** (5 mol %), EtOH, rt
2. $NaBH_4$ (1 eq), TBAF (4 eq)



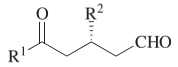
| R | Time (h) | | er | |
|---|---|---|---|---|
| *n*-Bu | 9 | (63) | 95.5:4.5 | 388 |
| Ph | 9 | (55) | 96.0:4.0 | |
| 4-$BrC_6H_4$ | 10 | (66) | 95.0:5.0 | |
| 4-$MeOC_6H_4$ | 20 | (40) | 93.5:6.5 | |
| 4-$O_2NC_6H_4$ | 9 | (57) | 97.0:3.0 | |

$C_{6-8}$





**145b** (5 mol %), benzene, rt, 8 d



389

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Ph | 48 | (74) | 97.0:3.0 |
| Ph | Ph | 48 | (74) | 98.0:2.0 |
| Ph | 4-$FC_6H_4$ | 48 | (73) | 97.0:3.0 |
| Ph | 2-$MeOC_6H_4$ | 24 | (77) | 99.0:1.0 |
| Ph | 4-$MeOC_6H_4$ | 36 | (78) | 98.0:2.0 |
| Ph | 3-$MeC_6H_4$ | 48 | (82) | 99.0:1.0 |
| Ph | 4-$MeC_6H_4$ | 48 | (82) | 99.0:1.0 |
| 3-$BrC_6H_4$ | 4-$BrC_6H_4$ | 24 | (76) | 98.0:2.0 |
| 3-$BrC_6H_4$ | 2-$ClC_6H_4$ | 24 | (69) | 98.5:1.5 |
| 3-$BrC_6H_4$ | 4-$ClC_6H_4$ | 24 | (79) | 98.0:2.0 |
| 3-$BrC_6H_4$ | 2-$MeOC_6H_4$ | 24 | (80) | 97.5:2.5 |
| 2-$ClC_6H_4$ | 2-$ClC_6H_4$ | 24 | (71) | 99.0:1.0 |
| 2-$FC_6H_4$ | 4-$BrC_6H_4$ | 24 | (73) | 98.0:2.0 |
| 2-$FC_6H_4$ | 2-$ClC_6H_4$ | 24 | (72) | 98.5:1.5 |
| 2-$FC_6H_4$ | 4-$ClC_6H_4$ | 24 | (73) | 98.5:1.5 |
| 2-$HOC_6H_4$ | 2-$MeOC_6H_4$ | 24 | (76) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 2-$MeOC_6H_4$ | 24 | (78) | 98.0.2.0 |

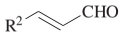
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

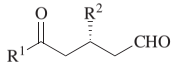
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{8-9}$



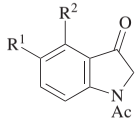


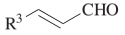
**146** (30 mol %), 4-$O_2NC_6H_4CO_2H$ (30 mol %), *t*-BuOH/*i*-PrOH (5:1), 0°, 4–18 h



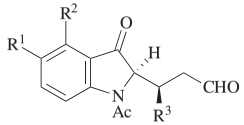
170

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Ph | (75) | 95.0:5.0 |
| Ph | 4-$NCC_6H_4$ | (59) | 95.0:5.0 |
| 4-$BrC_6H_4$ | Ph | (58) | 93.0:7.0 |
| 4-$MeOC_6H_4$ | Ph | (56) | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 4-$FC_6H_4$ | (63) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 4-$MeOC_6H_4$ | (63) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 4-$NCC_6H_4$ | (61) | 97.0:3.0 |
| 4-$MeC_6H_4$ | Me | (60) | 93.5:6.5 |
| 4-$MeC_6H_4$ | Ph | (62) | 97.5:2.5 |
| 4-$MeC_6H_4$ | 4-$FC_6H_4$ | (71) | 96.0:4.0 |





**145b** (20 mol %), $H_2O$ (2 eq), THF, –10°

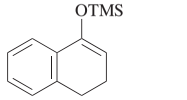


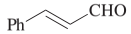
390

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| H | H | Me | 24 | (90) | 1:1 | 93.0:7.0 |
| H | H | 2-$C_4H_3O$ | 48 | (92) | 6:1 | 88.0:12.0 |
| H | H | Ph | 48 | (84) | 6:1 | 97.0:3.0 |
| H | H | 4-$BrC_6H_4$ | 36 | (81) | 4:1 | 97.0:3.0 |
| H | H | 2-$ClC_6H_4$ | 24 | (91) | 4:1 | 97.0:3.0 |
| H | H | 3-$ClC_6H_4$ | 48 | (91) | 6:1 | 95.0:5.0 |
| H | H | 4-$ClC_6H_4$ | 48 | (88) | 4:1 | 97.5:2.5 |
| H | H | 2-$MeOC_6H_4$ | 36 | (85) | 4:1 | 98.0:2.0 |

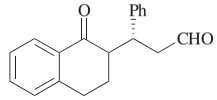
| | | | | | | |
|---|---|---|---|---|---|---|
| H | H | 4-$MeOC_6H_4$ | 48 | (92) | 5:1 | 97.0:3.0 |
| H | H | 2-$O_2NC_6H_4$ | 72 | (89) | 6:1 | 96.0:4.0 |
| Br | H | Ph | 24 | (92) | 11:1 | 91.0:9.0 |
| H | H | 4-$MeC_6H_4$ | 48 | (94) | 6:1 | 93.0:7.0 |
| H | Me | Ph | 60 | (91) | 5:1 | 97.5:2.5 |

$C_{10}$

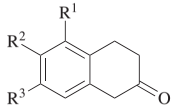


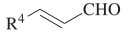




**146** (30 mol %), 4-$O_2NC_6H_4CO_2H$ (30 mol %), *t*-BuOH/*i*-PrOH (5:1), 20°, 4–18 h

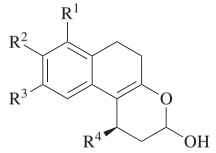



(87) er 92.5:7.5 170




**145b** (10 mol %), DABCO (20 mol %), DMSO




391

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Temp (°) | Time (d) | | dr | er |
|---|---|---|---|---|---|---|---|---|
| H | H | H | Me | 0 | 1 | (99) | 2:1 | 96.5:3.5 |
| H | H | H | Et | –20 | 2 | (62) | 3:1 | 96.5:3.5 |
| H | H | H | 2-$C_4H_3O$ | 0 | 1 | (50) | 9:1 | 91.5:8.5 |
| H | H | H | Ph | 0 | 1 | (97) | 5:1 | 95.0:5.0 |
| H | H | H | 4-$BrC_6H_4$ | –20 | 2 | (60) | 4:1 | 90.0:10.0 |
| H | H | H | 4-$MeOC_6H_4$ | 0 | 1 | (99) | 6:1 | 93.0:7.0 |
| H | H | H | 4-$O_2NC_6H_4$ | –20 | 2 | (67) | 3:1 | 97.5:2.5 |
| H | H | MeO | Me | 0 | 1 | (77) | 3:1 | 98.0:2.0 |
| H | H | MeO | Ph | 0 | 1 | (99) | 5:1 | 96.5:3.5 |
| H | Br | H | Me | 0 | 1 | (99) | 3:1 | 97.5:2.5 |
| H | Br | H | Ph | 0 | 1 | (99) | 4:1 | 95.5:4.5 |
| H | Cl | H | Me | 0 | 1 | (80) | 3:1 | 97.5:2.5 |
| H | Cl | H | Ph | 0 | 1 | (95) | 4:1 | 95.0:5.0 |
| H | MeO | H | Ph | 0 | 1 | (77) | 5:1 | 94.0:6.0 |
| MeO | H | H | Me | 0 | 1 | (77) | 3:1 | 98.0:2.0 |
| MeO | H | H | Ph | 0 | 1 | (99) | 5:1 | 96.5:3.5 |

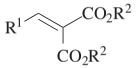
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

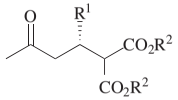
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





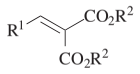
Catalyst (20 mol %),
THF, rt, 4 d



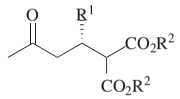
253

| $R^1$ | $R^2$ | Catalyst | | er |
|---|---|---|---|---|
| *i*-Pr | Bn | **6** | (16) | 58.5:41.5 |
| *i*-Pr | Bn | **147** | (53) | 59.5:40.5 |
| 2-$C_4H_3O$ | Et | **6** | (84) | 66.5:33.5 |
| 2-$C_4H_3O$ | Et | **147** | (95) | 51.0:49.0 |
| *n*-$C_5H_{11}$ | Bn | **6** | (16) | 62.0:38.0 |
| *n*-$C_5H_{11}$ | Bn | **147** | (41) | 60.0:40.0 |
| *c*-$C_6H_{11}$ | Bn | **6** | (27) | 57.0:43.0 |
| *c*-$C_6H_{11}$ | Bn | **147** | (64) | 58.5:41.5 |
| Ph | Me | **6** | (55) | 78.0:22.0 |
| Ph | Me | **147** | (88) | 78.5:22.5 |
| Ph | Et | **6** | (47) | 79.5:20.5 |
| Ph | Et | **147** | (80) | 80.5:19.5 |

| $R^1$ | $R^2$ | Catalyst | | er |
|---|---|---|---|---|
| Ph | *i*-Pr | **6** | (22) | 80.5:19.5 |
| Ph | *i*-Pr | **147** | (42) | 81.0:19.0 |
| Ph | Bn | **147** | (85) | 75.5:24.5 |
| 2-$MeC_6H_4$ | Et | **6** | (17) | 85.0:15.0 |
| 2-$MeC_6H_4$ | Et | **147** | (36) | 86.0:14.0 |
| 2-$CF_3C_6H_4$ | Et | **6** | (46) | 85.0:15.0 |
| 2-$CF_3C_6H_4$ | Et | **147** | (62) | 86.5:13.5 |
| 1-Np | Et | **6** | (31) | 82.0:18.0 |
| 1-Np | Et | **147** | (45) | 85.5:14.5 |
| 2-Np | Et | **6** | (60) | 77.5:22.5 |
| 2-Np | Et | **147** | (87) | 79.0:21.0 |

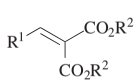


**6** (20 mol %), THF

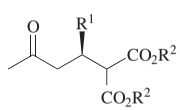


138

| $R^1$ | $R^2$ | Temp | | er |
|---|---|---|---|---|
| *i*-Pr | Bn | rt | (16) | 58.5:41.5 |
| 2-$C_4H_3O$ | Et | rt | (84) | 66.5:33.5 |
| *n*-$C_5H_{11}$ | Bn | rt | (16) | 62.0:38.0 |
| *c*-$C_6H_{11}$ | Bn | rt | (27) | 57.0:43.0 |
| Ph | Et | –25° | (5) | 86.0:14.0 |
| Ph | Et | 4° | (16) | 84.5:15.5 |
| Ph | Et | rt | (47) | 79.5:20.5 |
| 2-$MeC_6H_4$ | Et | rt | (17) | 85.0:15.0 |
| 2-$CF_3C_6H_4$ | Et | –25° | (14) | 95.5:4.5 |
| 2-$CF_3C_6H_4$ | Et | 4° | (46) | 90.0:10.0 |
| 2-$CF_3C_6H_4$ | Et | rt | (46) | 85.0:15.0 |
| 1-Np | Et | –25° | (5) | 92.0:8.0 |
| 1-Np | Et | 4° | (21) | 88.0:12.0 |
| 1-Np | Et | rt | (31) | 82.0:18.0 |
| 2-Np | Et | rt | (60) | 77.5:22.5 |



**29c** (20 mol %),
2-HO-3,5-$(O_2N)_2C_6H_2CO_2H$
(20 mol %), 30°, 4–5 d



368

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 3-$O_2NC_6H_4$ | Me | (92) | 92.0:8.0 |
| 3-$O_2NC_6H_4$ | Et | (81) | 93.0:7.0 |
| 4-$O_2NC_6H_4$ | Me | (90) | 93.5:6.5 |
| 4-$O_2NC_6H_4$ | Et | (85) | 93.0:7.0 |
| 4-$O_2NC_6H_4$ | *i*-Pr | (33) | 93.5:6.5 |
| 4-$O_2NC_6H_4$ | Bn | (78) | 92.5:7.5 |

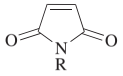
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

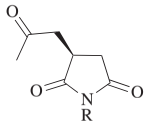
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



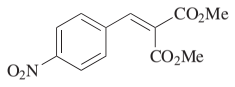


**150a** (10 mol %), $PhCO_2H$ (10 mol %), toluene, rt

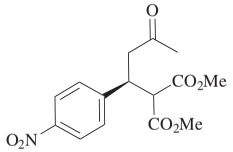


392

| R | Time (h) | | er |
|---|---|---|---|
| *n*-Pr | 72 | (94) | 99.5:0.5 |
| *i*-Pr | 120 | (92) | 96.0:4.0 |
| *t*-Bu | 120 | (69) | 99.5:0.5 |
| Ph | 48 | (87) | 99.0:1.0 |
| 4-$BrC_6H_4$ | 48 | (93) | 96.5:3.5 |
| 3-$ClC_6H_4$ | 48 | (94) | 99.0:1.0 |
| 4-$ClC_6H_4$ | 48 | (94) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 48 | (96) | 99.0:1.0 |
| 3-$MeC_6H_4$ | 48 | (97) | 98.0:2.0 |
| 4-$MeC_6H_4$ | 48 | (91) | 99.0:1.0 |
| 3-$CF_3C_6H_4$ | 48 | (98) | 98.0:2.0 |
| 4-$CF_3C_6H_4$ | 48 | (99) | 98.0:2.0 |
| Bn | 48 | (86) | 99.5:0.5 |

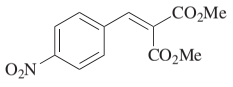


Catalyst (20 mol %), *n*-$PrCO_2H$ (10 mol %), neat

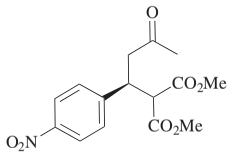


393

| Catalyst | Temp | Time (d) | | er |
|---|---|---|---|---|
| **16b** | rt | 2 | (74) | 77.0:23.0 |
| **148** | 0° | — | (36) | 81.0:19.0 |



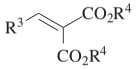
**149** (30 mol %),
$Zn(SbF_6)_2$ (15 mol %),
MeCN, rt



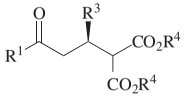
(96) er 85.5:14.5 394

$C_{3-12}$





1. **155** (5.5 mol %),
$Cu(OTf)_2$ (5 mol %), additive
$CH_2Cl_2$
2. HBr, THF



395

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Additive | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|---|---|
| Me | $EtO_2C$ | 4-$MeC_6H_4$ | Me | — | –78 | 10 | (35) | 90.0:10.0 |
| Et | $EtO_2C$ | 4-$MeC_6H_4$ | Me | — | –78 | 10 | (88) | 91.5:8.5 |
| 2-$C_4H_3S$ | Ac | 4-$MeC_6H_4$ | Et | — | –78 | 48 | (64) | 85.0:15.0 |
| Ph | Ac | 4-$MeC_6H_4$ | Me | — | –78 | 10 | (90) | 95.0:5.0 |
| Ph | Ac | 4-$MeC_6H_4$ | Et | — | –78 | 24 | (85) | 97.0:3.0 |
| Ph | Ac | 4-$MeC_6H_4$ | *i*-Pr | — | –40 | 24 | (63) | 90.0:10.0 |
| Ph | Cbz | Ph | Me | 4 Å MS | –78 | 18 | (85) | 91.0:9.0 |
| Ph | Cbz | 4-$MeOC_6H_4$ | Me | 4 Å MS | –78 | 6 | (98) | 91.5:8.5 |
| Ph | Cbz | 2-$MeC_6H_4$ | Me | 4 Å MS | –78 | 48 | (80) | 64.0:36.0 |
| Ph | Cbz | 3-$MeC_6H_4$ | Me | 4 Å MS | –78 | 10 | (79) | 91.0:9.0 |
| Ph | Cbz | 4-$MeC_6H_4$ | Me | 4 Å MS | –78 | 7 | (88) | 90.0:10.0 |
| 4-$ClC_6H_4$ | Ac | 4-$MeC_6H_4$ | Me | — | –78 | 24 | (80) | 94.0:6.0 |
| 4-$ClC_6H_4$ | Ac | 4-$MeC_6H_4$ | Et | — | –78 | 46 | (64) | 96.5:3.5 |
| 4-$MeC_6H_4$ | Ac | 4-$MeC_6H_4$ | Me | — | –78 | 24 | (80) | 94.0:6.0 |
| 2-Np | Ac | 4-$MeC_6H_4$ | Me | — | –78 | 18 | (87) | 94.0:6.0 |
| 2-Np | Ac | 4-$MeC_6H_4$ | Et | — | –78 | 48 | (64) | 85.0:15.0 |

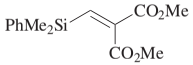
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

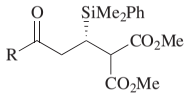
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{3-13}$





**6** (30 mol %),
TFA (10 mol %), NMP

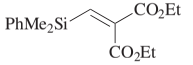


396

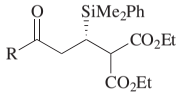
| R | Temp (°) | Time (d) | | er |
|---|---|---|---|---|
| Me | –10 | 7 | (76) | 95.0:5.0 |
| $(MeO)_2CH$ | –10 | 7 | (78) | 92.7:7.3 |
| Et | –10 | 7 | (81) | 96.4:3.6 |
| *n*-Pr | –10 | 7 | (85) | 95.6:4.4 |
| *i*-Pr | –10 | 7 | (82) | 99.8:0.2 |
| *i*-Bu | –10 | 6 | (82) | 98.4:1.6 |
| *n*-$C_5H_{11}$ | –10 | 3 | (94) | 99.8:0.2 |
| $BnO(CH_2)_6$ | –10 | 6 | (92) | 95.7:4.3 |
| *c*-$C_6H_{11}(CH_2)_2$ | –10 | 5 | (76) | 95.2:4.8 |
| *n*-$C_9H_{19}$ | –10 | 3 | (88) | 95.6:4.4 |
| *n*-$C_{11}H_{23}$ | 4 | 6 | (80) | 93.5:6.5 |

$C_{3-11}$





**6** (30 mol %),
TFA (10 mol %), NMP, –10°

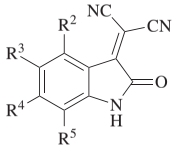


397

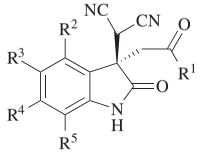
| R | Time (d) | | er |
|---|---|---|---|
| Me | 7 | (76) | 95.0:5.0 |
| $(MeO)_2CH$ | 7 | (78) | 92.7:7.3 |
| Et | 7 | (81) | 96.4:3.6 |
| *n*-Pr | 7 | (85) | 95.6:4.4 |
| *i*-Pr | 7 | (82) | 99.8:0.2 |
| *i*-Bu | 6 | (82) | 98.4:1.6 |
| *n*-$C_5H_{11}$ | 3 | (94) | 99.8:0.2 |
| $BnO(CH_2)_6$ | 6 | (92) | 95.7:4.3 |
| *n*-$C_9H_{19}$ | 3 | (88) | 95.6:4.4 |

$C_{3-4}$





**80d** (*x* mol %),
**154** (20–40 mol %),
THF, rt



398

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|---|---|---|
| Me | H | H | H | H | 10 | 24 | (96) | 98.5:1.5 |
| Me | H | H | H | $CF_3$ | 10 | 5 | (99) | 97.5:2.5 |
| Me | H | H | Br | H | 10 | 10 | (99) | 99.0:1.0 |
| Me | H | Br | H | H | 10 | 15 | (94) | 98.5:1.5 |
| Me | H | Cl | H | H | 10 | 12 | (98) | 98.5:1.5 |
| Me | H | F | H | H | 10 | 10 | (96) | 98.5:1.5 |
| Me | H | F | F | H | 10 | 10 | (96) | 98.5:1.5 |
| Me | H | I | H | H | 20 | 72 | (98) | 97.0:3.0 |
| Me | H | MeO | H | H | 10 | 10 | (98) | 99.0:1.0 |
| Me | H | Me | H | H | 10 | 20 | (94) | 98.5:1.5 |
| Me | H | Me | H | Me | 20 | 24 | (90) | 98.0:2.0 |
| Me | Br | H | H | H | 20 | 7 | (81) | 99.5:0.5 |
| Me | Cl | H | H | H | 20 | 9 | (93) | 99.5:0.5 |
| Et | H | H | H | H | 20 | 72 | (98) | >99.5:0.5 |

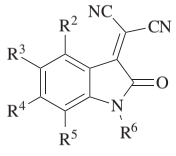
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

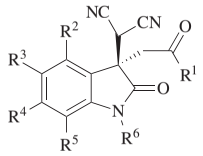
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{3-4}$





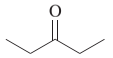
**152** (20 mol %),
**153** (40 mol %),
THF, rt

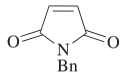


399

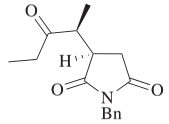
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | Time (h) | | er |
|---|---|---|---|---|---|---|---|---|
| Me | H | H | H | H | H | 9 | (95) | 96.0:4.0 |
| Me | H | H | H | H | Bn | 7 | (92) | 73.0:27.0 |
| Me | H | H | H | Cl | H | 9 | (91) | 93.0:7.0 |
| Me | H | H | Cl | H | H | 8 | (91) | 92.5:7.5 |
| Me | H | Br | H | H | H | 6 | (93) | 97.0:3.0 |
| Me | H | Cl | H | H | H | 4.5 | (90) | 95.5:4.5 |
| Me | H | F | H | H | H | 5 | (95) | 97.5:2.5 |
| Me | H | MeO | H | H | H | 6 | (95) | 97.5:2.5 |
| Me | H | $O_2N$ | H | H | H | 6 | (92) | 96.5:3.5 |
| Me | H | Me | H | H | H | 8 | (95) | 97.0:3.0 |
| Et | Cl | H | H | H | H | 6 | (91) | 98.0:2.0 |

$C_5$



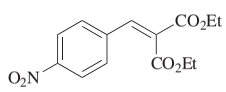


**6** (10 mol %),
*i*-PrOH/$Et_2O$ (1:1),
0°, 24 h

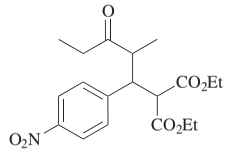


(80) dr 4.1:1
er 50.0:50.0

400



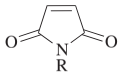
**29a** (20 mol %),
2-HO-3,5-$(O_2N)_2C_6H_2CO_2H$
(20 mol %), 30°, 4 d



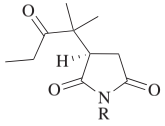
(14) *syn*/*anti* = 9:1
er 90.5:9.5

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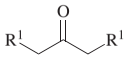


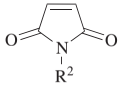
**150a** (10 mol %),
$PhCO_2H$ (10 mol %),
toluene, rt, 140 h



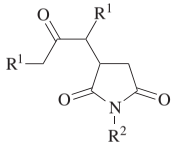
| R | | er | |
|---|---|---|---|
| Ph | (93) | 96.5:3.5 | |
| 4-$BrC_6H_4$ | (99) | 99.5:0.5 | 392 |
| 3-$ClC_6H_4$ | (98) | 99.0:1.0 | |
| 4-$CF_3C_6H_4$ | (73) | 98.0:2.0 | |

$C_{5-9}$





**150a** (10 mol %),
$PhCO_2H$ (10 mol %),
1 M in toluene, rt

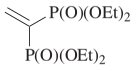


392

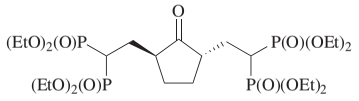
| $R^1$ | $R^2$ | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| Me | 3-$MeC_6H_4$ | 48 | (96) | 1:1 | 98.5:1.5 | 99.5:0.5 |
| Et | Ph | 48 | (96) | >4:1 | 99.5:0.5 | 97.5:2.5 |
| Pr | Ph | 72 | (80) | >4.1 | 99.5:0.5 | 97.0:3.0 |

$C_5$



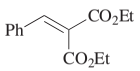


**6** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt, 17 h

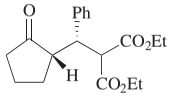


(70) *cis*/*trans* = 1:99, er 99.5:0.5

401



Catalyst (20 mol %),
THF, rt, 4 d



| Catalyst | | *syn*/*anti* | er (*syn*) | er (*anti*) | |
|---|---|---|---|---|---|
| **6** | (61) | 9:1 | 76.5:23.5 | 77.5:22.5 | 138, 253 |
| **147** | (28) | 7:1 | 69.5:30.5 | — | 253 |

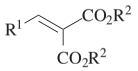
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

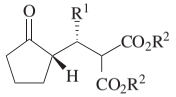
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_5$



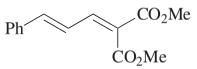


**149** (30 mol %), $Zn(SbF_6)_2$ (15 mol %), solvent, rt

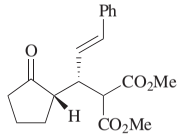


394

| $R^1$ | $R^2$ | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Ph | Me | MeCN | (92) | >99:1 | >99.5:0.5 |
| 4-$ClC_6H_4$ | Me | MeCN | (83) | >99:1 | >99.5:0.5 |
| 4-$MeOC_6H_4$ | Me | MeCN | (80) | 99:1 | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | Me | THF | (99) | 96:4 | 99.0:1.0 |
| 4-$O_2NC_6H_4$ | Et | MeCN | (80) | 99:1 | >99.5:0.5 |

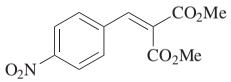


**149** (20 mol %), $Zn(OTf)_2$ (10 mol %), $CH_2Cl_2$, rt

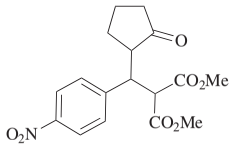


(50) dr 4:1
er 90.0:10.0 (major)
er 87.0:13.0 (minor)

394

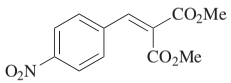


**29c** (20 mol %), 2-HO-3,5-$(O_2N)_2C_6H_2CO_2H$ (20 mol %), 30°, 5 d

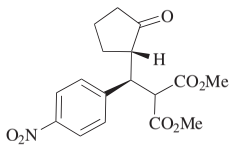


(51) *syn*/*anti* = 2:1
er 87.5:12.5

368

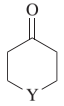


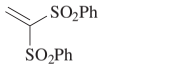
**156** (20 mol %), toluene, rt, 2–5 d



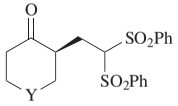
(73) dr 75:25
er 75.0:25.0

402



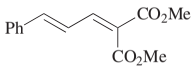


**225a** (20 mol %), $PhCO_2H$ (20 mol %), $CHCl_3$, 0°, 2 h

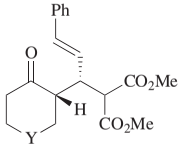


| Y | | er |
|---|---|---|
| O | (89) | 95.5:4.5 |
| S | (76) | 97.5:2.5 |

403

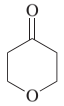


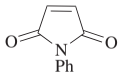
**149** (20 mol %), $Zn(OTf)_2$ (10 mol %), $CH_2Cl_2$, rt



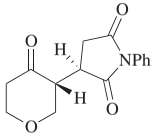
| Y | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| O | (62) | 2.3:1 | 95.5:4.5 | 78.5:21.5 |
| S | (64) | 3.5:1 | 78.5:21.5 | 84.5:15.5 |

394



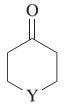


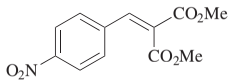
**16b** (10 mol %), *i*-PrOH/$Et_2O$ (1:1), 0°, 48 h



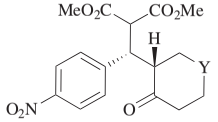
(86) dr 3.9:1
er 92.5:7.5

400





**156** (20 mol %), solvent, rt, 2–5 d



| Y | Solvent | | dr | er |
|---|---|---|---|---|
| O | neat | (87) | 80:20 | 96.0:4.0 |
| S | toluene | (88) | 86:14 | 98.0:2.0 |

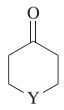
402

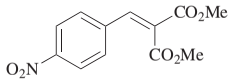
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

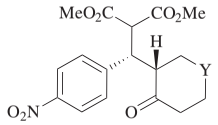
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_5$



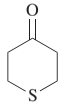


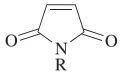
**149** (30 mol %), $Zn(SbF_6)_2$ (15 mol %), HFIP (1 eq), THF, rt



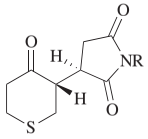
| Y | | *syn*/*anti* | er |
|---|---|---|---|
| O | (60) | 86:14 | >99.5:0.5 |
| S | (70) | 99:1 | >99.5:0.5 |

394





**16b** (10 mol %), *i*-PrOH/$Et_2O$ (1:1), 0°

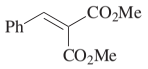


| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 4-$BrC_6H_4$ | 48 | (76) | 2.2:1 | 92.5:7.5 |
| Bn | 60 | (82) | 4.3:1 | 97.0:3.0 |
| $BnCH_2$ | 60 | (61) | 12:1 | 88.0:12.0 |

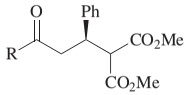
400

$C_{6-8}$





**151** (10 mol %), HFIP (2 eq), $CH_2Cl_2$, –78°



| R | Conv. (%) | er |
|---|---|---|
| *t*-Bu | 15 | 79.0:21.0 |
| Ph | 50 | 67.0:33.0 |

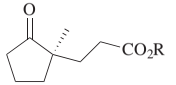
404

$C_6$



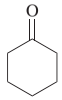


**131** (20 mol %), toluene, 90°



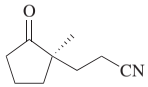
| R | Time (h) | | er |
|---|---|---|---|
| Me | 46 | (70) | 99.5:0.5 |
| Bn | 48 | (96) | 99.5:0.5 |

405

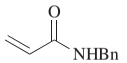




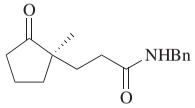
**157a** (20 mol %),
toluene, 90°, 46 h



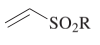
(54) er 86.0:14.0 405



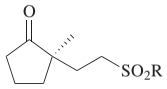
**131** (20 mol %),
toluene, 90°, 46 h



(31) er 90.0:10.0 405

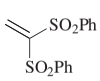


**157a** (20 mol %),
toluene, 90°, 46 h

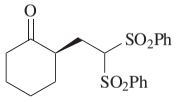


| R | | er |
|---|---|---|
| Me | (50) | >97.5:2.5 |
| Ph | (34) | 94.5:5.5 |

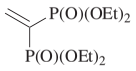
405



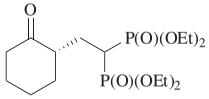
**225a** (20 mol %),
$PhCO_2H$ (20 mol %),
$CHCl_3$, 0°, 2 h



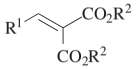
(94) er 96.0:4.0 403



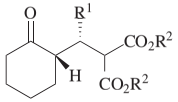
**6** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt, 17 h



(61) er 70.0:30.0 401



**16b** (20 mol %),
*n*-$PrCO_2H$ (10 mol %),
neat, rt, 2 d



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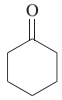
| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Bu | Me | (27) | — | — |
| Ph | Et | (36) | 90:10 | 94.0:6.0 |
| 4-$BrC_6H_4$ | Et | (71) | 93:7 | 95.0:5.0 |
| 2-$ClC_6H_4$ | Et | (48) | 95:5 | 94.0:6.0 |
| 3-$O_2NC_6H_4$ | Et | (95) | 91:9 | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | Me | (98) | 93:7 | 95.0:5.0 |
| 1-Np | Et | (20) | 95:5 | 93.5:6.5 |

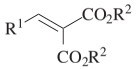
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

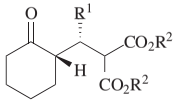
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



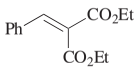


**29a** (20 mol %), 2-HO-3,5-$(O_2N)_2C_6H_2CO_2H$ (20 mol %), $H_2O$, 30°, 3–9 d

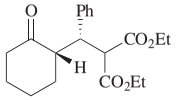


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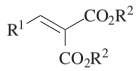
| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Bu | Et | (82) | 95:5 | 65.5:34.5 |
| Ph | Et | (72) | 98:2 | 98.0:2.0 |
| 4-$BrC_6H_4$ | Et | (78) | 98:2 | 98.0:2.0 |
| 4-$ClC_6H_4$ | Et | (90) | 98:2 | 96.0:4.0 |
| 3,4-$Cl_2C_6H_3$ | Et | (96) | 97:3 | 97.5:2.5 |
| 3-$O_2NC_6H_4$ | Me | (99) | 99:1 | 97.5:2.5 |
| 3-$O_2NC_6H_4$ | Et | (99) | 97:3 | 97.5:2.5 |
| 4-$O_2NC_6H_4$ | Me | (98) | 96:4 | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | Et | (99) | 98:2 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | Et | (44) | 99:1 | 97.5:2.5 |
| 2-$MeC_6H_4$ | Et | (58) | 95:5 | 97.0:3.0 |
| 4-$CF_3C_6H_4$ | Et | (94) | 97:3 | 97.5:2.5 |
| 4-$NCC_6H_4$ | Et | (99) | 96:4 | 97.5:2.5 |
| 2-Np | Et | (70) | 98:2 | 97.5:2.5 |



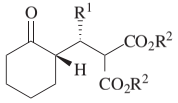
Catalyst (20 mol %), THF, rt



| Catalyst | Time (d) | | *syn*/*anti* | er (*syn*) | Refs. |
|---|---|---|---|---|---|
| **6** | 14 | (24) | >20:1 | 82.5:17.5 | 253, 138 |
| **147** | 7 | (32) | 19:1 | 88.5:11.5 | 253 |

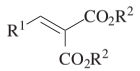


**156** (20 mol %),
neat, rt, 2–12 d

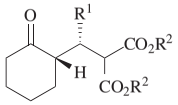


402

| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | Me | (88) | 90:10 | 91.0:9.0 |
| 2-$C_5H_4N$ | Me | (87) | >99:1 | 77.0:23.0 |
| Ph | Me | (86) | 91:9 | 95.0:5.0 |
| 4-$BrC_6H_4$ | Me | (88) | 91:9 | 97.0:3.0 |
| 4-$BrC_6H_4$ | Et | (90) | 90:10 | 97.0:3.0 |
| 4-$ClC_6H_4$ | Me | (84) | 89:11 | 98.0:2.0 |
| 2-$O_2NC_6H_4$ | Me | (61) | >99:1 | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | Me | (87) | 86:14 | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | Me | (95) | 95:5 | 98.0:2.0 |
| 4-$O_2NC_6H_4$ | Et | (95) | 90:10 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | Me | (64) | 91:9 | 96.0:4.0 |
| 4-$NCC_6H_4$ | Me | (84) | 88:12 | 96.0:4.0 |
| 1-Np | Me | (80) | 91:9 | 93.0:7.0 |



**149** (30 mol %),
$Zn(SbF_6)_2$ (15 mol %),
HFIP (*x* eq), solvent, rt



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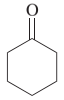
| $R^1$ | $R^2$ | *x* | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| Ph | Me | 0 | THF | (80) | 99:1 | 99.0:1.0 |
| 4-$BrC_6H_4$ | Me | 0 | THF | (90) | 98:2 | 99.0:1.0 |
| 4-$ClC_6H_4$ | Me | 0 | THF | (99) | 99:1 | >99.5:0.5 |
| 4-$MeOC_6H_4$ | Me | 1 | THF | (95) | 99:1 | >99.5:0.5 |
| 2-$O_2NC_6H_4$ | Me | 1 | THF | (65) | >99:1 | >99.5:0.5 |
| 3-$O_2NC_6H_4$ | Me | 0 | MeCN | (87) | 98:2 | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | Me | 0 | THF | (88) | 98:2 | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | Et | 0 | THF | (88) | 98:2 | >99.5:0.5 |
| 4-$MeC_6H_4$ | Me | 0 | THF | (85) | 98:2 | 99.5:0.5 |
| 4-$NCC_6H_4$ | Me | 0 | THF | (85) | 99:1 | 99.5:0.5 |
| 4-$MeO_2CC_6H_4$ | Me | 0 | THF | (99) | >99:1 | >99.5:0.5 |

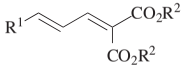
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

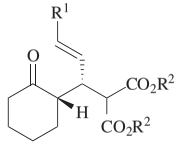
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



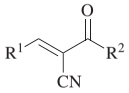


**149** (20 mol %), $Zn(OTf)_2$ (10 mol %), $CH_2Cl_2$, rt

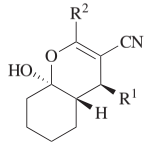


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| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| *n*-Pr | Me | (83) | 1.4:1 | 99.0:1.0/98.5:1.5 |
| Ph | Me | (90) | 1.9:1 | 99.0:1.0/97.5:2.5 |
| Ph | Et | (99) | 1.6:1 | 97.5:2.5/97.5:2.5 |
| 4-$BrC_6H_4$ | Me | (74) | 1.7:1 | 97.5:2.5/99.0:1.0 |
| 4-$ClC_6H_4$ | Me | (78) | 1.7:1 | 96.0:4.0/98.0:2.0 |
| 4-$MeOC_6H_4$ | Me | (80) | 1.4:1 | 96.5:3.5/98.5:1.5 |
| 4-$O_2NC_6H_4$ | Me | (80) | 1.6:1 | 98.0:2.0/95.5:4.5 |



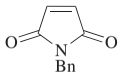
**80d** (20 mol %), 2-$FC_6H_4CO_2H$ (20 mol %), $CH_2Cl_2$, rt



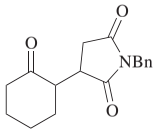
406

| $R^1$ | $R^2$ | Time (d) | | dr | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | Ph | 1 | (88) | 5.2:1 | 96.5:3.5 |
| 2-$C_4H_3S$ | Ph | 2 | (85) | 3.2:1 | 97.5:2.5 |
| Ph | Ph | 3.5 | (78) | 4.9:1 | 97.5:2.5 |
| 2-$BrC_6H_4$ | Ph | 4 | (32) | 3.6:1 | 93.0:7.0 |
| 4-$BrC_6H_4$ | Ph | 2.5 | (84) | 4.8:1 | 97.0:3.0 |
| 4-$BrC_6H_4$ | 4-$BrC_6H_4$ | 2 | (81) | 4.6:1 | 82.5:17.5 |
| 4-$BrC_6H_4$ | 4-$MeOC_6H_4$ | 4 | (86) | 9:1 | 87.5:12.5 |
| 4-$ClC_6H_4$ | Ph | 3.5 | (85) | 3.7:1 | 97.0:3.0 |

| | | | | | |
|---|---|---|---|---|---|
| 4-$MeOC_6H_4$ | Ph | 4 | (78) | 4.5:1 | 97.0:3.0 |
| 3-$O_2NC_6H_4$ | Ph | 4 | (79) | 5.4:1 | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | Ph | 2 | (77) | 5.6:1 | 98.0:2.0 |
| 4-$MeC_6H_4$ | Ph | 4 | (81) | 5:1 | 96.5:3.5 |
| 4-$NCC_6H_4$ | Ph | 2.5 | (90) | 5.4:1 | 98.0:2.0 |
| 2-Np | Ph | 4 | (82) | 4.3:1 | 80.0:20·0 |

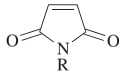


**150a** (10 mol %),
$PhCO_2H$ (10 mol %),
1 M in toluene, rt, 48 h

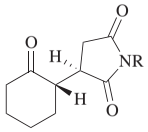


(96) dr 3:1
er 96.5:3.5 (major)
er 97.0:3.0 (minor)

392

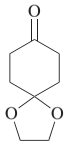


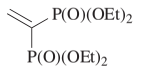
**16b** (10 mol %),
*i*-PrOH/$Et_2O$ (1:1), 0°



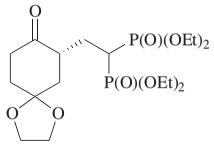
400

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| Ph | 24 | (85) | 2.5:1 | 99.5:0.5 |
| 4-$BrC_6H_4$ | 24 | (79) | 3.7:1 | 90.5:9.5 |
| 4-Br-3-$MeOC_6H_3$ | 36 | (77) | 2:1 | 86.0:14.0 |
| Bn | 48 | (70) | 8.5:1 | 95.5:4.5 |



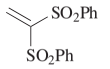


**6** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt, 25 h

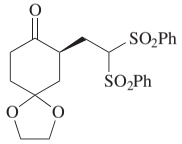


(62) er 82.0:18.0

401



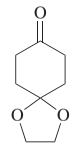
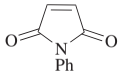
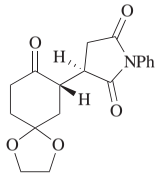
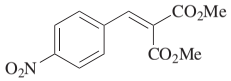
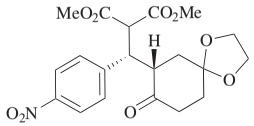
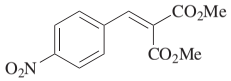
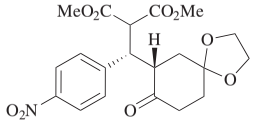
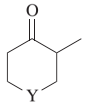
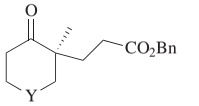
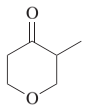
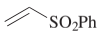
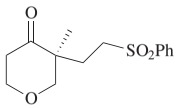
**225a** (20 mol %),
$PhCO_2H$ (20 mol %),
$CHCl_3$, 0°, 2 h



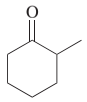
(87) er 95.0:5.0

403

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

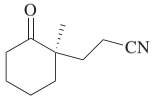
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_6$ | | | | |
|  |  | **16b** (10 mol %), *i*-PrOH/$Et_2O$ (1:1), 0°, 48 h |  (70) dr 4.5:1 er 93.5:6.5 | 400 |
| |  | **16b** (20 mol %), *n*-$PrCO_2H$ (10 mol %), neat, rt, 2 d |  (60) *syn*/*anti* = 89:11 er 97.0:3.0 | 393 |
| |  | **156** (20 mol %), toluene, rt, 2–5 d |  (85) dr 90:10 er 80.0:20.0 | 402 |
|  |  | **131** (20 mol %), toluene, 90°, 48 h |  Y: O (91) er 99.0:1.0; S (64) er 98.5:1.5 | 405 |
|  |  | **157b** (20 mol %), toluene, 90°, 46 h |  (65) er 99.0:1.0 | 405 |

$C_7$





**131** (20 mol %),
toluene, 90°, 46 h

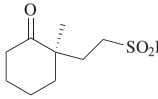


(75) er 92.5:7.5

405



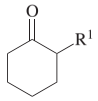
**157a** (20 mol %),
toluene, 90°, 46 h



| R | | er |
|---|---|---|
| Me | (50) | >97.5:2.5 |
| Ph | (65) | 97.0:3.0 |

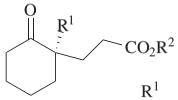
405

$C_{7-8}$





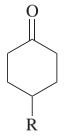
**131** (20 mol %),
toluene, 90°

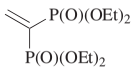


405

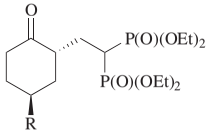
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Me | 46 | (91) | 99.0:1.0 |
| Me | Bn | 48 | (95) | 99.0:1.0 |
| Et | Bn | 48 | (42) | 99.5:0.5 |

$C_{7-12}$



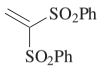


**6** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt

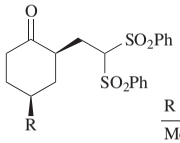


401

| R | Time (h) | | *cis*/*trans* | er (*cis*) | er (*trans*) |
|---|---|---|---|---|---|
| Me | 17 | (86) | 18:82 | 91.5:8.5 | 85.5:14.5 |
| Et | 17 | (72) | 30:70 | 93.0:7.0 | 88.5:11.5 |
| *t*-Bu | 17 | (92) | 30:70 | 94.0:6.0 | 89.0:11.0 |
| Ph | 7 | (78) | 8:92 | 81.0:19.0 | 88.0:12.0 |



**225a** (20 mol %),
$PhCO_2H$ (20 mol %),
$CHCl_3$, 0°, 2 h



403

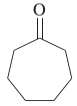
| R | | dr | er |
|---|---|---|---|
| Me | (84) | 5:1 | 98.0:2.0 |
| $EtO_2C$ | (85) | 5:1 | 94.0:6.0 |
| *n*-Pr | (90) | 4:1 | 97.0:3.0 |
| *t*-Bu | (93) | 3:1 | 97.5:2.5 |
| *n*-$C_5H_{11}$ | (78) | 2.5:1 | 95.0:5.0 |
| Ph | (92) | 6:1 | 98.5:1.5 |

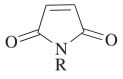
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

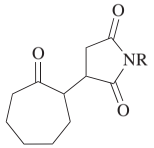
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_7$





**150a** (10 mol %), $PhCO_2H$ (10 mol %), 1 M in toluene, rt

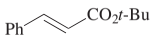


392

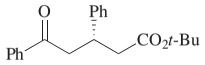
| R | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| Ph | 72 | (93) | 2:1 | 98.0:2.0 | 96.0:4.0 |
| 4-$CF_3C_6H_4$ | 120 | (93) | 2:1 | 99.5:0.5 | 98.0:2.0 |

$C_8$



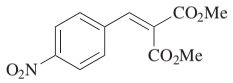


**159** (1 mol %), MeOH, 0° to rt, 6 h

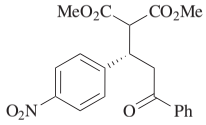


(82) er 98.5:1.5

407



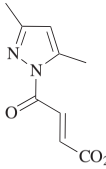
**156** (20 mol %), neat, rt, 2–5 d



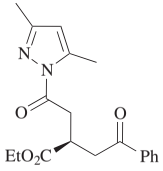
(75) er 60.0:40.0

402





**158** (11 mol %), $Cu(OTf)_2$ (10 mol %), MeCN, rt, 44.5 h

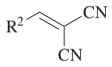


(70) er 98.0:2.0

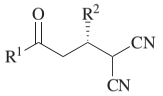
408

$C_{8-12}$





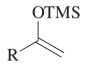
**80b** (20 mol %),
PTSA (40 mol %), THF, 45°

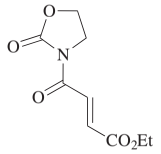


409

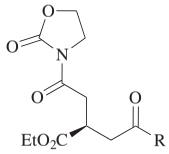
| $R^1$ | $R^2$ | Time (d) | | er |
|---|---|---|---|---|
| Ph | Ph | 6 | (73) | 85.5:14.5 |
| 3-$BrC_6H_4$ | Ph | 4 | (79) | 89.0:11.0 |
| 4-$BrC_6H_4$ | Ph | 6 | (69) | 90.5:9.5 |
| 4-$BrC_6H_4$ | 4-$FC_6H_4$ | 6 | (65) | 90.0:10.0 |
| 4-$BrC_6H_4$ | 4-$MeOC_6H_4$ | 6 | (69) | 85.5:14.5 |
| 4-$BrC_6H_4$ | 4-$O_2NC_6H_4$ | 6 | (75) | 92.0:8.0 |
| 4-$ClC_6H_4$ | Ph | 6 | (72) | 89.0:11.0 |
| 4-$FC_6H_4$ | Ph | 6 | (72) | 87.5:12.5 |
| 4-$MeOC_6H_4$ | Ph | 4 | (76) | 85.5:14.5 |
| 4-$O_2NC_6H_4$ | Ph | 6 | (85) | 86.0:14.0 |
| 4-$MeC_6H_4$ | Ph | 6 | (77) | 87.0:13.0 |
| 2-Np | 4-$O_2NC_6H_4$ | 6 | (48) | 86.0:14.0 |

$C_8$





**151** (10 mol %),
$CH_2Cl_2$, –78°, 4 d



55

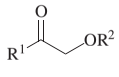
| R | | er |
|---|---|---|
| *c*-$C_6H_{11}$ | (31) | 99.0:1.0 |
| Ph | (54) | 99.5:0.5 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

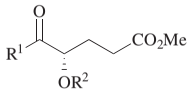
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_8$



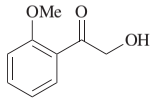


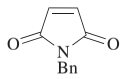
**138** (20 mol %),
0.3 M CsOH•$H_2O$, THF



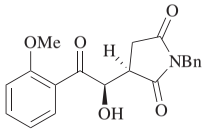
384

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | $Ph_2CH$ | –40 | 0.5 | (56) | 74.0:26.0 |
| 2-$MeOC_6H_4$ | $Ph_2CH$ | –40 | 1.5 | (65) | 86.0:14.0 |
| 4-$MeOC_6H_4$ | $Ph_2CH$ | –40 | 4.5 | (60) | 84.5:15.5 |
| 2,4-$(MeO)_2C_6H_3$ | $Ph_2CH$ | –40 | 6 | (51) | 82.5:17.5 |
| 2,5-$(MeO)_2C_6H_3$ | Bn | –40 | 5.5 | (52) | 91.5:9.5 |
| 2,5-$(MeO)_2C_6H_3$ | $Ph_2CH$ | –40 | 1.5 | (54) | 91.0:9.0 |
| 2,5-$(MeO)_2C_6H_3$ | $Ph_2CH$ | –20 | 0.75 | (62) | 89.0:11.0 |
| 2,5-$(MeO)_2C_6H_3$ | $Ph_2CH$ | 0 | 0.24 | (70) | 82.0:18.0 |



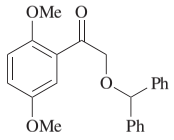


**139** (1 mol %),
$Et_2Zn$ (4 mol %),
THF, 3 Å MS, –20°, 18 h



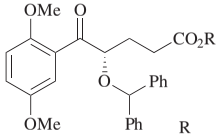
(84) dr 94:6
er >99.5:0.5

48





**138** (20 mol %),
50% of KOH,
THF/toluene (7:3), –40°

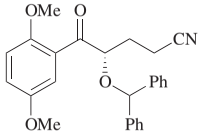


384

| R | Time (h) | | er |
|---|---|---|---|
| Me | 7 | (75) | 93.5:6.5 |
| Et | 6 | (68) | 91.0:9.0 |
| *t*-Bu | 24 | (63) | 89.0:11.0 |

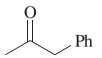


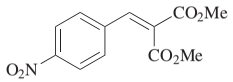
**138** (20 mol %), 50% of KOH, THF, –40°, 6 h



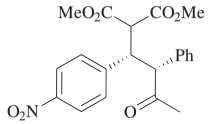
(25) er 95.0:5.0 384

$C_9$

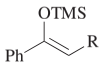


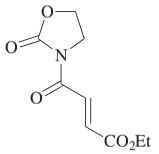


**149** (30 mol %), $Zn(SbF_6)_2$ (15 mol %), HFIP (1 eq), THF, rt

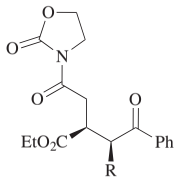


(20) 394





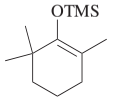
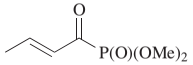
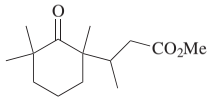
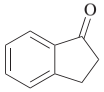
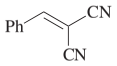
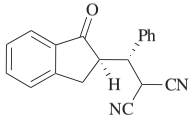
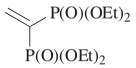
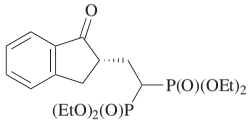
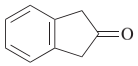
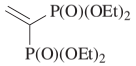
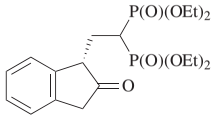
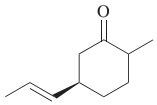
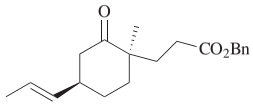
**151** (10 mol %), additive, $CH_2Cl_2$

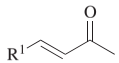


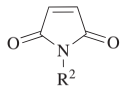
55

| R | Additive | Temp (°) | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|---|---|
| Me | none | –40 | 96 | (95) | 99:1 | 98.0:2.0 |
| Me | HFIP | –40 | 3 | (94) | 99:1 | 98.0:2.0 |
| Me | HFIP | –20 | 1.5 | (95) | 97:3 | 97.5:2.5 |
| Me | HFIP | –5 | 1.2 | (94) | 97:3 | 97.0:3.0 |
| Me | HFIP | 0 | 0.17 | (99) | 95:5 | 96.0:4.0 |
| Et | HFIP | 0 | 0.33 | (99) | 99:1 | 97.0:3.0 |
| *i*-Pr | HFIP | 0 | 1 | (99) | 99:1 | 97.0:3.0 |

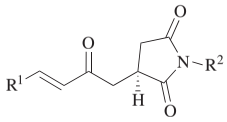
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_9$ | | | | |
|  |  | 1. **161** (10 mol %), $CH_2Cl_2$, rt<br>2. TBAF/MeOH |  (54) dr >30:1<br>er 90.0:10.0 | 410 |
|  |  | **80b** (20 mol %), PTSA (40 mol %), THF, 45°, 3 d |  (60) dr 17:1<br>er 90.5:9.5 | 409 |
| |  | **6** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt |  (92) | 401 |
|  |  | **6** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$ |  (70) | 401 |
| $C_{10}$ | | | | |
|  |  | **131** (20 mol %), toluene, 90°, 48 h |  (96) dr >97.5:2.5 | 405 |





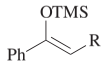
**150b** (20 mol %), $PhCO_2H$ (20 mol %), toluene, 50°

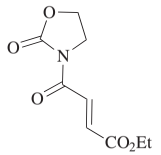


392

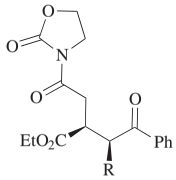
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Ph | (72) | 97.0:3.0 |
| Ph | 4-$ClC_6H_4$ | (62) | 99.0:1.0 |
| Ph | 4-$MeC_6H_4$ | (76) | 97.5:2.5 |
| 2-$FC_6H_4$ | Ph | (63) | 98.5:1.5 |
| 4-$BrC_6H_4$ | 4-$ClC_6H_4$ | (72) | 95.5:4.5 |

$C_{10-11}$





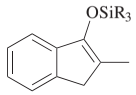
**151** (10 mol %), HFIP (1 eq), $CH_2Cl_2$

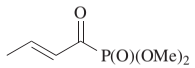


54

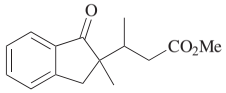
| R | Temp (°) | Time (min) | | *anti*/*syn* | er |
|---|---|---|---|---|---|
| Et | –78 | 120 | (89) | 95:5 | 95.0:5.0 |
| Et | 0 | 20 | (99) | >99:1 | 97.0:3.0 |
| *i*-Pr | 0 | 60 | (99) | >99:1 | 97.0:3.0 |

$C_{10}$





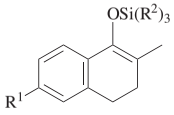
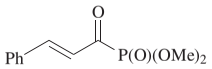
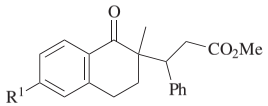
1. **161** (10 mol %), $CH_2Cl_2$
2. TBAF/MeOH



410

| R | Temp | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| Me | rt | (84) | 1.7:1 | 99.5:0.5 | 89.5:10.5 |
| EtO | 0° | (84) | 3.4:1 | 99.5:0.5 | 86.0:14.0 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{11}$  |  | 1. **161** (10 mol %), $CH_2Cl_2$<br>2. TBAF/MeOH |  | 410 |

| $R^1$ | $R^2$ | Temp | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| H | Me | rt | (59) | 6:1 | 98.0:2.0 | 75.0:25.0 |
| H | EtO | 0° | (56) | 30:1 | 99.5:0.5 | 91.5:8.5 |
| BzO | Me | rt | (87) | 7:1 | 98.0:2.0 | 90.5:9.5 |

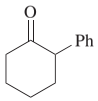
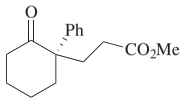
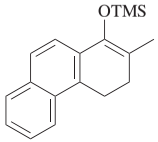
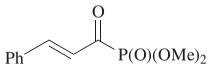
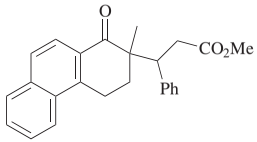
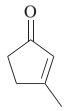
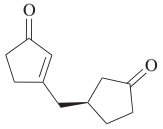
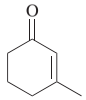
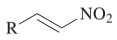
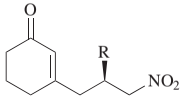
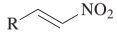
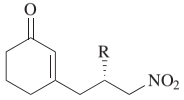
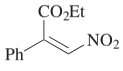
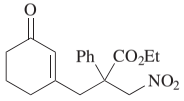
| | | | | | |
|---|---|---|---|---|---|
| $C_{12}$  |  | **144a** (5.6 mol %), 50% of NaOH, toluene, 20° |  | (13) er 60.0:40.0 | 386 |
| $C_{15}$  |  | 1. **161** (10 mol %), $CH_2Cl_2$, rt<br>2. TBAF/MeOH |  | (97) dr 8:1<br>er 98.0:2.0 (major)<br>er 79.0:21.0 (minor) | 410 |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS *(Continued)*
E. VINYLOGOUS REACTIONS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_6$  |  | **144b** (25 mol %), 50% of KOH, toluene, 4 d |  (15) er 92.5:7.5 | 382 |
| $C_7$  |  | **80c** (10 mol %), 2-$FC_6H_4CO_2H$ (20 mol %), 0.2 M in toluene, 40°, 48 h |  | 145 |
| |  | **225b** (10 mol %), 2-$FC_6H_4CO_2H$ (20 mol %), 0.2 M in toluene, 40°, 48 h |  | 145 |
| |  | **225b** (10 mol %), 2-$FC_6H_4CO_2H$ (20 mol %), 0.2 M in toluene, 40°, 96 h |  (58) er 95.0:5.0 | 145 |

| R | | er |
|---|---|---|
| Ph | (55) | 97.5:2.5 |
| 2-$BnOC_6H_4$ | (68) | 98.0:2.0 |

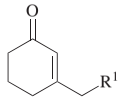
| R | | er |
|---|---|---|
| 2-$C_4H_3S$ | (68) | 99.0:1.0 |
| Ph | (77) | 99.0:1.0 |
| 4-$BrC_6H_4$ | (73) | 98.5:1.5 |
| 2-$ClC_6H_4$ | (84) | 98.0:2.0 |
| 2-$FC_6H_4$ | (83) | 98.5:1.5 |
| 4-$MeOC_6H_4$ | (70) | 98.5:1.5 |
| 2-$BnOC_6H_4$ | (87) | 98.5:1.5 |
| 4-$MeC_6H_4$ | (70) | 99.0:1.0 |

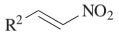
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

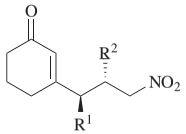
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{8-14}$





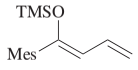
**225b** (20 mol %),
2-$R^3C_6H_4CO_2H$ (*x* mol %),
0.2 M in toluene, rt, 48 h

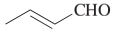


145

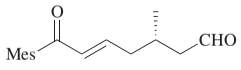
| $R^1$ | $R^2$ | $R^3$ | *x* | | dr | er |
|---|---|---|---|---|---|---|
| Me | 2-$C_4H_3S$ | HO | 40 | (90) | 3.3:1 | 97.0:3.0 |
| Me | Ph | F | 30 | (72) | 9:1 | 96.0:4.0 |
| Me | Ph | HO | 40 | (80) | 6:1 | 97.0:3.0 |
| Me | 4-$BrC_6H_4$ | HO | 40 | (81) | 5:1 | 96.5:3.5 |
| Me | 2-$FC_6H_4$ | HO | 40 | (80) | 6:1 | 95.0:5.0 |
| Me | 4-$MeOC_6H_4$ | F | 30 | (78) | 10:1 | 97.0:3.0 |
| Me | 4-$O_2NC_6H_4$ | HO | 40 | (65) | 3:1 | 97.5:2.5 |
| Me | 4-$MeC_6H_4$ | F | 30 | (76) | 10:1 | 96.0:4.0 |
| *n*-Pr | Ph | HO | 40 | (86) | 11.5:1 | 97.5:2.5 |
| *n*-Pr | 4-$BrC_6H_4$ | HO | 40 | (50) | 10:1 | 97.0:3.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | HO | 40 | (72) | 13.5:1 | 95.5:4.5 |
| allyl | Ph | HO | 40 | (44) | 11.5:1 | 97.0:3.0 |
| Ph | Ph | HO | 40 | (86) | 2:1 | 95.0:5.0 |
| Bn | Ph | HO | 40 | (65) | 7:1 | 92.5:7.5 |

$C_{13}$



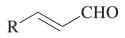


**145b** (20 mol %),
$PhCO_2H$ (20 mol %),
EtOH, rt, 48 h

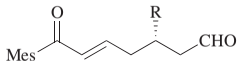


(50) er 85.5:14.5

411



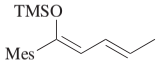
**145b** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (20 mol %), toluene/$H_2O$ (10:1), rt

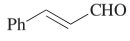


| R | Time (h) | | er |
|---|---|---|---|
| $PhMe_2Si$ | 28 | (90) | >99.5:0.5 |
| 2-$C_4H_3S$ | 34 | (72) | 99.5:0.5 |
| Ph | 48 | (74) | 99.5:0.5 |
| 4-$BrC_6H_4$ | 38 | (76) | 99.0:1.0 |
| 4-$ClC_6H_4$ | 33 | (77) | 99.5:0.5 |
| 3-$MeOC_6H_4$ | 38 | (76) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 36 | (70) | 99.5:0.5 |
| 2-$O_2NC_6H_4$ | 36 | (72) | 99.5:0.5 |
| 4-$O_2NC_6H_4$ | 36 | (73) | 99.5:0.5 |
| 2-$MeC_6H_4$ | 48 | (72) | 99.5:0.5 |

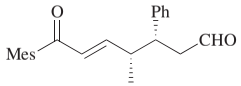
411

$C_{14}$





**145b** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (20 mol %), EtOH, rt, 45 h



(65) *syn*/*anti* = 77:23, er 98.0:2.0

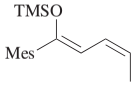
411

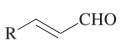
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

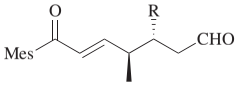
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{14}$



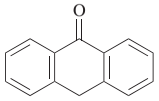



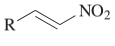

**145b** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (20 mol %), toluene/$H_2O$ (10:1), rt



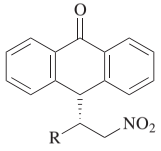

411

| R | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 40 | (70) | 89:11 | 99.5:0.5 |
| Ph | 48 | (77) | 92:8 | 99.5:0.5 |
| 4-$BrC_6H_4$ | 40 | (74) | 89:11 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 40 | (73) | 86:14 | 99.5:0.5 |
| 3-$MeOC_6H_4$ | 42 | (74) | 84:16 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 38 | (69) | 88:12 | 99.5:0.5 |
| 2-$O_2NC_6H_4$ | 40 | (78) | 82:18 | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | 38 | (80) | 82:18 | 98.0:2.0 |
| 2-$MeC_6H_4$ | 48 | (73) | 88:12 | 99.5:0.5 |
| 3-$MeC_6H_4$ | 48 | (75) | 87:13 | 99.5:0.5 |

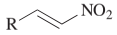


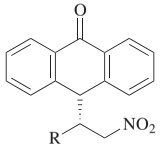

**163** (5 mol %), $CH_2Cl_2$, –40°, 12 h




| R | | er | Refs. |
|---|---|---|---|
| *n*-Pr | (91) | 95.5:4.5 | 412 |
| 2-$C_4H_3O$ | (93) | 97.5:2.5 | |
| Ph | (94) | 98.0:2.0 | |
| 4-$BrC_6H_4$ | (99) | 97.0:3.0 | |
| 2-$ClC_6H_4$ | (99) | 98.5:1.5 | |
| 4-$ClC_6H_4$ | (98) | 98.5:1.5 | |
| 2,4-$Cl_2C_6H_3$ | (99) | 99.5:0.5 | |
| 3-$FC_6H_4$ | (99) | 99.0:1.0 | |
| 4-$FC_6H_4$ | (99) | 98.0:2.0 | |
| 4-$MeOC_6H_4$ | (98) | 95.5:4.5 | |
| 4-$O_2NC_6H_4$ | (96) | 99.5:0.5 | |
| PhCH=CH | (96) | 90.0:10.0 | |
| 1-Np | (94) | 99.0:1.0 | |

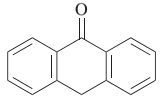
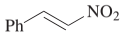
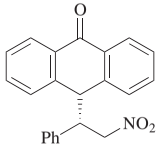
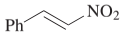
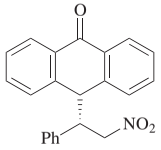
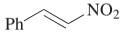
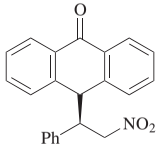
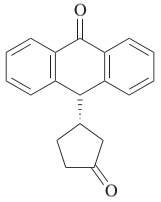


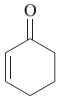
**164b** (10 mol %),
toluene, –10°, 36 h



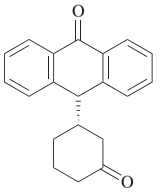
| R | | er | |
|---|---|---|---|
| *i*-Pr | (49) | 92.0:8.0 | 413 |
| *i*-Bu | (80) | 93.0:7.0 | |
| 2-$C_4H_3O$ | (97) | 95.0:5.0 | |
| 2-$C_4H_3S$ | (84) | 95.5:4.5 | |
| *c*-$C_6H_{11}$ | (57) | 92.5:7.5 | |
| Ph | (88) | 96.5:3.5 | |
| 2-$BrC_6H_4$ | (95) | 91.5:8.5 | |
| 3-$BrC_6H_4$ | (65) | 95.0:5.0 | |
| 4-$BrC_6H_4$ | (83) | 95.5:4.5 | |
| 2-$ClC_6H_4$ | (96) | 92.0:8.0 | |
| 4-$ClC_6H_4$ | (93) | 96.5:3.5 | |
| 2,4-$Cl_2C_6H_3$ | (92) | 90.5:9.5 | |
| 3-$FC_6H_4$ | (80) | 95.0:5.0 | |
| 4-$FC_6H_4$ | (90) | 97.0:3.0 | |
| 2-$MeOC_6H_4$ | (89) | 94.5:5.5 | |
| 4-$MeOC_6H_4$ | (94) | 93.0:7.0 | |
| 2-$O_2NC_6H_4$ | (91) | 95.0:5.0 | |
| 3-$O_2NC_6H_4$ | (60) | 95.0:5.0 | |
| 4-$O_2NC_6H_4$ | (77) | 90.0:10.0 | |
| 3-$MeC_6H_4$ | (87) | 95.5:4.5 | |
| 4-$MeC_6H_4$ | (97) | 92.5:7.5 | |
| 3-$CF_3C_6H_4$ | (65) | 95.0:5.0 | |
| 4-$NCC_6H_4$ | (82) | 95.5:4.5 | |
| 1-Np | (90) | 80.0:20.0 | |

TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

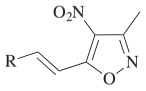
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_{14}$ | | | | |
|  |  | **61** (10 mol %), $PhCO_2H$ (10 mol %), brine, rt, 10 h |  | (94) er 92.0:8.0 | 297 |
| |  | **165** (10 mol %), THF, rt, 24 h |  | (54) er 62.5:37.5 | 414 |
| |  | *ent*-**164b** (5 mol %), $CO_2$ (l), 100 bar, rt, 24 h |  | (65) er 88.0:12.0 | 415 |
| |  | **69a** (10 mol %), toluene, rt, 72 h |  | (85) er 89.0:11.0 | 416 |



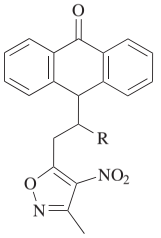
**69a** (10 mol %),
toluene, rt, 72 h



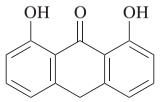
(91) er 72.0:28.0 416

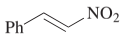


**164a** (10 mol %),
$CH_2Cl_2$, –20°, 24 h

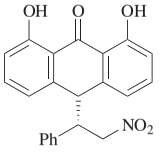


| R | | er | |
|---|---|---|---|
| *c*-$C_3H_5$ | (85) | 96.5:3.5 | |
| 2-$C_4H_3O$ | (99) | 98.0:2.0 | |
| 2-$C_4H_3S$ | (93) | 97.0:3.0 | 417 |
| Ph | (99) | 98.0:2.0 | |
| 2-$BrC_6H_4$ | (99) | 97.0:3.0 | |
| 3-$BrC_6H_4$ | (99) | 97.0:3.0 | |
| 4-$BrC_6H_4$ | (82) | 96.0:4.0 | |
| 2-$ClC_6H_4$ | (87) | 92.0:8.0 | |
| 3-$ClC_6H_4$ | (99) | 94.5:5.5 | |
| 4-$ClC_6H_4$ | (99) | 94.5:5.5 | |
| 4-$MeOC_6H_4$ | (69) | 96.0:4.0 | |
| 3-$MeC_6H_4$ | (73) | 97.5:2.5 | |
| 4-$MeC_6H_4$ | (73) | 96.5:3.5 | |
| 1-Np | (57) | 86.0:14.0 | |





**163** (5 mol %),
$CH_2Cl_2$, –40°, 12 h



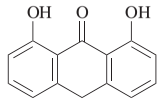
(99) er 54.5:45.5 412

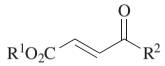
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

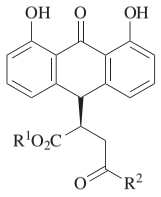
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{14}$



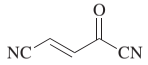


**160c** (10 mol %), $CH_2Cl_2$, –20°

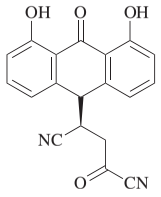


| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Me | 6 | (92) | 99.0:1.0 |
| Et | Ph | 7 | (92) | 97.5:2.5 |

418

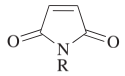


**160c** (10 mol %), $CH_2Cl_2$, –20°, 7 h

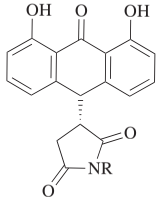


(90) er 97.0:3.0

418

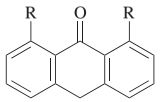


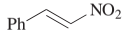
**160c** (10 mol %), $CH_2Cl_2$, –20°



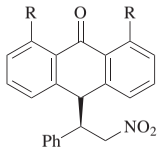
| R | Time (h) | | er |
|---|---|---|---|
| Ph | 7 | (80) | 99.5:0.5 |
| 3,4-$Cl_2C_6H_3$ | 8 | (89) | 99.0:1.0 |
| 2-$O_2NC_6H_4$ | 8 | (87) | 98.5:1.5 |
| Bn | 8 | (86) | 96.5:3.5 |

418

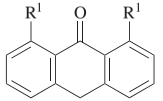


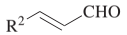


*ent*-**164b** (10 mol %),
toluene, rt, 14 h

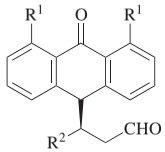


| R | | er | |
|---|---|---|---|
| H | (92) | 94.5:5.5 | 419 |
| HO | (77) | 67.5:32.5 | |





**145b** (10 mol %),
toluene, –40°



420

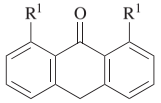
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| H | Me | 10 | (95) | 97.0:3.0 |
| H | Et | 10 | (82) | 98.0:2.0 |
| H | *n*-Pr | 10 | (84) | 98.0:2.0 |
| H | *n*-Bu | 10 | (92) | 93.0:7.0 |
| H | Ph | 36 | (88) | 90.0:10.0 |
| H | 2-$BrC_6H_4$ | 53 | (32) | 51.5:48.5 |
| H | 2-$O_2NC_6H_4$ | 53 | (35) | 53.5:46.5 |
| H | 4-$O_2NC_6H_4$ | 36 | (75) | 89.0:11.0 |
| H | 4-$NCC_6H_4$ | 5 | (85) | 99.5:0.5 |
| HO | Me | 10 | (88) | 98.5:1.5 |
| HO | Et | 10 | (95) | 99.5:0.5 |
| HO | *n*-Pr | 10 | (93) | 99.5:0.5 |
| HO | *n*-Bu | 10 | (92) | 99.5:0.5 |

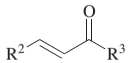
TABLE 1. KETONES, SILYL ENOL ETHERS, AND ENAMINES AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

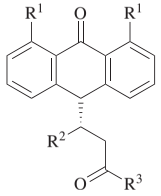
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{14}$



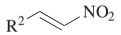


**69a** (10 mol %), toluene, rt, 72 h

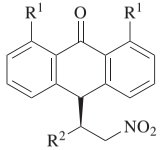


416

| $R^1$ | $R^2$ | $R^3$ | | er |
|---|---|---|---|---|
| H | Ph | Me | (95) | 93.0:7.0 |
| H | Ph | Et | (81) | 85.0:15.0 |
| H | 2-$BrC_6H_4$ | Me | (97) | 95.5:4.5 |
| H | 3-$BrC_6H_4$ | Me | (98) | 95.5:4.5 |
| H | 4-$BrC_6H_4$ | Me | (88) | 95.0:5.0 |
| H | 2-$ClC_6H_4$ | Me | (98) | 95.5:4.5 |
| H | 3-$ClC_6H_4$ | Me | (97) | 95.5:4.5 |
| H | 4-$ClC_6H_4$ | Me | (97) | 95.5:4.5 |
| H | 2-$FC_6H_4$ | Me | (97) | 95.0:5.0 |
| H | 3-$FC_6H_4$ | Me | (97) | 93.0:7.0 |
| H | 4-$FC_6H_4$ | Me | (74) | 93.5:6.5 |
| H | 2-$MeOC_6H_4$ | Me | (90) | 95.0:5.0 |
| H | 3-$MeOC_6H_4$ | Me | (80) | 95.5:4.5 |
| H | 4-$MeOC_6H_4$ | Me | (85) | 95.0:5.0 |
| H | 2-$MeC_6H_4$ | Me | (83) | 96.5:3.5 |
| H | 3-$MeC_6H_4$ | Me | (97) | 95.0:5.0 |
| H | 4-$MeC_6H_4$ | Me | (83) | 92.0:8.0 |
| Cl | Ph | Me | (92) | 95.5:4.5 |
| HO | 4-$BrC_6H_4$ | Me | (83) | 78.5:21.5 |

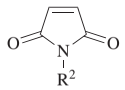


*ent*-**164b** (10 mol %), toluene, 14 h

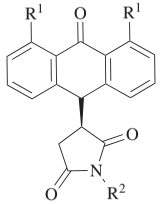


420

| $R^1$ | $R^2$ | Temp | | er |
|---|---|---|---|---|
| H | Ph | rt | (92) | 94.5:5.5 |
| H | 2-$FC_6H_4$ | rt | (95) | 96.0:4.0 |
| H | 4-$MeOC_6H_4$ | rt | (94) | 95.0:5.0 |
| H | 4-$O_2NC_6H_4$ | rt | (91) | 92.5:7.5 |
| H | 4-$MeC_6H_4$ | rt | (92) | 95.0:5.0 |
| HO | Ph | –40° | (77) | 68.0:32.0 |
| HO | 2-$FC_6H_4$ | –40° | (89) | 60.5:39.5 |
| HO | 4-$MeOC_6H_4$ | –40° | (70) | 70.0:30.0 |
| HO | 4-$O_2NC_6H_4$ | –40° | (87) | 56.5:43.5 |
| HO | 4-$MeC_6H_4$ | –40° | (85) | 69.0:31.0 |

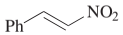
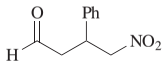
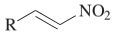
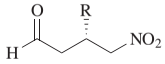


*ent*-**164b** (10 mol %), toluene, rt, 14 h

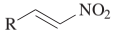
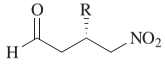


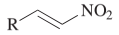
| $R^1$ | $R^2$ | | er | |
|---|---|---|---|---|
| H | 4-$CF_3C_6H_4$ | (94) | 98.5:1.5 | 419, 420 |
| HO | Ph | (93) | 99.5:0.5 | 419, 420 |
| HO | 4-$BrC_6H_4$ | (91) | 98.0:2.0 | 419, 420 |
| HO | 3-$ClC_6H_4$ | (92) | 61.0:39.0 | 420 |
| HO | 4-$MeOC_6H_4$ | (94) | 98.5:1.5 | 419, 420 |
| HO | Bn | (92) | 92.5:7.5 | 419, 420 |
| HO | $Ph_2CH$ | (78) | — | 420 |

TABLE 2. ALDEHYDES AS DONORS
A. NITROALKENES AS ACCEPTORS

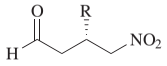
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.* | | | | |
| $C_2$ | | | | |
|  |  | **81** (20 mol %), 2-$MeC_6H_4CO_2H$ (20 mol %), *n*-hexane, rt, 48 h |  (93) er 61.5:38.5 | 319 |
| |  | **145b** (10 mol %), 1,4-dioxane, rt |  | 123 |

| R | Time (h) | | er |
|---|---|---|---|
| *n*-Bu | 36 | (54) | 99.5:0.5 |
| *i*-Bu | 72 | (61) | >99.5:0.5 |
| 2-$C_4H_3O$ | 48 | (72) | 98.5:1.5 |
| Ph | 18 | (75) | 98.0:2.0 |
| 4-$BrC_6H_4$ | 18 | (73) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 36 | (75) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 27 | (69) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 42 | (72) | 97.5:2.5 |
| 4-$CF_3C_6H_4$ | 24 | (77) | 96.5:3.5 |
| 2-Np | 28 | (70) | 96.0:4.0 |

| | | | | |
|---|---|---|---|---|
|  | **145b** (20 mol %), *i*-PrOH (10 eq), DMF, rt, 24–40 h |  | R (38) er<br>Me (38) 94.0:6.0<br>*i*-Bu (52) 97.0:3.0<br>*t*-Bu (41) 97.0:3.0<br>*c*-$C_6H_{11}$ (61) 96.0:4.0<br>$BnCH_2$ (56) 96.0:4.0 | 122 |

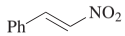


**145b** (20 mol %), MeCN, 0°, 62–93 h

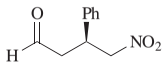


| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (49) | 95.0:5.0 |
| Ph | (51) | 96.0:4.0 |
| 4-$BrC_6H_4$ | (53) | 95.0:5.0 |
| 2-$ClC_6H_4$ | (57) | 95.0:5.0 |
| 3-$ClC_6H_4$ | (51) | 96.0:4.0 |
| 4-$ClC_6H_4$ | (58) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | (44) | 96.0:4.0 |
| 3-(*c*-$C_5H_9$)O-4-$MeOC_6H_3$ | (50) | 94.0:6.0 |

122

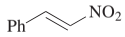


**166** (10 mol %), $CH_2Cl_2$, rt, 72 h

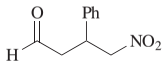


(44) er 98.0:2.0

421



**167** (10 mol %), $CH_2Cl_2$, rt, 48 h



(58) er 50.0:50.0

422

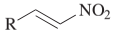
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

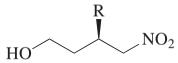
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_2$



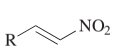


1. **168a** (10 mol %), $PhCO_2H$ (10 mol %), brine, rt
2. $NaBH_4$, MeOH

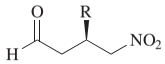


423

| R | Temp | Time (h) | | er |
|---|---|---|---|---|
| *n*-Bu | rt | 72 | (34) | 94.0:6.0 |
| 2-$C_4H_3O$ | rt | 72 | (43) | 92.0:8.0 |
| Ph | 4° | 72 | (57) | 95.5:4.5 |
| 2-$BrC_6H_4$ | rt | 22 | (41) | 91.0:9.0 |
| 4-$ClC_6H_4$ | rt | 36 | (40) | 92.5:7.5 |
| 3-$MeOC_6H_4$ | rt | 60 | (56) | 92.0:8.0 |
| 4-$MeOC_6H_4$ | rt | 72 | (61) | 90.0:10.0 |
| 3,4-$(OCH_2O)C_6H_3$ | rt | 96 | (40) | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | rt | 96 | (42) | 94.0:6.0 |
| 4-$MeC_6H_4$ | rt | 60 | (42) | 92.0:8.0 |
| $BnCH_2$ | rt | 72 | (30) | 98.5:1.5 |

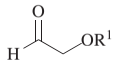


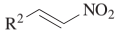
**177** (0.7 mol %), pH 7.3 $Na_2HPO_4$, EtOH, $H_2O$, 22°, 3 h



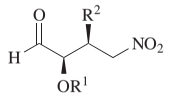
424, 425

| R | | er |
|---|---|---|
| Ph | (46) | 94.5:5.5 |
| 4-$HOC_6H_4$ | (65) | 75.5:24.5 |





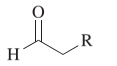
**145b** (10 mol %),
toluene, rt, 96 h

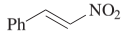


426

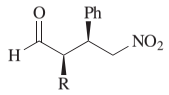
| $R^1$ | $R^2$ | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| $CF_3CH_2$ | Ph | (55) | 56:44 | 97.0:3.0 | 97.0:3.0 |
| TBS | Ph | (43) | 59:41 | 92.0:8.0 | 92.0:8.0 |
| Ph | Ph | (58) | 61:39 | 98.0:2.0 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Ph | (73) | 54:46 | 97.0:3.0 | 97.0:3.0 |
| Bn | $EtO_2C$ | (88) | 71:29 | 97.5:2.5 | 96.5:3.5 |
| Bn | *i*-Pr | (30) | 79:21 | 91.0:9.0 | 96.5:3.5 |
| Bn | 2-$C_4H_3S$ | (88) | 60:40 | 96.5:3.5 | 95.5:4.5 |
| Bn | 4-$ClC_6H_4$ | (95) | 54:46 | 98.0:2.0 | 97.5:2.5 |
| Bn | 4-$CF_3C_6H_4$ | (51) | 63:37 | 98.0:2.0 | 96.5:4.5 |
| Bn | ferrocenyl | (14) | 56:44 | — | — |

$C_{2-9}$





**145b** (5 mol %),
additive, toluene, rt



66

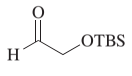
| R | Additive | Time (h) | | dr | er |
|---|---|---|---|---|---|
| BnO | none | 312 | (50) | 1:1 | — |
| BnO | 4-$O_2NC_6H_4OH$ | 55 | (65) | 1:1 | — |
| *i*-Pr | none | 336 | (77) | 15:1 | — |
| *i*-Pr | 4-$O_2NC_6H_4OH$ | 20 | (95) | 14:1 | 99.5:0.5 |
| Bn | none | 18 | (90) | 8:1 | 99.5:0.5 |
| Bn | 4-$O_2NC_6H_4OH$ | 6 | (90) | 11:1 | 99.5:0.5 |

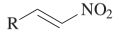
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

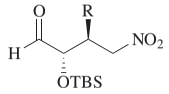
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_2$

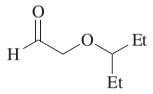


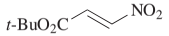


*ent*-**164b** (*x* mol %), 1 M in $CH_2Cl_2$, rt

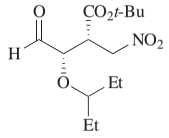


| R | *x* | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3S$ | 20 | 6 | (75) | 97:3 | 98.5:1.5 |
| Ph | 20 | 4 | (83) | 98:2 | 99.0:1.0 |
| 3-$BrC_6H_4$ | 20 | 6 | (66) | 96:4 | 98.5:1.5 |
| 4-$BrC_6H_4$ | 20 | 6 | (70) | 97:3 | 99.0:1.0 |
| 2,6-$Cl_2C_6H_3$ | 50 | 24 | (68) | 98:2 | 99.0:1.0 |
| 3,4-$Cl_2C_6H_3$ | 20 | 2 | (72) | 96:4 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 20 | 24 | (67) | 97:3 | 99.0:1.0 |
| *n*-$C_7H_{15}$ | 50 | 6 | (57) | 92:8 | 98.5:1.5 |
| 4-$MeC_6H_4$ | 20 | 6 | (81) | 97:3 | 98.5:1.5 |
| 2-$CF_3C_6H_4$ | 20 | 24 | (74) | 98:2 | 99.5:0.5 |





**145b** (1 mol %), $ClCH_2CO_2H$ (20 mol %), toluene, rt, 6 h

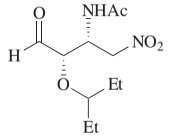


(99) *syn*/*anti* = 7.8:1
er 98.5:1.5

428

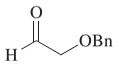
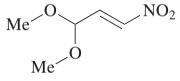


**145b** (10 mol %), *rac*-$PhCH(OH)CO_2H$, $H_2O$, $CHCl_3$, rt

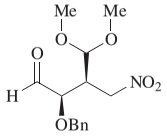


89% conv., *syn*/*anti* = 5.3:1
er (*syn*) 97.5:2.5
er (*anti*) 90.5:9.5

429

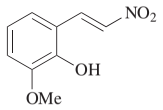



**16a** (10 mol %), *i*-PrOH, 48 h

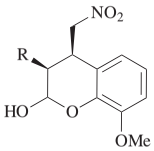


(99) *syn*/*anti* = 1.5:1 — 430

$C_{2\text{-}9}$

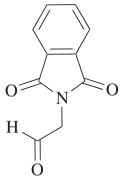
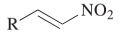
**145b** (20 mol %), $PhCO_2H$ (20 mol %), 0.25 M in $CH_2Cl_2$, rt



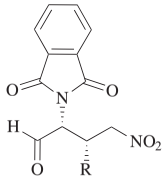
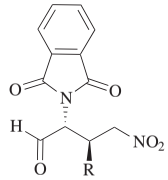
431

| R | Time (h) | | dr | er |
|---|---|---|---|---|
| BnO | 6 | (99) | 70.5:29.5 | 93.5:6.5 |
| *n*-Pr | 6 | (97) | 86.5:13.5 | 99.5:0.5 |
| *n*-Bu | 6 | (95) | 91.5:8.5 | 95.0:5.0 |
| Bn | 9 | (93) | 91.5:8.5 | 99.7:0.4 |

$C_2$

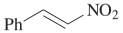
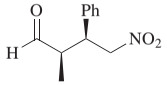
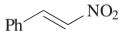
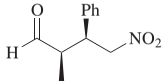
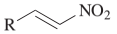
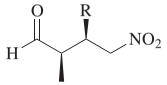
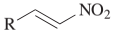
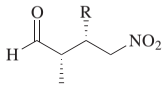
**145a** (20 mol %), **169a** (20 mol %), $CHCl_3$/brine (1:1), rt


+


432

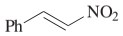
| R | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| Ph | 24 | (—) | 2:1 | 99.0:1.0 | 84.0:16.0 |
| Ph | 48 | (95) | 2:1 | 92.5:7.5 | 84.0:16.0 |
| 4-$BrC_6H_4$ | 4 | (70) | 2:1 | — | — |
| 2,4-$Cl_2C_6H_3$ | 4 | (97) | 2:1 | — | — |
| 3,4-$Cl_2C_6H_3$ | 3 | (92) | 2:1 | 93.0:7.0 | 93.0:7.0 |
| 4-$MeC_6H_4$ | 7 | (99) | 2:1 | — | — |
| 4-$CF_3C_6H_4$ | 1 | (45) | 1:1 | — | — |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

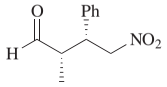
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.* | | | | |
| $C_3$  |  | **1** (15 mol %), [bmim][$BF_4$], rt, 24 h |  (77) *syn*/*anti* = 95:5; er 59.5:40.5 | 433 |
| |  | **1** (10 mol %), **118** (10 mol %), toluene, 0°, 17 h |  (96) *syn*/*anti* = 70:30; er (*syn*) 97.0:3.0; er (*anti*) 97.5:2.5 | 343 |
| |  | **1** (20 mol %), **169b** (5 mol %), benzene, rt |  | 434 |
| |  | **3** (15 mol %), $CHCl_3$ |  | 251 |

| R | | dr | er |
|---|---|---|---|
| Ph | (85) | 12:1 | 88.0:12.0 |
| 4-$BrC_6H_4$ | (80) | 10:1 | 80.0:20.0 |
| 4-$MeOC_6H_4$ | (79) | 11:1 | 80.0:20.0 |

| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| $CF_3$ | rt | 24 | (42) | 77:23 | 95.5:4.5 |
| $(MeO)_2CH$ | –25 | 72 | (73) | 77:23 | 95.5:4.5 |
| *n*-Bu | –25 | 15 | (70) | 90:10 | 96.5:3.5 |
| 2-$C_4H_3S$ | –25 | 48 | (66) | 94:6 | 96.5:3.5 |
| *c*-$C_6H_{11}$ | –25 | 72 | (76) | 85:15 | 98.0:2.0 |
| Ph | –25 | 48 | (71) | 94:6 | 96.5:3.5 |
| Ph | rt | 1.5 | (99) | 75:25 | 88.5:11.5 |
| 4-$MeOC_6H_4$ | –25 | 72 | (64) | 94:6 | 96.5:3.5 |
| 4-$MeC_6H_4$ | –25 | 72 | (88) | 95:5 | 97.0:3.0 |
| 2-$CF_3C_6H_4$ | –25 | 72 | (74) | 92:8 | 97.5:2.5 |

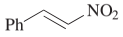


**3** (15 mol %), additive (15 mol %), $CHCl_3$

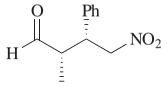


250

| Additive | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| none | –25° | 48 | (71) | 95:5 | 91.5:8.5 |
| none | rt | 0.5 | (99) | 75:25 | 83.0:17.0 |
| HCl | 0° | 48 | (83) | 94:6 | 92.5:7.5 |
| HCl | rt | 3 | (86) | 85:15 | 89.5:11.5 |

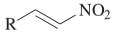


**6** (15 mol %), $CHCl_3$, –25°, 15 h

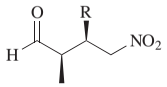


(86) *syn*/*anti* = 94:6, er 80.0:20.0

251

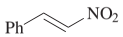


**16b** (20 mol %), solvent, 0°, 24 h

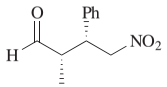


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| R | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|
| TrN-5-$C_3H_2N_2$ | *i*-PrOH/$CH_2Cl_2$ (1:1) | (78) | 20:1 | 99.5:0.5 |
| Ph | *i*-PrOH | (77) | 12:1 | 98.5:1.5 |

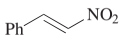


**25** (10 mol %), $Me_2PEG$ (10 mol %), $H_2O$, 4°, 24 h

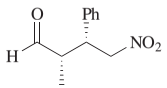


(81) *syn*/*anti* = 96:4, er 81.0:19.0

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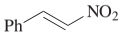
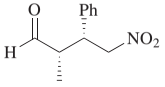
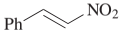
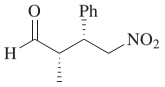
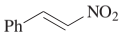
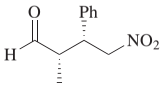
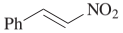
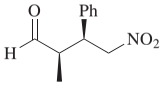
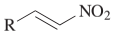
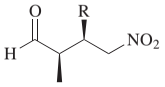
**61** (10 mol %), $PhCO_2H$ (10 mol %), brine, 20°, 12 h



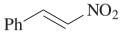
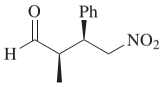
(95) *syn*/*anti* = 92:8, er 91.5:8.5

297

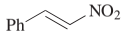
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$  |  | **62** (10 mol %), TFA (2 mol %), neat, rt, 18 h |  (82) *syn*/*anti* = 93:7 er 89.0:11.0 | 298 |
| |  | **65** (5 mol %), MeOH, rt |  (87) *syn*/*anti* = 95:5 er 93.5:6.5 | 301 |
| |  | **68** (30 mol %), $PhCO_2H$ (20 mol %), toluene, rt, 4 d |  (71) *syn*/*anti* = 2:1 er 74.0:26.0 | 279 |
| |  | **75** (20 mol %), $PhCO_2H$ (20 mol %), neat, rt, 1 h |  (93) dr 65:35 er 63.0:37.0 | 315 |
| |  | **79** (*x* mol %), benzene, 2° |  | 267 |

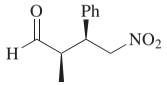
| R | *x* | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|
| *i*-Pr | 10 | 120 | (51) | 72:28 | 87.5:12.5 | 93.5:6.5 |
| Ph | 5 | 40 | (90) | 78:22 | 97.0:3.0 | 99.0:1.0 |
| 4-$BrC_6H_4$ | 5 | 40 | (89) | 78:22 | 95.5:4.5 | 98.5:1.5 |
| 4-$MeC_6H_4$ | 5 | 48 | (91) | 73:27 | 97.0:3.0 | 98.0:2.0 |

| | | | | | | |
|---|---|---|---|---|---|---|
|  | **113** (*x* mol %), $CHCl_3$ |  | | | | 355 |

| *x* | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 10 | –25° | 72 | (81) | 90:10 | 93.5:6.5 |
| 20 | rt | 15 | (84) | 75:25 | 89.5:10.5 |



Catalyst (5 mol %), $CH_2Cl_2$, rt, 48 h

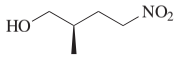


| Catalyst | | *syn*/*anti* | er (*syn*) |
|---|---|---|---|
| **123** | (60) | 59:41 | 68:0:32.0 |
| **124** | (55) | 62:38 | 62.0:38.0 |

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1. **145b** (2 mol %), 3-$O_2NC_6H_4CO_2H$ (20 mol %), toluene, 48 h
2. $NaBH_4$, MeOH, 0°

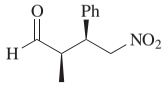


(95) er 99.0:1.0

124

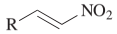


**145b** (10 mol %), hexane, 0°, 48 h

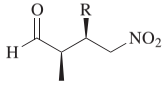


(84) *syn*/*anti* = 96:4, er 99.5:0.5

60



**145b** (*x* mol %), hexane



60

| R | *x* | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 10 | 0 | 5 | (81) | 94:6 | 99.5:0.5 |
| *n*-Bu | 10 | 0 | 25 | (52) | 84:16 | 99.5:0.5 |
| *c*-$C_6H_{11}$ | 20 | rt | 48 | (56) | 96:4 | 99.5:0.5 |
| Ph | 10 | 0 | 5 | (85) | 94:6 | 99.5:0.5 |
| 4-$BrC_6H_4$ | 10 | 0 | 1 | (72) | 95:5 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 10 | 0 | 5 | (80) | 95:5 | 99.5:0.5 |

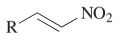
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

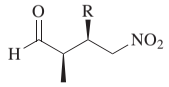
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_3$



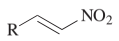


**145b** (5 mol %), toluene, rt

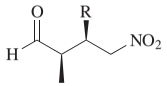


66

| R | Additive | Time (h) | | dr | er |
|---|---|---|---|---|---|
| *t*-$BuO_2C$ | none | 4 | (92) | 7:1 | 99.0:1.0 |
| *t*-$BuO_2C$ | 4-$O_2NC_6H_4OH$ | 0.75 | (90) | 9:1 | 99.0:1.0 |
| *i*-Pr | none | 168 | (79) | 6.5:1 | 99.5:0.5 |
| *i*-Pr | 4-$O_2NC_6H_4OH$ | 12 | (90) | 5:1 | 99.5:0.5 |
| *c*-$C_6H_{11}$ | none | 240 | (43) | 1.5:1 | 98.5:1.5 |
| *c*-$C_6H_{11}$ | 4-$O_2NC_6H_4OH$ | 22 | (85) | 2:1 | 98.5:1.5 |
| Ph | none | 6 | (98) | 15:1 | 99.5:0.5 |
| Ph | 4-$O_2NC_6H_4OH$ | 0.25 | (98) | 15:1 | 99.5:0.5 |
| 4-$BrC_6H_4$ | none | 16 | (90) | 10:1 | 99.5:0.5 |
| 4-$BrC_6H_4$ | 4-$O_2NC_6H_4OH$ | 0.58 | (95) | 14:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | none | 3 | (95) | 7:1 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 4-$O_2NC_6H_4OH$ | 3 | (95) | 5:1 | 97.5:2.5 |
| 3,4-$(OCH_2O)C_6H_3$ | none | 1.5 | (92) | 15:1 | 99.0:1.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 4-$O_2NC_6H_4OH$ | 0.5 | (95) | 15:1 | 99.5:0.5 |
| 4-$CF_3C_6H_4$ | none | 1 | (92) | 9:1 | 98.5:1.5 |
| 4-$CF_3C_6H_4$ | 4-$O_2NC_6H_4OH$ | 0.25 | (90) | 5:1 | 99.5:0.5 |
| $BnCH_2$ | none | 12 | (88) | 3:1 | 98.5:1.5 |
| $BnCH_2$ | 4-$O_2NC_6H_4OH$ | 1.5 | (92) | 5:1 | 99.0:1.0 |



**166** (10 mol %), $CH_2Cl_2$, rt

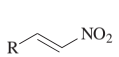


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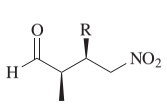
Catalyst Recycling (R = 4-$BrC_6H_4$)

| Run | Time (h) | Conv. (%) | | *syn/anti* | er |
|---|---|---|---|---|---|
| 1 | 6 | >99 | (98) | 93:7 | 99.5:0.5 |
| 2 | 6 | >99 | (96) | 93:7 | 99.5:0.5 |
| 3 | 6 | 96 | (96) | 92:8 | 98.5:1.5 |
| 4 | 6 | 94 | (94) | 92:8 | 98.5:1.5 |
| 5 | 6 | 92 | (92) | 93:7 | 99.0:1.0 |
| 6 | 6 | 89 | (89) | 92:8 | 98.5:1.5 |

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| *i*-Pr | 96 | (84) | 70:30 | 99.5:0.5 |
| 2-$C_4H_3O$ | 4 | (96) | 85:15 | 95.0:5.0 |
| *c*-$C_6H_{11}$ | 64 | (89) | 70:30 | 98.5:1.5 |
| Ph | 7 | (98) | >99:1 | >99.5:0.5 |
| 4-$BrC_6H_4$ | 4 | (98) | 91:9 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 8 | (94) | 89:11 | 99.5:0.5 |
| $BnCH_2$ | 24 | (94) | 81:19 | 97.5:2.5 |



**167** (10 mol %), $CH_2Cl_2$, rt



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Catalyst Recycling (R = Ph)

| Run | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 1 | 22 | (89) | 89:11 | 98.5:1.5 |
| 2 | 48 | (83) | 76:24 | 95.0:5.0 |
| 3 | 48 | (81) | 78:22 | 97.0:3.0 |
| 4 | 48 | (57) | 72:28 | 96.0:4.0 |

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 48 | (74) | 84:16 | 95.5:4.5 |
| 4-$BrC_6H_4$ | 48 | (85) | 80:20 | 97.0:3.0 |
| 2-$MeOC_6H_4$ | 30 | (75) | 85:15 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 24 | (80) | 74:26 | 95.5:4.5 |
| 2,3-$(OCH_2O)C_6H_3$ | 48 | (79) | 75:25 | 95.0:5.0 |
| 4-$MeC_6H_4$ | 48 | (80) | 80:20 | 87.5:12.5 |

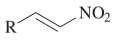
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

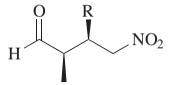
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_3$





**168b** (10 mol %), $CF_3C_6H_5$, rt

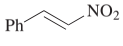


436

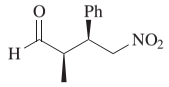
Catalyst Recycling (R = Ph)

| Run | Time (h) | | dr | er |
|---|---|---|---|---|
| 1 | 4 | (89) | 21:1 | >99.5:0.5 |
| 2 | 5 | (86) | 24:1 | >99.5:0.5 |
| 3 | 10 | (90) | 23:1 | >99.5:0.5 |
| 4 | 20 | (90) | 24:1 | >99.5:0.5 |
| 5 | 23 | (89) | 23:1 | >99.5:0.5 |
| 6 | 36 | (86) | 28:1 | >99.5:0.5 |

| R | Time (h) | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 4 | (84) | 5:1 | 98.5:1.5 |
| Ph | 4 | (89) | 21:1 | >99.5:0.5 |
| 4-$BrC_6H_4$ | 2 | (81) | 19:1 | >99.5:0.5 |
| 2-$MeOC_6H_4$ | 12 | (85) | 6:1 | >99.5:0.5 |
| 4-$MeOC_6H_4$ | 5 | (84) | 14:1 | 99.5:0.5 |
| 2-$CF_3C_6H_4$ | 8 | (84) | 29:1 | >99.5:0.5 |
| $BnCH_2$ | 13 | (82) | 18:1 | >99.5:0.5 |

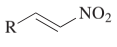


**170** (20 mol %), THF, rt, 3 h

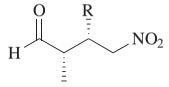


(85) *syn*/*anti* = 90:10
er 78.0:22.0

139, 253

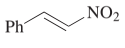


**171** (15 mol %), $CHCl_3$, –3°

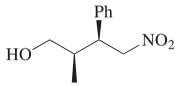


437

| R | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 3 | (89) | 89:11 | 89.5:10.5 |
| *c*-$C_6H_{11}$ | 13 | (23) | 85:15 | 92.5:7.5 |
| Ph | 3 | (86) | 90:10 | 90.0:10.0 |
| 4-$ClC_6H_4$ | 3 | (84) | 80:20 | 87.5:12.5 |
| 4-$MeOC_6H_4$ | 3 | (81) | 84:16 | 89.0:11.0 |

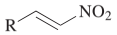


1. **172** (20 mol %),
   $PhCO_2H$ (20 mol %),
   solvent, rt, 20 h
2. $NaBH_4$, EtOH, 0°

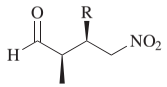


167

| Solvent | | er |
|---|---|---|
| $H_2O$ | (62) | 99.0:1.0 |
| EtOH/$H_2O$ (1:1) | (52) | 96.5:3.5 |

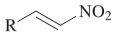


**173** (20 mol %),
DMAP (20 mol %),
*i*-PrOH, 0°

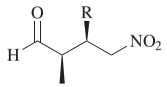


438

| R | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| Ph | 2 | (77) | 80:20 | 97.0:3.0 | — |
| 3-BnO-4-$MeOC_6H_3$ | 48 | (78) | 71:29 | 86.5:13.5 | 79.0:21.0 |



**174** (10 mol %),
$CH_2Cl_2$/hexane, 0°



439

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 41 | (52) | 94:6 | 84.5:15.5 |
| Ph | 17 | (78) | 97:3 | 90.5:9.5 |
| 4-$MeOC_6H_4$ | 40 | (68) | 94:6 | 87.0:13.0 |

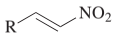
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

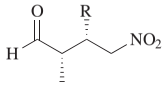
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_3$



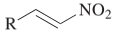


**175** (*x* mol %), NMM (1–5 mol %), $CHCl_3$/*i*-PrOH (9:1)

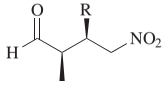


| R | *x* | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| 2-$C_4H_3S$ | 3 | –15° | 84 | (94) | 30:1 | 97.5:2.5 |
| 2-$C_4H_3S$ | 1 | rt | 12 | (84) | 6:1 | 94.0:6.0 |
| *c*-$C_6H_{11}$ | 5 | –15° | 48 | (55) | 4:1 | 99.0:1.0 |
| *c*-$C_6H_{11}$ | 3 | rt | 36 | (88) | 4:1 | 99.0:1.0 |
| Ph | 5 | –15° | 48 | (70) | >99:1 | 98.5:1.5 |
| Ph | 1 | rt | 24 | (98) | 9:1 | 95.5:4.5 |

130

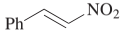


**176** (10 mol %), hexane/benzene, 5°, 7 d

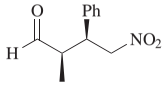


| R | | dr | er |
|---|---|---|---|
| Ph | (87) | 98:2 | 99.5:0.5 |
| 4-$BrC_6H_4$ | (82) | >99:1 | 97.0:3.0 |
| 4-$MeC_6H_4$ | (85) | >99:1 | 94.5:5.5 |

440

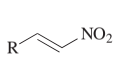


**178** (10 mol %), $CCl_4$, rt, 4 h

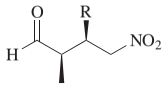


(79) *syn*/*anti* = 91:9
er 99.5:0.5

441

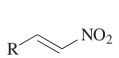


**179** ($x$ mol %), $CH_2Cl_2$

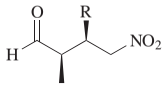


442

| R | $x$ | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 10 | 0 | 16 | (83) | 89:11 | 99.5:0.5 |
| 2-$C_4H_3O$ | 10 | 20 | 12 | (87) | 72:28 | 99.5:0.5 |
| 2-$C_4H_3S$ | 10 | 0 | 15 | (82) | 85:15 | 99.5:0.5 |
| *i*-Bu | 20 | 0 | 48 | (65) | 99:1 | 99.5:0.5 |
| *i*-Bu | 20 | 20 | 36 | (72) | 99:1 | 97.0:3.0 |
| *c*-$C_6H_{11}$ | 20 | 20 | 30 | (81) | 99:1 | 99.5:0.5 |
| Ph | 10 | 0 | 15 | (87) | 95:5 | 99.5:0.5 |
| Ph | 10 | 20 | 8 | (93) | 92:8 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 10 | 0 | 36 | (81) | 93:7 | 99.5:0.5 |
| 2-$MeOC_6H_4$ | 10 | 20 | 2 | (95) | 88:12 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 10 | 20 | 2 | (91) | 90:10 | 99.5:0.5 |
| 1-Np | 20 | 20 | 36 | (65) | 99:1 | 99.5:0.5 |



**180** (1–2 mol %), additive, solvent, rt



443

| R | Additive | Solvent | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *c*-$C_6H_{11}$ | $PhCO_2H$ | $CH_2Cl_2$ | 22 | (66) | 89:11 | 99.5:0.5 |
| Ph | none | $H_2O$ | 2 | (98) | 93:7 | 99.5:0.5 |
| 4-$BrC_6H_4$ | none | $H_2O$ | 4 | (98) | 92:8 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | none | $H_2O$ | 4 | (96) | 91:9 | 99.5:0.5 |

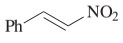
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

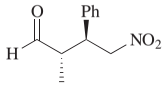
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_3$



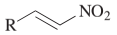


**181** (20 mol %), imidazole (20 mol %), $CH_2Cl_2$, rt, 23 h

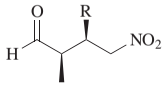


(96) dr 2:1
er (major) 89.0:11.0
er (minor) 85.0:15.0

444

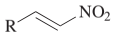


**182** (10 mol %), $CHCl_3$/MeOH (9:1), 0°

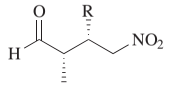


445

| R | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 4 | (74) | 98:2 | >99.5:0.5 |
| 2-$C_4H_3S$ | 3 | (94) | 91:9 | 98.5:1.5 |
| *i*-Bu | 4 | (46) | 89:11 | 99.5:0.5 |
| Ph | 2 | (92) | 95:5 | 97.0:3.0 |
| 2-$BrC_6H_4$ | 2.5 | (88) | 95:5 | 98.0:2.0 |
| 3-$BrC_6H_4$ | 1.5 | (89) | 95:5 | 94.5:5.5 |
| 4-$BrC_6H_4$ | 3 | (88) | 98:2 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 2.5 | (88) | 91:9 | 98.5:1.5 |
| 2-$MeOC_6H_4$ | 4 | (84) | 98:2 | 93.0:7.0 |
| 4-$MeOC_6H_4$ | 3 | (76) | 97:3 | 98.0:2.0 |
| 4-$MeC_6H_4$ | 2.5 | (75) | 97:3 | 97.0:3.0 |
| 3-$CF_3C_6H_4$ | 5 | (83) | 95:5 | 98.0:2.0 |
| $BnCH_2$ | 4 | (64) | 99:1 | 97.5:2.5 |

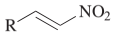


**183** (15 mol %), $CHCl_3$

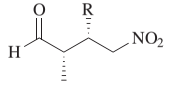


446

| R | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Ph | rt | 1 | (91) | 91:9 | 95.5:4.5 |
| 4-$BrC_6H_4$ | rt | 1 | (99) | 87:13 | 95.0:5.0 |
| 4-$MeOC_6H_4$ | rt | 6 | (82) | 87:13 | 94.0:6.0 |
| 4-$CF_3OC_6H_4$ | –20° | 30 | (78) | 87:13 | 94.5:5.5 |
| 4-$CF_3OC_6H_4$ | rt | 1 | (90) | 84:16 | 94.5:5.5 |

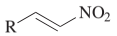


**184** (*x* mol %), NMM (1–2 mol %), $CHCl_3$/*i*-PrOH (9:1), rt, 12–24 h

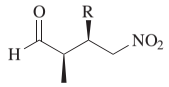


447

| R | *x* | | *syn*/*anti* | er |
|---|---|---|---|---|
| *c*-$C_6H_{11}$ | 2 | (84) | 6:1 | 99.0:1.0 |
| Ph | 1 | (98) | 7:1 | 97.5:2.5 |

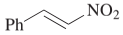


**185** (10 mol %), $CHCl_3$, –45 to 0°, 48 h

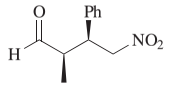


448

| R | | *syn*/*anti* | er |
|---|---|---|---|
| Ph | (71) | 99:1 | 96.5:3.5 |
| 4-$ClC_6H_4$ | (65) | 96:4 | 97.0:3.0 |



**187** (5 mol %), $PhCO_2H$ (5 mol %), $CH_2Cl_2$, –20°, 36 h



(88) dr 96:4
er 98.0:2.0

449

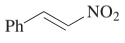
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

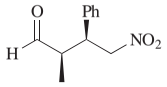
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_3$



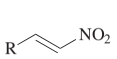


Catalyst (*x* mol %), $CH_2Cl_2$, rt

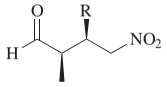


450

| Catalyst | *x* | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| **188** | 20 | 2 | (100) | 86:14 | 86.0:14.0 |
| **188** | 10 | 5 | (98) | 91:9 | 85.5:14.5 |
| **193** | 20 | 4 | (68) | 71:29 | 94.0:6.0 |



**189** (20 mol %), solvent, rt, 72 h

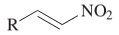


451

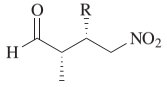
Catalyst Recycling (R = Ph)

| Run | | *syn*/*anti* | er |
|---|---|---|---|
| 1 | (80) | 84:16 | 95.0:5.0 |
| 2 | (83) | 86:14 | 94.0:6.0 |
| 3 | (54) | 83:17 | 92.5:7.5 |
| 4 | (42) | 80:20 | 92.0:8.0 |

| R | Solvent | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | $H_2O$ | (96) | 80:20 | 88.0:12.0 |
| Ph | $H_2O$ | (85) | 84:16 | 92.0:8.0 |
| 2-$BrC_6H_4$ | $H_2O$ | (70) | 75:25 | 88.5:11.5 |
| 2-$ClC_6H_4$ | $H_2O$ | (67) | 76:24 | 87.5:12.5 |
| 4-$ClC_6H_4$ | $H_2O$ | (79) | 85:15 | 90.0:10.0 |
| 4-$MeOC_6H_4$ | $H_2O$ | (53) | 86:14 | 91.5:8.5 |
| 4-$MeOC_6H_4$ | EtOH/$H_2O$ (1:1) | (74) | 79:21 | 92.5:7.5 |
| 2-$O_2NC_6H_4$ | $H_2O$ | (64) | 82:18 | 95.0:5.0 |
| 3-$MeC_6H_4$ | $H_2O$ | (64) | 86:14 | 90.5:9.5 |
| 1-Np | $H_2O$ | (67) | 77:23 | 92.0:8.0 |

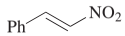


**190a** (10 mol %), toluene/THF (5:1), 0°

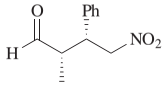


452

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 22 | (88) | 96:4 | 89.0:11.0 |
| Ph | 17 | (96) | 95:5 | 94.0:6.0 |
| 4-$BrC_6H_4$ | 22 | (87) | 97:3 | 93.0:7.0 |
| 2-$ClC_6H_4$ | 15 | (96) | 92:8 | 93.0:7.0 |
| 4-$ClC_6H_4$ | 19 | (99) | 95:5 | 93.0:7.0 |
| 2-$FC_6H_4$ | 15 | (96) | 97:3 | 92.0:8.0 |
| 4-$FC_6H_4$ | 22 | (93) | 95:5 | 92.0:8.0 |
| 4-$MeOC_6H_4$ | 22 | (93) | 96:4 | 94.0:6.0 |
| 4-$MeC_6H_4$ | 22 | (98) | 96:4 | 95.0:5.0 |

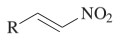


**190b** (10 mol %), hexane, –20°, 48 h

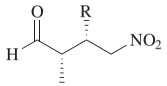


(97) *syn/anti* = 95:5, er 97.0:3.0

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**191** (*x* mol %), DMAP (5–10 mol %), MeOH, rt



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| R | *x* | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 5 | 8 | (94) | 82:18 | 98.0:2.0 |
| *c*-$C_6H_{11}$ | 10 | 72 | (60) | 60:40 | 99.0:1.0 |
| Ph | 5 | 8 | (96) | 91:9 | >99.5:0.5 |
| 4-$BrC_6H_4$ | 5 | 8 | (87) | 86:14 | 98.0:2.0 |
| 4-$MeC_6H_4$ | 5 | 8 | (79) | 72:28 | 96.5:3.5 |
| $BnCH_2$ | 10 | 72 | (70) | 80:20 | 98.0:2.0 |
| 1-Np | 5 | 24 | (92) | 91:9 | 98.0:2.0 |

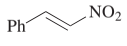
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

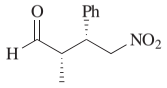
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_3$



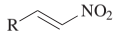


**192** (5 mol %), $CH_2Cl_2$, rt, 72 h

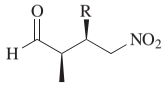


(77) *syn*/*anti* = 62:38, er 67.0:33.0

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Catalyst (10 mol %), TFA (5 mol %), solvent, rt

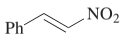


456

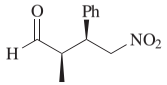
Catalyst **194b** Recycling (R = Ph)

| Run | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| 1 | 12 | (95) | 77:23 | 94.0:6.0 | 94.5:5.5 |
| 2 | 18 | (93) | 73:27 | 92.5:7.5 | 92.0:8.0 |
| 3 | 48 | (86) | 68:32 | 93.0:7.0 | 93.5:6.5 |

| R | Catalyst | Solvent | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|---|
| 2-$C_4H_3S$ | **194a** | THF | 17 | (93) | 61:39 | 92.0:8.0 | 93.0:7.0 |
| 2-$C_4H_3S$ | **194b** | $CH_2Cl_2$ | 17 | (97) | 68:32 | 94.0:6.0 | 94.5:5.5 |
| Ph | **194a** | THF | 12 | (95) | 68:32 | 92.0:8.0 | 90.5:9.5 |
| Ph | **194b** | $CH_2Cl_2$ | 12 | (95) | 77:23 | 94.0:6.0 | 94.5:5.5 |
| 4-$BrC_6H_4$ | **194a** | THF | 17 | (93) | 62:38 | 92.5:7.5 | — |
| 4-$BrC_6H_4$ | **194b** | $CH_2Cl_2$ | 17 | (95) | 65:35 | 94.0:6.0 | — |
| 4-$MeOC_6H_4$ | **194a** | THF | 36 | (87) | 74:26 | 91.0:9.0 | 92.5:7.5 |
| 4-$MeOC_6H_4$ | **194b** | $CH_2Cl_2$ | 36 | (96) | 73:27 | 93.0:7.0 | 93.0:7.0 |
| 2-$MeC_6H_4$ | **194a** | THF | 36 | (86) | 75:25 | 91.0:9.0 | 90.5:9.5 |
| 2-$MeC_6H_4$ | **194b** | $CH_2Cl_2$ | 36 | (87) | 77:23 | 95.0:5.0 | 94.0:6.0 |
| 4-$MeC_6H_4$ | **194a** | THF | 36 | (91) | 73:27 | 91.5:8.5 | — |
| 4-$MeC_6H_4$ | **194b** | $CH_2Cl_2$ | 36 | (99) | 73:27 | 94.5:5.5 | — |



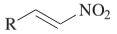
**195** (5 mol %),
$PhCO_2H$ (5 mol %),
$CH_2Cl_2/H_2O$ (2.5:1), rt



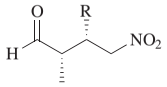
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Catalyst Recycling

| Run | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 45 | (98) | 87:13 | 96.0:4.0 |
| 2 | 24 | (82) | 92:8 | 96.0:4.0 |
| 3 | 24 | (48) | 92:8 | 96.0:4.0 |

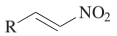


**196** (10 mol %),
DMAP (10 mol %),
MeOH, rt

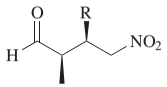


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 96 | (71) | 70:30 | 54.0:46.0 |
| Ph | 76 | (87) | 80:20 | 99.0:1.0 |
| 4-$BrC_6H_4$ | 76 | (48) | 68:32 | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 96 | (87) | 63:37 | 94.0:6.0 |
| 1-Np | 48 | (45) | 74:26 | 94.0:6.0 |
| 2-Np | 56 | (48) | 64:36 | 91.5:8.5 |



**197a** (10 mol %),
**202** (10 mol %),
toluene, rt



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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 3 | (80) | 87:13 | 97.5:2.5 |
| 2-$BrC_6H_4$ | 2 | (90) | 84:16 | 99.0:1.0 |
| 3-$BrC_6H_4$ | 2 | (95) | 97:3 | 84.0:16.0 |
| 4-$BrC_6H_4$ | 2 | (83) | 72:28 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 2 | (81) | 99:1 | 84.0:16.0 |
| 4-$MeOC_6H_4$ | 2 | (85) | 77:23 | 95.0:5.0 |
| 4-$MeC_6H_4$ | 2 | (78) | 82:18 | 94.5:5.5 |

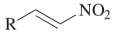
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

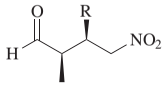
*Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.*

$C_3$



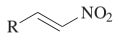


**198** (5 mol %), DIPEA (5 mol %), $CH_2Cl_2$, 0°

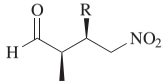


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 72 | (99) | 86:14 | 98.0:2.0 |
| 2-$C_4H_3S$ | 120 | (83) | 87:13 | 97.0:3.0 |
| 3-$C_5H_4N$ | 36 | (99) | 65:35 | 97.5:2.5 |
| Ph | 24 | (97) | 92:8 | 99.0:1.0 |
| 3-$ClC_6H_4$ | 48 | (95) | 94:6 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 10 | (99) | 91:9 | 98.5:1.5 |
| 4-$FC_6H_4$ | 16 | (98) | 92:8 | 98.5:1.5 |
| 2-$MeOC_6H_4$ | 96 | (99) | 97:3 | 98.0:2.0 |
| 3-$MeOC_6H_4$ | 120 | (85) | 93:7 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 96 | (96) | 94:6 | 98.0:2.0 |
| 3,4-$(MeO)_2C_6H_3$ | 168 | (45) | 91:9 | 98.0:2.0 |
| 2-$MeC_6H_4$ | 168 | (57) | 93:7 | 98.5:1.5 |
| 4-$CF_3C_6H_4$ | 12 | (99) | 87:13 | 98.0:2.0 |
| 1-Np | 96 | (84) | 92:8 | 92.5:7.5 |
| 2-Np | 72 | (93) | 89:11 | 98.0:2.0 |



**199** (10 mol %),
$PhCO_2H$ (1 eq),
$EtOH/H_2O$ (1:1), rt

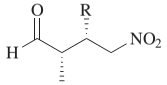


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| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 1 | (98) | 88:12 | 97.5:2.5 |
| Ph | 1.5 | (99) | 92:8 | 99.0:1.0 |
| 2-$ClC_6H_4$ | 1.5 | (98) | 90:10 | 98.5:1.5 |
| 4-$ClC_6H_4$ | 2 | (96) | 92:8 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 3 | (88) | 91:9 | 99.0:1.0 |
| 2-$O_2NC_6H_4$ | 3.5 | (84) | 74:26 | 97.0:3.0 |
| 3-$O_2NC_6H_4$ | 5 | (67) | 82:18 | 96.5:3.5 |
| 3,5-$Me_2C_6H_3$ | 16 | (75) | 88:12 | 98.0:2.0 |



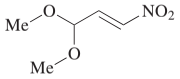
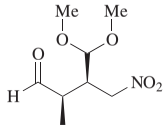
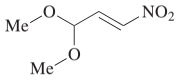
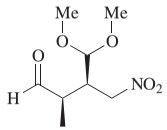
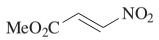
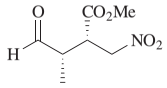
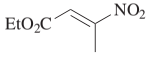
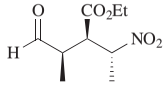
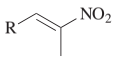
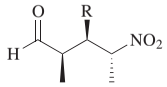
**200** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$



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| R | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *i*-Bu | rt | 3 | (94) | 84:16 | 93.0:7.0 |
| 2-$C_4H_3O$ | 0° | 12 | (92) | 85:15 | 99.0:1.0 |
| 2-$C_4H_3O$ | rt | 4 | (94) | 76:24 | 94.0:6.0 |
| 2-$C_4H_3S$ | 0° | 24 | (94) | 85:15 | 98.5:1.5 |
| 2-$C_4H_3S$ | rt | 24 | (82) | 90:10 | 97.5:2.5 |
| Ph | rt | 3 | (89) | 85:15 | >99.5:0.5 |
| 4-$BrC_6H_4$ | rt | 3 | (90) | 80:20 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | rt | 3 | (95) | 84:16 | >99.5:0.5 |
| 1-Np | rt | 4 | (88) | 75:25 | 96.0:4.0 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **16a** (10 mol %), *i*-PrOH, 12 h |  (74) *syn*/*anti* = 1.7:1 er 90.0:10.0 | 430 |
| |  | **145b** (10 mol %), DMF, $H_2O$ (2 eq), rt, 24 h |  (86) *syn*/*anti* = 6.0:1 er >99.5:0.5 | 116 |
| |  | *ent*-**145b** (5 mol %), $PhCO_2H$ (50 mol %), $H_2O$, 0°, 1 h; then rt, 7 h |  (74) *syn*/*anti* = 97:3 er 99.0:1.0 | 118 |
| |  | **145b** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 12–24 h |  (37) dr 48:26:17:9 er 98.5:1.5 | 463 |
| |  | **145b** (10 mol %), 4-$O_2NC_6H_4OH$ (40 mol %), $CHCl_3$, rt |  | 464 |

| R | Time (h) | | dr | er |
|---|---|---|---|---|
| Ph | 30 | (68) | 92:7:1:<1 | >99.5:0.5 |
| 4-$ClC_6H_4$ | 21 | (71) | 84:15:1:<1 | >99.5:0.5 |
| 4-$FC_6H_4$ | 23 | (70) | 92:8:<1:<1 | >99.5:0.5 |
| 4-$MeC_6H_4$ | 24 | (63) | 91:8:1:<1 | >99.5:0.5 |

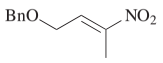
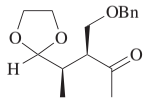
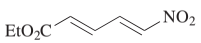
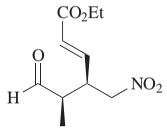
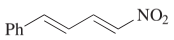
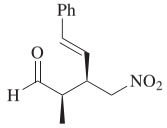
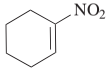
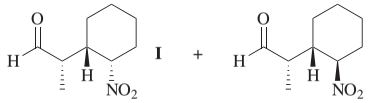
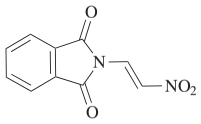
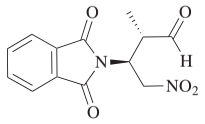
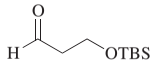
| | | | | |
|---|---|---|---|---|
|  (*E*)/(*Z*) = 93:7 | 1. *ent*-**3** (15 mol %), $CHCl_3$, –10°, 7 d<br>2. Ethylene glycol, PPTS (10 mol %), benzene, Dean–Stark<br>3. $NaNO_2$, isoamyl nitrite, DMSO, rt, 4 d |  | (50) *syn*/*anti* = 57:43<br>er (*syn*) 96.5:3.5<br>er (*anti*) 87.0:13.0 | 465 |
|  | **145b** (5 mol %), toluene, –10°, 1–2.5 d |  | (94) *syn*/*anti* = 95:5<br>er >99.5:0.5 | 466 |
|  | **145b** (5 mol %), 5% $H_2O$/EtOH, rt, 10 h |  | (81) *syn*/*anti* = 80:20<br>er 98.0:2.0 | 121 |
|  | *ent*-**145b** (20 mol %), 3-$O_2NC_6H_4CO_2H$ (10 mol %), $CHCl_3$, rt, 36 h |  **I** + **II** | **I** + **II** (84) dr **I**/**II** 8:1, er 98.5:1.5 | 467 |
|  | **186** (10–20 mol %), AcOH (25 mol %), MeCN, 0°, 3.5 h |  | (95) *syn*/*anti* = 10:1<br>er 99.5:0.5 | 468 |

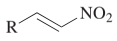
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

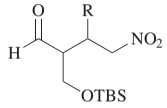
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_3$





**181** (20 mol %), imidazole (20 mol %), $CH_2Cl_2$, rt, 20 h

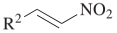


469

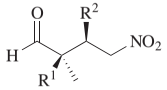
| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| Ph | (62) | 76:24 | 96.0:4.0 | 89.0:11.0 |
| 4-$BrC_6H_4$ | (66) | 75:25 | 99.0:1.0 | 96.0:4.0 |
| 2,4-$Cl_2C_6H_3$ | (42) | 60:40 | 99.0:1.0 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | (65) | 70:30 | 99.0:1.0 | 99.5:0.5 |
| 4-$MeC_6H_4$ | (46) | 68:32 | 99.5:0.5 | 99.0:1.0 |
| 4-$CF_3C_6H_4$ | (48) | 74:26 | 99.5:0.5 | 99.5:0.5 |

$C_{3-10}$





**17** (20 mol %), $H_2O$ (5 eq), $CH_2Cl_2$, rt, 24 h

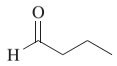


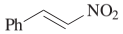
72

| $R^1$ | $R^2$ | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| PhO | Ph | (78) | 10.4:1 | 97.0:3.0 | 96.0:4.0 |
| $TBSOCH_2$ | 2-$C_4H_3O$ | (79) | 5.4:1 | 99.5:0.5 | 97.5:2.5 |
| $TBSOCH_2$ | 2-$C_4H_3S$ | (85) | 6.6:1 | 99.5:0.5 | 98.5:1.5 |
| $TBSOCH_2$ | 3-$C_5H_4N$ | (94) | 5.6:1 | 99.5:0.5 | 98.0:2.0 |
| $TBSOCH_2$ | Ph | (87) | 6.3:1 | 99.5:0.5 | 99.0:1.0 |
| $TBSOCH_2$ | 4-$FC_6H_4$ | (86) | 6.6:1 | 99.5:0.5 | 97.0:3.0 |
| $TBSOCH_2$ | 4-$MeOC_6H_4$ | (85) | 7.1:1 | 99.5:0.5 | 97.5:2.5 |
| *n*-Pr | Ph | (98) | 2.1:1 | 99.5:0.5 | 98.5:1.5 |
| $Me_2C{=}CH(CH_2)_2$ | Me | (61) | 3.3:1 | 99.5:0.5 | 99.5:0.5 |
| $Me_2C{=}CH(CH_2)_2$ | Ph | (82) | 3.9:1 | 99.5:0.5 | 99.5:0.5 |

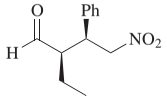
| | | | | | |
|---|---|---|---|---|---|
| Ph | Me | (91) | 23:1 | 99.5:0.5 | — |
| Ph | $CF_3$ | (34) | >50:1 | 99.5:0.5 | 98.5:1.5 |
| Ph | $BnOCH_2$ | (87) | >50:1 | 99.5:0.5 | — |
| Ph | *n*-Bu | (54) | 28:1 | 98.0:2.0 | — |
| 4-$MeOC_6H_4CH_2$ | Ph | (78) | 13:1 | 98.0:2.0 | — |
| 3,4-$(OCH_2O)C_6H_3CH_2$ | Ph | (82) | 3.1:1 | 99.5:0.5 | 99.5:0.5 |
| 3,4-$(OCH_2O)C_6H_3CH_2$ | 4-$BrC_6H_4$ | (81) | 3.8:1 | 99.5:0.5 | 99.5:0.5 |
| 3,4-$(OCH_2O)C_6H_3CH_2$ | 2-$CF_3C_6H_4$ | (63) | 4.7:1 | 99.0:1.0 | 96.0:4.0 |

$C_4$



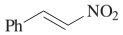


**1** (15 mol %), [bmim][$BF_4$], rt, 24 h

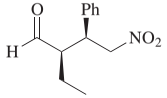


(80) *syn*/*anti* = 94:6
er 60.0:40.0

433

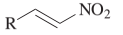


**1** (10 mol %),
**118** (10 mol %),
toluene, 0°, 20 h

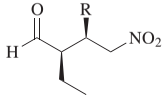


(91) *syn*/*anti* = 81:19
er (*syn*) 95.5:4.5
er (*anti*) 94.5:5.5

343

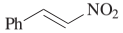


**1** (20 mol %),
**169b** (5 mol %),
benzene, rt

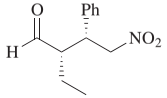


| R | | dr | er |
|---|---|---|---|
| Ph | (77) | 20:1 | 83.5:16.5 |
| 4-$BrC_6H_4$ | (79) | 17:1 | 84.5:15.5 |

434

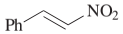


**3** (15 mol %), $CHCl_3$, rt, 4 d

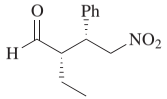


(70) *syn*/*anti* = 90:10
er 85.0:15.0

251



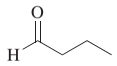
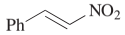
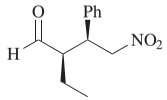
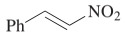
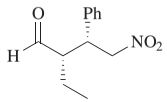
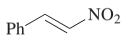
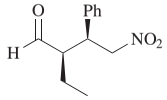
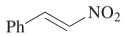
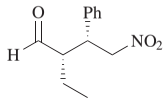
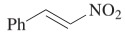
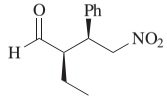
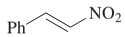
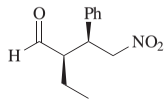
**3** (15 mol %),
additive (15 mol %), $CHCl_3$

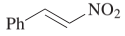
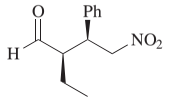
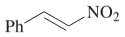
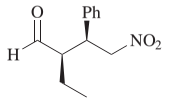
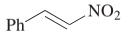
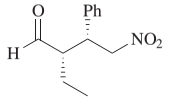
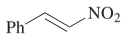
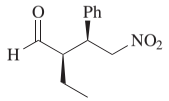


| Additive | Temp (°) | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| none | –25 | 4 | (70) | 90:10 | 85.0:15.0 |
| HCl | 0 | 2 | (82) | 88:12 | 84.0:16.0 |

250

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **5** (10 mol %), TFA (10 mol %), brine, rt, 24 h |  (99) *syn*/*anti* = 65:35 er 69.0:31.0 | 252 |
| |  | **6** (15 mol %), $CHCl_3$ –25°, 15 h |  (93) *syn*/*anti* = 94:6 er 76.5:23.5 | 251 |
| |  | **51** (10 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), $H_2O$ |  | 288 |
| | | Temp / Time (h) / (76) / *syn*/*anti* 97:3 / er 90.5:9.5 | | |
| | | 0° / 72 | | |
| | | rt / 12 / (99) / 97:3 / 88.5:11.5 | | |
| |  | **65** (5 mol %), MeOH, rt |  (90) *syn*/*anti* = 97:3 er 95.0:5.0 | 301 |
| |  | **79** (5 mol %), benzene, 2°, 42 h |  (88) *syn*/*anti* = 76:24 er (*syn*) 97.0:3.0 er (*anti*) 97.5:2.5 | 267 |
| |  | **82** (10 mol %), $PhCO_2H$ (10 mol %), EtOH, rt, 48 h |  (73) *syn*/*anti* = 75:25 er 61.0:39.0 | 320 |

| | | | | |
|---|---|---|---|---|
|  | **86** (10 mol %), $CH_2Cl_2$, 0°, 46 h |  | (70) *syn*/*anti* = 99:1<br>er 99.5:0.5 | 327 |
|  | **92** (2 mol %),<br>4-$MeOC_6H_4CO_2H$<br>(2 mol %), brine, rt, 24 h |  | (90) *syn*/*anti* = 90:10<br>er 90.5:9.5 | 332 |
|  | **106b** (20 mol %),<br>toluene, rt, 24 h |  | (95) *syn*/*anti* = 83:17<br>er 81.5:18.5 | 350 |
|  | **113** (*x* mol %), $CHCl_3$ |  | | 355 |

| *x* | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 10 | –25° | 72 | (76) | 80:20 | 93.5:6.5 |
| 20 | rt | 5.5 | (100) | 72:28 | 87.0:13.0 |

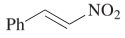
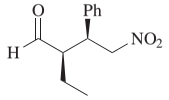
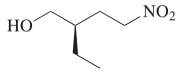
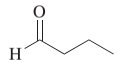
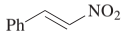
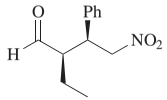
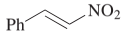
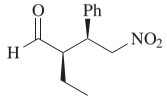
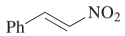
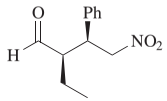
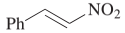
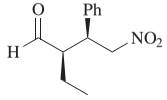
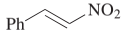
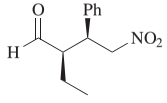
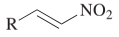
| | | | | |
|---|---|---|---|---|
|  | **121** (15 mol %),<br>TFA (5 mol %),<br>neat, rt, 72 h |  | (88) *syn*/*anti* = 99:1<br>er 87.0:13.0 | 361 |
|  | 1. **145b** (2 mol %),<br>3-$O_2NC_6H_4CO_2H$<br>(20 mol %), toluene, 48 h<br>2. $NaBH_4$, MeOH, 0° |  | (96) er 99.0:1.0 | 124 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

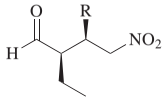
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **145b** (10 mol %), hexane, 0°, 48 h |  (66) *syn*/*anti* = 93:7 er 99.5:0.5 | 60 |
| |  | **145b** (5 mol %), additive, toluene, rt |  | 66 |

| Additive | Time (h) | | dr | er |
|---|---|---|---|---|
| none | 28 | (98) | 8:1 | 97.5:2.5 |
| 4-$O_2NC_6H_4OH$ | 0.75 | (95) | 15:1 | 98.0:2.0 |

| | | | | |
|---|---|---|---|---|
| |  | **166** (10 mol %), $CH_2Cl_2$, rt, 5 h |  (93) *syn*/*anti* = 90:10 er >99.5:0.5 | 435, 421 |
| |  | **170** (20 mol %), THF, rt, 27 h |  (94) *syn*/*anti* = 86:14 er 82.5:17.5 | 139, 253 |
| |  | **173** (20 mol %), DMAP (20 mol %), *i*-PrOH, 0°, 24 h |  (76) *syn*/*anti* = 77:23 er 97.5:2.5 | 438 |

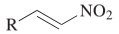


**174** (10 mol %),
$CH_2Cl_2$/hexane

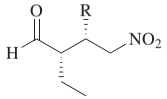


439

| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3S$ | 0 | 42 | (78) | 95:5 | 88.5:11.5 |
| Ph | 0 | 48 | (63) | 97:3 | 92.0:8.0 |
| 4-$MeOC_6H_4$ | 0 | 44 | (57) | 97:3 | 92.0:8.0 |
| 2-$CF_3C_6H_4$ | rt | 68 | (67) | 80:20 | 92.5:7.5 |



**175** (*x* mol %),
NMM (1–5 mol %),
$CHCl_3$/*i*-PrOH (9:1)



130

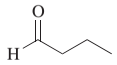
| R | *x* | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| H | 1 | rt | 48 | (65) | — | 90.5:9.5 |
| *n*-$C_5H_{11}$ | 3 | rt | 12 | (82) | 15:1 | 96.5:3.5 |
| *n*-$C_5H_{11}$ | 5 | –15° | 48 | (80) | 20:1 | 97.0.3.0 |
| Ph | 1 | rt | 12 | (93) | 25:1 | 97.5:2.5 |
| Ph | 3 | –15° | 48 | (92) | >99:1 | 98.5:1.5 |
| 4-$BrC_6H_4$ | 1 | rt | 12 | (99) | 25:1 | 97.5:2.5 |
| 4-$BrC_6H_4$ | 5 | –15° | 48 | (95) | 90:1 | 98.5:1.5 |
| 4-$ClC_6H_4$ | 1 | rt | 12 | (99) | 30:1 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 3 | –15° | 48 | (97) | >99:1 | 98.5:1.5 |
| 2,4-$Cl_2C_6H_3$ | 1 | rt | 12 | (90) | 20:1 | 97.5:2.5 |
| 2,4-$Cl_2C_6H_3$ | 3 | –15° | 48 | (97) | 50:1 | 98.5:1.5 |
| 4-$FC_6H_4$ | 1 | rt | 12 | (99) | 25:1 | 97.5:2.5 |
| 4-$FC_6H_4$ | 5 | –15° | 48 | (99) | >99:1 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 3 | rt | 12 | (99) | 15:1 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 5 | –15° | 48 | (97) | 70:1 | 97.0:3.0 |
| 2-$CF_3C_6H_4$ | 1 | rt | 12 | (88) | >99:1 | 99.0:1.0 |
| 2-$CF_3C_6H_4$ | 3 | –15° | 48 | (95) | >99:1 | 99.5:0.5 |

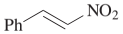
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

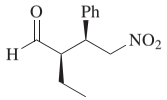
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_4$



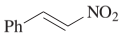


**176** (10 mol %), hexane/benzene, 5°, 7 d

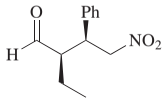


(85) *syn*/*anti* = 95:5
er 99.5:0.5

440

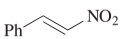


**178** (10 mol %), $CCl_4$, rt, 30 h

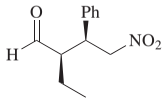


(80) *syn*/*anti* = 92:8
er 99.5:0.5

441

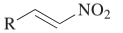


**179** (10 mol %), $CH_2Cl_2$

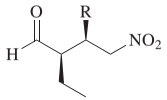


442

| Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 0 | 18 | (88) | 96:4 | 99.5:0.5 |
| 20 | 12 | (93) | 93:7 | 99.5:0.5 |

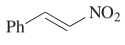


**180** (1–2 mol %), additive, $H_2O$, rt

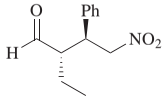


443

| R | Additive | Time (h) | | dr | er |
|---|---|---|---|---|---|
| *c*-$C_6H_{11}$ | none | 22 | (50) | 89:11 | 97.5:2.5 |
| *c*-$C_6H_{11}$ | $PhCO_2H$ | 22 | (81) | 79:21 | 98.5:1.5 |
| Ph | $PhCO_2H$ | 2 | (94) | 94:6 | >99.8:0.2 |
| 4-$BrC_6H_4$ | none | 4 | (94) | 95:5 | >99.5:0.5 |
| 4-$BrC_6H_4$ | none | 4 | (86) | 96:4 | >99.5:0.5 |
| 4-$MeOC_6H_4$ | none | 4 | (92) | 92:8 | 99.5:0.5 |

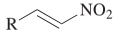


**181** (20 mol %), imidazole (20 mol %), $CH_2Cl_2$, rt, 24 h

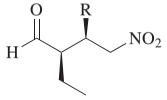


(72) dr 2:1
er (major) 95.5:4.5
er (minor) 96.5:3.5

444

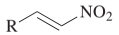


**182** (10 mol %), $CHCl_3$/MeOH (9:1)

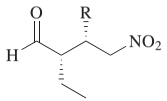


445

| R | Temp (°) | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *i*-Bu | 0 | 5 | (92) | 99:1 | 94.5:5.5 |
| Ph | 0 | 4 | (86) | 98:2 | 98.0:2.0 |
| 4-$BrC_6H_4$ | 0 | 4 | (87) | 97:3 | 96.5:3.5 |
| 4-$ClC_6H_4$ | 0 | 3.5 | (82) | 93:7 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 0 | 5 | (80) | 99:1 | 94.5:5.5 |
| 2-$CF_3C_6H_4$ | rt | 3 | (90) | 95:5 | 95.0:5.0 |
| $BnCH_2$ | 0 | 5 | (60) | 95:5 | 98.0:2.0 |



**184** (*x* mol %), NMM (1–2 mol %), solvent, rt, 12–24 h



447

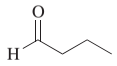
| R | *x* | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| $(MeO)_2CH$ | 1 | $CHCl_3$ | (99) | 68:1 | 96.0:4.0 |
| *i*-Bu | 1 | $CHCl_3$/*i*-PrOH (9:1) | (90) | 24:1 | 98.5:1.5 |
| Ph | 1 | $CHCl_3$/*i*-PrOH (9:1) | (96) | 42:1 | 98.5:1.5 |
| 2,4-$Cl_2C_6H_3$ | 1 | $CHCl_3$/*i*-PrOH (9:1) | (97) | 36:1 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 2 | $CHCl_3$/*i*-PrOH (9:1) | (99) | 21:1 | 97.5:2.5 |
| 2-$CF_3C_6H_4$ | 1 | $CHCl_3$/*i*-PrOH (9:1) | (95) | >99:1 | 99.0:1.0 |

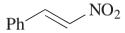
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

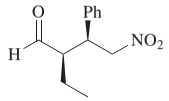
*Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.*

$C_4$



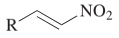


**185** (*x* mol %), $CHCl_3$

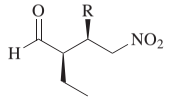


448

| *x* | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2.5 | 8 | 72 | (54) | 93:7 | 99.0:1.0 |
| 5 | –45 to 0 | 48 | (72) | 95:5 | 99.0:1.0 |
| 10 | –45 to 0 | 20 | (89) | 96:4 | 98.0:2.0 |
| 20 | –45 to 0 | 20 | (98) | 95:5 | 99.0:1.0 |

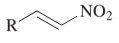


**187** (5 mol %), $PhCO_2H$ (5 mol %), $CH_2Cl_2$, –20°

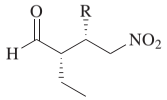


443

| R | Time (h) | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 40 | (96) | 98:2 | 90.5:9.5 |
| *c*-$C_6H_{11}$ | 60 | (75) | 91:9 | 98.5:1.5 |
| Ph | 36 | (92) | 98:2 | 96.5:3.5 |
| 4-$ClC_6H_4$ | 20 | (96) | 98:2 | 97.5:2.5 |
| 2,4-$Cl_2C_6H_4$ | 28 | (94) | 99:1 | 97.5:2.5 |
| 4-$FC_6H_4$ | 24 | (98) | 98:2 | 96.5:3.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 60 | (96) | 97:3 | 96.5:3.5 |
| 4-$MeSC_6H_4$ | 35 | (94) | 99:1 | 95.5:4.5 |
| 4-$MeC_6H_4$ | 36 | (97) | 99:1 | 96.5:3.5 |
| 4-$CF_3C_6H_4$ | 12 | (99) | 98:2 | 97.5:2.5 |
| $BnCH_2$ | 36 | (93) | 95:5 | 96.0:4.0 |

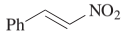


**190a** (10 mol %),
toluene/THF (5:1), 0°

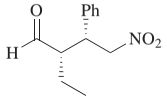


| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 46 | (95) | 95:5 | 94.0:6.0 |
| 4-$MeC_6H_4$ | 48 | (90) | 94:6 | 95.0:5.0 |

452

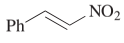


**191** (5 mol %),
DMAP (5 mol %),
MeOH, rt

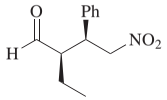


(89) *syn*/*anti* = 91:9
er 99.0:1.0

454

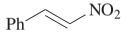


Catalyst (10 mol %),
TFA (5 mol %),
solvent, rt, 12 h

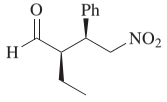


456

| Catalyst | Solvent | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| **194a** | THF | (96) | 82:18 | 88.0:12.0 | 87.5:12.5 |
| **194b** | $CH_2Cl_2$ | (99) | 89:11 | 93.5:6.5 | 91.0:9.0 |



**195** (5 mol %),
$PhCO_2H$ (5 mol %),
$CH_2Cl_2/H_2O$ (2.5:1),
rt, 24 h

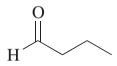
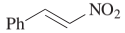
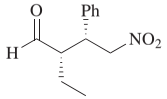
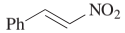
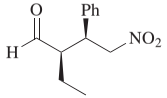


457

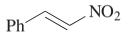
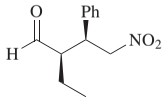
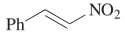
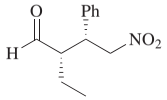
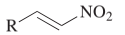
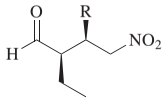
Catalyst Recycling

| Run | | *syn*/*anti* | er |
|---|---|---|---|
| 1 | (96) | 92:8 | 92.0:8.0 |
| 2 | (78) | 93:7 | 92.0:8.0 |
| 3 | (97) | 92:8 | 92.0:8.0 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

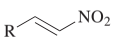
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$  |  | **196** (10 mol %), DMAP (10 mol %), MeOH, rt, 96 h |  (42) *syn*/*anti* = 81:19 er 96.5:3.5 | 458 |
| |  | **197b** (*x* mol %), $CH_2Cl_2$ |  | 132 |

| *x* | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 5 | 0° | 20 | (90) | 99:1 | >99.5:0.5 |
| 10 | rt | 2 | (75) | 98:2 | 97.0:3.0 |

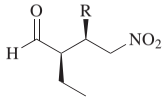
| | | | | |
|---|---|---|---|---|
|  | **198** (5 mol %), DIPEA (5 mol %), $CH_2Cl_2$, 0°, 15 h |  (95) *syn*/*anti* = 96:4 er 98.5:1.5 | 460 |
|  | **200** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 40 h |  (85) *syn*/*anti* = 92:8 er (*syn*) 98.5:1.5 | 462 |
|  | **201** (1 mol %), **202** (1 mol %), $CH_2Cl_2$, 0° |  | 470 |

| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (95) | 95:5 | 99.0:1.0 |
| 2-$C_4H_3S$ | (93) | >99:1 | 97.5:2.5 |
| Ph | (95) | 97:3 | 98.5:1.5 |

| | | | |
|---|---|---|---|
| 4-$BrC_6H_4$ | (96) | 99:1 | >99.5:0.5 |
| 4-$ClC_6H_4$ | (95) | 97:3 | 98.0:2.0 |
| 3-$MeOC_6H_4$ | (95) | 98:2 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | (92) | 96:4 | 98.5:1.5 |
| 2-$O_2NC_6H_4$ | (92) | >99:1 | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | (93) | 97:3 | 98.0:2.0 |
| 4-$MeC_6H_4$ | (94) | 98:2 | 98.0:2.0 |



**203** (2 mol %), $HCO_2H$ (20 mol %), $H_2O$, rt, 12–18 h

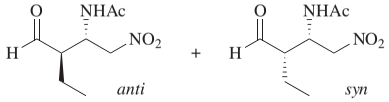


471

| R | | *syn*/*anti* | er |
|---|---|---|---|
| Ph | (93) | 92:8 | 98.0:2.0 |
| 4-$BrC_6H_4$ | (90) | 90:10 | 97.5:2.5 |



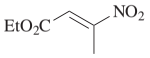
**145b** (5 mol %), AcOH (20 mol %), $CHCl_3$, –10°



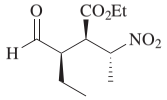
*anti* + *syn*

468

(95) *anti*/*syn* = 9:1, er 99.0:1.0

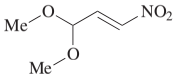


**145b** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 12–24 h

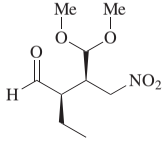


(80) dr 90:5:4:1
er >99.5:0.5

463



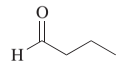
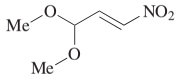
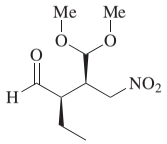
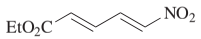
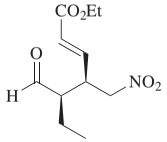
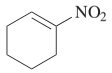
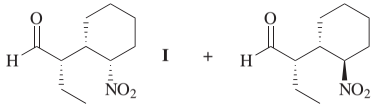
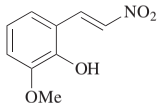
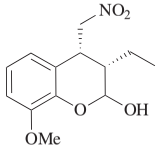
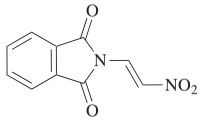
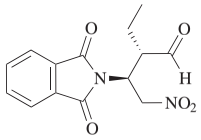
**16a** (10 mol %), *i*-PrOH, 48 h, rt



(75) *syn*/*anti* = 5:1
er 90.0:10.0

430

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

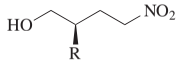
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **145b** (10 mol %), DMF, $H_2O$ (2 eq), rt, 48 h |  (63) *syn/anti* = 11:1 er >99.5:0.5 | 116 |
| |  | **145b** (5 mol %), toluene, 0° to rt, 1–2.5 d |  (87) *syn/anti* = 93:7 er >99.5:0.5 | 466 |
| |  | *ent*-**145b** (20 mol %), 3-$O_2NC_6H_4CO_2H$ (10 mol %), $CHCl_3$, rt, 38 h |  **I** +  **II** (87) dr **I/II** 17:1, er 99.5:0.5 | 467 |
| |  | **145b** (20 mol %), $PhCO_2H$ (20 mol %), 0.25 M in $CH_2Cl_2$, rt, 9 h |  (97) dr 74.5:25.5 er >99.9:0.1 | 431 |
| |  | **186** (10–20 mol %), AcOH (25 mol %), MeCN, 0°, 3.5 h |  (99) *syn/anti* = 14:1 er 99.5:0.5 | 468 |

$C_{4-9}$



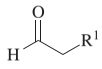


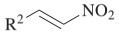
1. **145b** (2 mol %), 3-$O_2NC_6H_4CO_2H$ (20 mol %), toluene
2. $NaBH_4$, MeOH, 0°



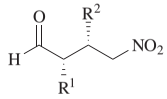
124

| R | Temp (°) | Time (h) | | er |
|---|---|---|---|---|
| $MeO_2CCH_2$ | 3 | 54 | (92) | 98.0:2.0 |
| *t*-$BuO_2C(CH_2)_2$ | 3 | 54 | (94) | 98.5:1.5 |
| *i*-Pr | rt | 32 | (94) | 98.5:1.5 |
| *n*-Bu | 3 | 48 | (95) | 99.5:0.5 |
| *i*-Bu | 3 | 54 | (94) | >99.5:0.5 |
| $(Boc)_2N(CH_2)_4$ | 3 | 48 | (92) | 99.0:1.0 |
| *c*-$C_6H_{11}CH_2$ | 3 | 48 | (93) | >99.5:0.5 |
| Bn | 3 | 32 | (93) | 99.5:0.5 |
| 4-*t*-$BuOC_6H_4CH_2$ | 3 | 32 | (94) | 99.0:1.0 |





**184** (*x* mol %), NMM (1–2 mol %), solvent, rt, 12–24 h

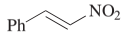


447

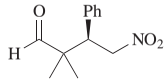
| $R^1$ | $R^2$ | *x* | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| $MeO_2CCH_2$ | $(MeO)_2CH$ | 1 | $CHCl_3$ | (95) | 16:1 | 95.0:5.0 |
| *i*-Pr | $(MeO)_2CH$ | 2 | $CHCl_3$ | (95) | >99:1 | 97.5:2.5 |
| *i*-Pr | Ph | 2 | $CHCl_3$/*i*-PrOH (9:1) | (93) | 61:1 | 98.0:2.0 |
| *n*-Bu | Ph | 1 | $CHCl_3$/*i*-PrOH (9:1) | (98) | 27:1 | 98.0:2.0 |
| Bn | Ph | 1 | $CHCl_3$/*i*-PrOH (9:1) | (94) | 25:1 | 98.5:1.5 |

$C_4$



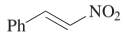


**1** (20 mol %), **169b** (20 mol %), benzene, rt

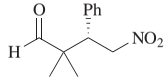


(66) er 86.0:14.0

449

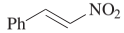


**3** (15 mol %), $CHCl_3$, rt, 3 d

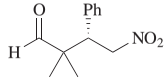


(72) er 90.0:10.0

251



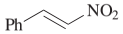
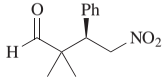
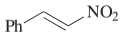
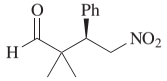
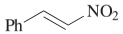
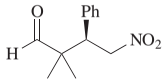
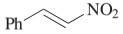
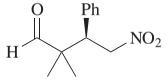
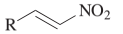
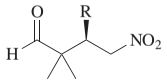
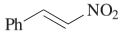
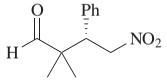
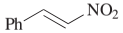
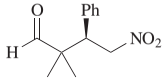
**3** (15 mol %), microwaves (15 W), 27°, 2 h

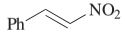


(76) er 88.5:11.5

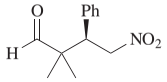
310

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

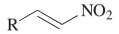
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$  |  | **5** (10 mol %), TFA (10 mol %), brine, rt, 30 h |  (76) er 88.0:12.0 | 252 |
| |  | **6** (15 mol %), TFA (15 mol %), *i*-PrOH, 4°, 48 h |  (87) er 90.0:10.0 | 472 |
| |  | **12** (10 mol %), TFA (2 mol %), neat, 24 h |  (98) er 86.0:14.0 | 275 |
| |  | Catalyst (15 mol %), TFA (5 mol %), rt, 96 h |  Catalyst (yield) er: **12** (51) 94.5:5.5; **13** (70) 93.0:7.0 | 255 |
| |  | **16b** (20 mol %), *i*-PrOH, 0° |  | 73, 258 |
| | | | R: 2-$C_4H_3S$ — Time (h) 6 — (75) — er 94.5:5.5; Ph — 4.5 — (85) — 95.0:5.0; 4-$MeC_6H_4$ — 6 — (67) — 95.0:5.0 | |
| |  | **18** (20 mol %), *n*-$PrCO_2H$ (10 mol %), $CH_2Cl_2$, rt |  (61) er 91.0:9.0 | 259 |
| |  | **33** (10 mol %), toluene, rt, 36 h |  (69) er 91.5:8.5 | 272 |



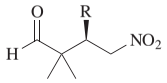
**47** (10 mol %), *i*-PrOH, rt, 16 h



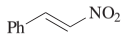
(85) er 87.5:12.5 284



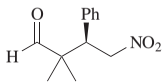
**52** (20 mol %), $CH_2Cl_2$, rt, 72 h



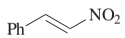
| R | | er | |
|---|---|---|---|
| 2-$C_4H_3O$ | (71) | 87.0:13.0 | 473 |
| 2-$C_4H_3S$ | (57) | 93.0:7.0 | |
| Ph | (58) | 95.5:4.5 | |
| 4-$BrC_6H_4$ | (52) | 95.5:4.5 | |
| 2-$ClC_6H_4$ | (75) | 95.5:4.5 | |
| 4-$ClC_6H_4$ | (51) | 93.0:7.0 | |
| 4-$FC_6H_4$ | (58) | 88.5:11.5 | |
| 4-$MeOC_6H_4$ | (56) | 92.5:7.5 | |
| 3-$O_2NC_6H_4$ | (68) | 91.0:9.0 | |
| 4-$O_2NC_6H_4$ | (47) | 95.0:5.0 | |
| 3-$MeC_6H_4$ | (55) | 93.0:7.0 | |
| 4-$MeC_6H_4$ | (49) | 88.5:11.5 | |
| 2-Np | (60) | 98.0:2.0 | |



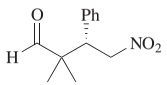
**54** (20 mol %), [bmim][$BF_4$], rt, 96 h



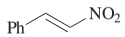
(41) er 90.5:9.5 291



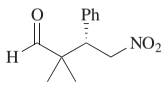
**62** (10 mol %), TFA (2 mol %), neat, rt, 18 h



(85) er 92.0:8.0 298



**65** (5 mol %), MeOH, rt



(79) er 81.0:19.0 301

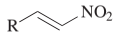
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

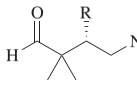
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_4$



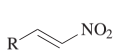


**68** (30 mol %), $PhCO_2H$ (20 mol %), toluene, rt, 4 d

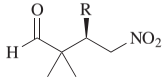


| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (93) | 99.5:0.5 |
| Ph | (70) | 99.5:0.5 |

279

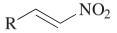


**74** (20 mol %), toluene, rt

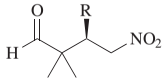


315

| R | Time (d) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 0.5 | (88) | 94.5:5.5 |
| 2-$C_4H_3S$ | 0.5 | (92) | 93.5:6.5 |
| Ph | 1 | (90) | 96.5:3.5 |
| 2-$BrC_6H_4$ | 2 | (85) | 94.5:5.5 |
| 3-$BrC_6H_4$ | 2 | (88) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 1 | (90) | 96.0:4.0 |
| 3-$ClC_6H_4$ | 1 | (92) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 1 | (90) | 96.5:3.5 |
| 2-$MeOC_6H_4$ | 5 | (73) | 86.0:14.0 |
| 3-$MeOC_6H_4$ | 1.5 | (89) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 2 | (88) | 90.5:9.5 |
| 4-$MeC_6H_4$ | 1.5 | (92) | 92.5:7.5 |
| 3-$CF_3C_6H_4$ | 1 | (89) | 97.0:3.0 |
| $BnCH_2$ | 5 | (43) | 98.5:1.5 |

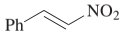


**75** (20 mol %), $PhCO_2H$ (20 mol %), neat

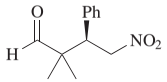


474

| R | Temp (°) | Time (d) | | er |
|---|---|---|---|---|
| Ph | 0 | 1 | (88) | 92.5:7.5 |
| 2-$BrC_6H_4$ | 0 | 1 | (88) | 80.0:20.0 |
| 3-$BrC_6H_4$ | 0 | 0.5 | (89) | 92.5:7.5 |
| 4-$BrC_6H_4$ | 0 | 0.5 | (98) | 92.0:8.0 |
| 3-$ClC_6H_4$ | 0 | 0.5 | (92) | 92.5:7.5 |
| 4-$ClC_6H_4$ | 0 | 0.5 | (88) | 92.0:8.0 |
| 2-$MeOC_6H_4$ | 0 | 3 | (92) | 85.5:14.5 |
| 3-$MeOC_6H_4$ | 0 | 0.5 | (88) | 92.5:7.5 |
| 4-$MeOC_6H_4$ | 0 | 0.5 | (96) | 91.5:8.5 |
| 4-$MeC_6H_4$ | 0 | 0.5 | (89) | 92.0:8.0 |
| 2-$CF_3C_6H_4$ | 0 | 3 | (66) | 76.0:24.0 |
| 3-$CF_3C_6H_4$ | 0 | 0.5 | (88) | 92.5:7.5 |
| $BnCH_2$ | rt | 3 | (56) | 95.0:5.0 |

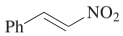


**77** (15 mol %), $H_2O$ (10 eq), NMP/DMSO (1:1), rt, 3 d

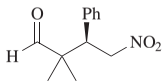


(57) er 79.0:21.0

312



**79** (5 mol %), benzene, 2°, 84 h



(71) er 92.5:7.5

267

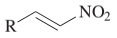
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

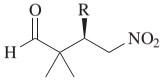
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_4$



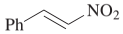


**80a** (10 mol %), $PhCO_2H$ (10 mol %), $H_2O$, neat, temp

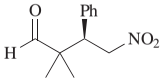


318

| R | Temp | Time (d) | | er |
|---|---|---|---|---|
| *i*-Bu | rt | 2.1 | (56) | 97.0:3.0 |
| 2-$C_4H_3O$ | rt | 1.8 | (95) | 95.5:4.5 |
| 2-$C_4H_3S$ | rt | 2.0 | (96) | 91.0:9.0 |
| Ph | 0° | 4.2 | (92) | 94.5:5.5 |
| Ph | rt | 1.8 | (93) | 94.0:6.0 |
| 4-$BrC_6H_4$ | rt | 2.6 | (95) | 92.5:7.5 |
| 2-$MeC_6H_4$ | rt | 3.5 | (91) | 97.0:3.0 |

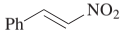


**84** (5 mol %), $CHCl_3$/MeOH (1:1), rt, 48 h

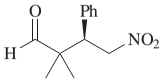


(45) er 53.5:46.5

323

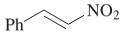


**86** (20 mol %), $CH_2Cl_2$, 0°, 72 h

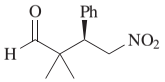


(60) er 88.0:12.0

421

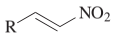


**87** (15 mol %), neat, 27°, 48 h

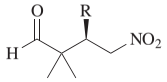


(78) er 77.5:22.5

324

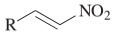


**91** (10 mol %), $H_2O$, rt

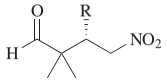


346

| R | Time (h) | | er |
|---|---|---|---|
| Ph | 72 | (80) | 91.5:8.5 |
| 4-$BrC_6H_4$ | 48 | (63) | 86.0:14.0 |
| 4-$ClC_6H_4$ | 48 | (76) | 84.5:15.5 |
| 4-$FC_6H_4$ | 48 | (73) | 83.5:16.5 |
| 3-$O_2NC_6H_4$ | 48 | (86) | 89.5:10.5 |
| 4-$MeC_6H_4$ | 96 | (67) | 77.5:22.5 |

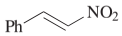


**93** (10 mol %),
2,4-$(O_2N)_2C_6H_3SO_3H$
(2.5 mol %),
4-(*n*-$C_{12}H_{25}$)$C_6H_4SO_3Na$
(10 mol %), 2 M in $CHCl_3$, rt

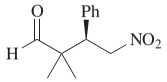


333

| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 45 | (70) | 95.0:5.0 |
| Ph | 36 | (58) | 89.0:11.0 |
| 4-$MeOC_6H_4$ | 52 | (59) | 95.0:5.0 |
| 4-$MeC_6H_4$ | 40 | (53) | 90.0:10.0 |

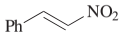


**95e** (10 mol %), $H_2O$, rt, 18 h

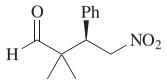


(60) er 93.0:7.0

337



**107** (20 mol %), $Et_2O$, 4°, 6 d



(58) er 91.0:9.0

351

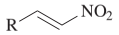
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

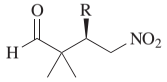
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_4$





Catalyst (*x* mol %),
additive (5 mol %), solvent



356

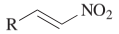
Catalyst **115a** Recycling (R = Ph)

| Run | Time (d) | | er |
|---|---|---|---|
| 1 | 6 | (58) | 91.0:9.0 |
| 2 | 6 | (57) | 90.5:9.5 |
| 3 | 6 | (55) | 91.0:9.0 |
| 4 | 6 | (50) | 90.0:10.0 |
| 5 | 7 | (45) | 88.5:11.5 |

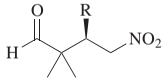
Catalyst **115b** Recycling (R = Ph)

| Run | Time (d) | | er |
|---|---|---|---|
| 1 | 3 | (90) | 92.0:8.0 |
| 2 | 3 | (87) | 91.0:9.0 |
| 3 | 3 | (85) | 91.5:8.5 |
| 4 | 3 | (83) | 90.5:9.5 |
| 5 | 4 | (80) | 89.0:11.0 |

| R | Catalyst | *x* | Additive | Solvent | Temp | Time (d) | | er |
|---|---|---|---|---|---|---|---|---|
| Ph | **115a** | 2 | none | $Et_2O$ | 0° | 6 | (58) | 91.0:9.0 |
| Ph | **115b** | 20 | TFA | MeOH | rt | 3 | (90) | 92.0:8.0 |
| 4-$BrC_6H_4$ | **115b** | 20 | TFA | MeOH | rt | 6 | (33) | 91.5:8.5 |
| 4-$MeC_6H_4$ | **115b** | 20 | TFA | MeOH | rt | 6 | (43) | 90.0:10.0 |



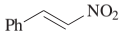
**131** (*x* mol %), $CH_2Cl_2$, rt



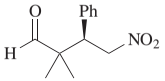
475

| R | *x* | Time (d) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 15 | 2 | (90) | >99.5:0.5 |
| Ph | 30 | 2 | (77) | >99.5:0.5 |
| 4-$BrC_6H_4$ | 15 | 2 | (75) | >99.5:0.5 |
| 2-$ClC_6H_4$ | 15 | 2 | (85) | >99.5:0.5 |
| 4-$ClC_6H_4$ | 15 | 2 | (85) | >99.5:0.5 |

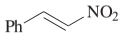
| | | | | |
|---|---|---|---|---|
| 4-$FC_6H_4$ | 15 | 2 | (72) | >99.5:0.5 |
| 4-$MeOC_6H_4$ | 30 | 2 | (76) | >99.5:0.5 |
| 2-$O_2NC_6H_4$ | 15 | 2 | (80) | 99.0:1.0 |
| 3-$O_2NC_6H_4$ | 15 | 2 | (95) | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | 10 | 2 | (90) | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | 15 | 1 | (98) | >99.5:0.5 |
| 4-$MeC_6H_4$ | 30 | 2 | (75) | >99.5:0.5 |
| 4-$NCC_6H_4$ | 15 | 2 | (90) | >99.5:0.5 |



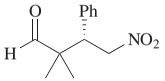
**145b** (20 mol %), hexane, rt, 96 h



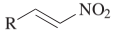
(85) er 84.0:16.0 — 60



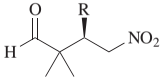
*ent*-**145b** (10 mol %), $PhCO_2H$ (5–20 mol %), $H_2O$, 0°, 1 h; then rt, 10 h



(97) er 96.0:4.0 — 118

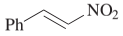


**173** (20 mol %), DMAP (20 mol %), *i*-PrOH, 0°, 72 h

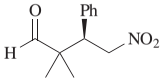


| R | | er |
|---|---|---|
| Ph | (73) | 83.5:16.5 |
| 4-$BrC_6H_4$ | (80) | 85.0:5.0 |

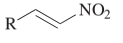
438



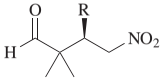
**174** (10 mol %), $CH_2Cl_2$/hexane, rt, 11 d



(36) er 87.5:12.5 — 439

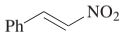


**178** (10 mol %), $CCl_4$, rt, 6 d

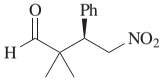


| R | | er |
|---|---|---|
| Ph | (80) | 94.5:5.5 |
| 4-$BrC_6H_4$ | (42) | 88.5:11.5 |

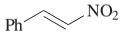
441



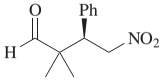
**179** (20 mol %), $CH_2Cl_2$, 20°, 120 h



(65) er 88.0:12.0 — 442



**180** (5 mol %), $H_2O$, rt, 22 h



(99) er 88.0:12.0 — 443

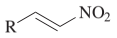
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

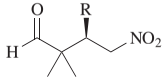
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_4$



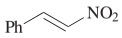


**181** (20 mol %), DMAP (20 mol %), $CHCl_3$, rt

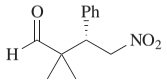


| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 6 | (94) | 99.0:1.0 |
| 2-$C_4H_3S$ | 24 | (99) | 99.5:0.5 |
| Ph | 3 | (83) | 99.5:0.5 |
| 4-$ClC_6H_4$ | 3 | (79) | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 2 | (79) | 99.5:0.5 |
| 4-$O_2NC_6H_4$ | 3 | (74) | 99.5:0.5 |
| PhCH=CH | 24 | (53) | 99.0:1.0 |

444

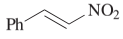


**183** (15 mol %), $CHCl_3$, rt, 7 d

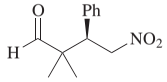


(14) er 70.5:29.5

446

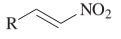


**187** (10 mol %), $PhCO_2H$ (5 mol %), $CH_2Cl_2$, rt, 60 h

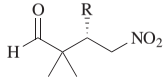


(71) er 90.0:10.0

449

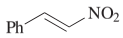


**191** (10 mol %), DMAP (10 mol %), MeOH, rt, 96 h

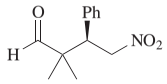


| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (85) | 97.5:2.5 |
| *c*-$C_6H_{11}$ | (86) | 97.5:2.5 |
| 4-$BrC_6H_4$ | (82) | 97.0:3.0 |

454

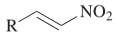


**203** (2 mol %), $HCO_2H$ (20 mol %), $H_2O$, rt, 12–18 h

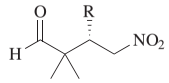


(90) er 96.5:3.5

471



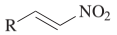
**204b** (20 mol %), $CH_2Cl_2$



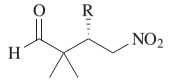
476

| R | Temp | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 0° | 72 | (71) | 98.0:2.0 |
| *c*-$C_6H_{11}$ | rt | 120 | (8) | 94.0:6.0 |
| Ph | 0° | 72 | (82) | 99.0:1.0 |
| Ph | rt | 0 | (92) | 97.0:3.0 |
| Ph | rt | 10 | (85) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 0° | 72 | (81) | 99.5:0.5 |
| 4-$BrC_6H_4$ | rt | 4 | (86) | 97.0:3.0 |
| 4-$FC_6H_4$ | 0° | 72 | (72) | 99.5:0.5 |
| 4-$FC_6H_4$ | rt | 5 | (87) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 0° | 72 | (49) | 99.0:1.0 |
| 4-$MeOC_6H_4$ | rt | 6 | (88) | 96.5:3.5 |
| $BnCH_2$ | rt | 120 | (41) | 94.0:6.0 |





**204b** (10 mol %), $CH_2Cl_2$



477

| R | Temp | Time (h) | | er |
|---|---|---|---|---|
| Me | rt | 24 | (60) | 95.5:4.5 |
| 2-$C_4H_3O$ | rt | 5 | (91) | 93.5:6.5 |
| 2-$C_4H_3O$ | 0° | 72 | (71) | 98.0:2.0 |
| 2-$C_4H_3S$ | 0° | 72 | (96) | 97.5:2.5 |
| 3-$C_5H_4N$ | 0° | 72 | (78) | 96.5:3.5 |
| *n*-PrCH=CH | rt | 16 | (91) | 97.0:3.0 |
| *c*-$C_6H_{11}$ | rt | 120 | (8) | 94.0:6.0 |
| Ph | 0° | 72 | (82) | 99.0:1.0 |
| Ph | rt | 5 | (92) | 97.0:3.0 |
| 2-$BrC_6H_4$ | 0° | 72 | (83) | 96.0:4.0 |
| 3-$BrC_6H_4$ | 0° | 72 | (86) | 96.0:4.0 |
| 3-$BrC_6H_4$ | rt | 5 | (89) | 93.0:7.0 |

| R | Temp | Time (h) | | er |
|---|---|---|---|---|
| 4-$BrC_6H_4$ | 0° | 72 | (81) | 99.5:0.5 |
| 4-$BrC_6H_4$ | rt | 4 | (86) | 97.0:3.0 |
| 4-$FC_6H_4$ | 0° | 72 | (72) | 99.5:0.5 |
| 4-$FC_6H_4$ | rt | 5 | (87) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 0° | 72 | (92) | 98.0:2.0 |
| 4-$O_2NC_6H_4$ | 0° | 72 | (87) | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | rt | 5 | (91) | 95.0:5.0 |
| 4-$(MeO_2C)C_6H_4$ | 0° | 72 | (94) | 98.0:2.0 |
| $BnCH_2$ | rt | 120 | (41) | 94.0:6.0 |
| PhCH=CH | 0° | 72 | (57) | 98.0:2.0 |
| PhCH=CH | rt | 8 | (89) | 95.5:4.5 |

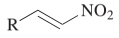
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

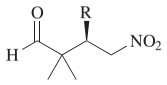
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_4$





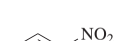
Catalyst (10 mol %), DABCO (40 mol %), $CHCl_3$, rt, 8–48 h



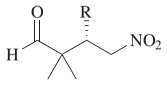
478

| R | Catalyst | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | **205b** | (95) | 98.5:1.5 |
| 2-$C_4H_3O$ | **206** | (85) | 98.5:1.5[a] |
| 2-$C_4H_3S$ | **205b** | (92) | 97.5:2.5 |
| 2-$C_4H_3S$ | **206** | (88) | 95.0:5.0[a] |
| Ph | **205b** | (88) | 98.5:1.5 |
| 2-$BrC_6H_4$ | **205b** | (91) | 97.5:2.5 |
| 4-$BrC_6H_4$ | **205b** | (86) | 98.0:2.0 |
| 4-$BrC_6H_4$ | **206** | (85) | 95.5:4.5[a] |
| 2-$ClC_6H_4$ | **205b** | (86) | 97.5:2.5 |
| 4-$ClC_6H_4$ | **205a** | (85) | 99.0:1.0 |
| 4-$ClC_6H_4$ | **205b** | (80) | 97.5:2.5 |
| 4-$FC_6H_4$ | **205b** | (87) | 97.5:2.5 |

| R | Catalyst | | er |
|---|---|---|---|
| 4-$FC_6H_4$ | **206** | (84) | 95.5:4.5[a] |
| 2-$MeOC_6H_4$ | **205b** | (93) | 97.0:3.0 |
| 2-$MeOC_6H_4$ | **206** | (96) | 96.5:3.5[a] |
| 4-$MeOC_6H_4$ | **205b** | (95) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | **206** | (86) | 96.5:3.5[a] |
| 3,4-$(MeO)_2C_6H_3$ | **205b** | (93) | 98.0:2.0 |
| 2-$O_2NC_6H_4$ | **205b** | (93) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | **205b** | (96) | 98.0:2.0 |
| 4-$MeC_6H_4$ | **205b** | (91) | 98.0:2.0 |
| 4-$MeC_6H_4$ | **206** | (85) | 97.5:2.5[a] |
| 4-$CF_3C_6H_4$ | **205b** | (85) | 95.0:5.0 |
| 1-Np | **205b** | (84) | 97.5:2.5 |



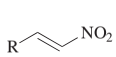
**208** (20 mol %), $CHCl_3$, rt



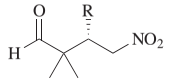
479

| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 2 | (92) | 98.0:2.0 |
| 5-Cl-2-$C_4H_2S$ | 2 | (92) | 96.5:3.5 |
| Ph | 3 | (89) | 98.5:1.5 |
| 4-$BrC_6H_4$ | 6 | (77) | 98.0:2.0 |
| 4-$ClC_6H_4$ | 6 | (82) | 98.5:1.5 |
| 4-$FC_6H_4$ | 6 | (82) | 98.5:1.5 |

| | | | |
|---|---|---|---|
| 2-$MeOC_6H_4$ | 12 | (74) | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 12 | (74) | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | 2 | (90) | 99.0:1.0 |
| 4-$O_2NC_6H_4$ | 2 | (88) | 98.5:1.5 |
| PhCH=CH | 24 | (70) | 98.0:2.0 |
| 1-Np | 24 | (64) | 98.0:2.0 |
| 2-Np | 24 | (57) | 98.0:2.0 |



**208** (10 mol %), $H_2O$, rt



| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 6 | (86) | 95.5:4.5 |
| 5-Cl-2-$C_4H_2S$ | 6 | (85) | 95.0:5.0 |
| Ph | 5 | (88) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 30 | (65) | 95.5:4.5 |
| 4-$ClC_6H_4$ | 30 | (65) | 96.0:4.0 |
| 4-$FC_6H_4$ | 30 | (78) | 96.0:4.0 |
| 2-$MeOC_6H_4$ | 48 | (86) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 48 | (89) | 96.0:4.0 |
| 3-$O_2NC_6H_4$ | 4 | (82) | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | 4 | (76) | 95.5:4.5 |
| PhCH=CH | 72 | (86) | 95.0:5.0 |
| 1-Np | 72 | (62) | 95.0:5.0 |
| 2-Np | 72 | (64) | 96.0:4.0 |

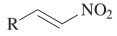
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

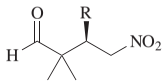
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_4$



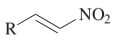


**209** (20 mol %), $CHCl_3$, rt

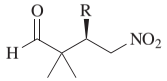


479

| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 2 | (89) | 98.0:2.0 |
| 5-Cl-2-$C_4H_2S$ | 2 | (90) | 97.5:2.5 |
| Ph | 3 | (91) | 99.0:1.0 |
| 4-$BrC_6H_4$ | 6 | (79) | 98.5:1.5 |
| 4-$ClC_6H_4$ | 6 | (84) | 98.5:1.5 |
| 4-$FC_6H_4$ | 6 | (83) | 99.0:1.0 |
| 2-$MeOC_6H_4$ | 12 | (76) | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 12 | (72) | 98.5:1.5 |
| 3-$O_2NC_6H_4$ | 2 | (87) | 99.0:1.0 |
| 4-$O_2NC_6H_4$ | 2 | (86) | 99.0:1.0 |
| PhCH=CH | 24 | (68) | 98.5:1.5 |
| 1-Np | 24 | (66) | 97.5:2.5 |
| 2-Np | 24 | (61) | 98.0:2.0 |

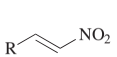


**209** (10 mol %), $H_2O$, rt

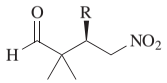


479

| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 6 | (87) | 96.0:4.0 |
| 5-Cl-2-$C_4H_2S$ | 6 | (82) | 95.0:5.0 |
| Ph | 5 | (89) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 30 | (68) | 95.0:5.0 |
| 4-$ClC_6H_4$ | 30 | (62) | 96.5:3.5 |
| 4-$FC_6H_4$ | 30 | (79) | 96.5:3.5 |
| 2-$MeOC_6H_4$ | 48 | (84) | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 48 | (86) | 96.0:4.0 |
| 3-$O_2NC_6H_4$ | 4 | (79) | 95.5:4.5 |
| 4-$O_2NC_6H_4$ | 4 | (78) | 96.0:4.0 |
| PhCH=CH | 72 | (88) | 95.5:4.5 |
| 1-Np | 72 | (65) | 95.5:4.5 |
| 2-Np | 72 | (65) | 96.0:4.0 |



**210** (20 mol %), [bmim][$BF_4$], rt



480

Catalyst Recycling (R = Ph)

| Run | Time (h) | | er |
|---|---|---|---|
| 1 | 24 | (80) | 89.0:11.0 |
| 2 | 30 | (96) | 89.5:10.5 |
| 3 | 36 | (81) | 89.5:10.5 |
| 4 | 48 | (88) | 88.0:12.0 |

| R | Time (h) | | er |
|---|---|---|---|
| Ph | 36 | (90) | 88.5:11.5 |
| 4-$ClC_6H_4$ | 36 | (90) | 88.5:11.5 |
| 2-$MeOC_6H_4$ | 72 | (80) | 87.0:13.0 |
| 4-$O_2NC_6H_4$ | 30 | (91) | 87.0:13.0 |
| 4-$MeC_6H_4$ | 36 | (91) | 87.5:12.5 |

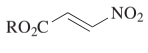
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

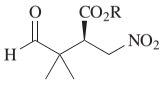
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_4$



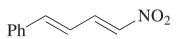


**204a** (16 mol %),
**204b** (4 mol %),
$CH_2Cl_2$, rt, 24 h

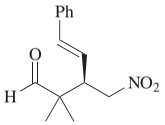


| R | | er |
|---|---|---|
| Me | (71) | 96.5:3.5 |
| Et | (76) | 96.0:4.0 |
| *t*-Bu | (74) | 94.5:5.5 |
| Bn | (80) | 96.0:4.0 |

481

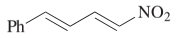


**34** (5 mol %),
**85** (5 mol %),
$CH_2Cl_2$, rt, 48 h

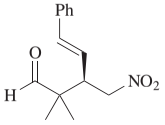


(77) er 84.0:16.0

325



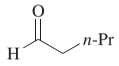
**145b** (10 mol %),
$H_2O$/EtOH (5 %), rt, 5 d

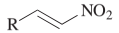


(72) er 94.0:6.0

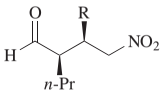
121

$C_5$



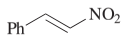


**1** (10 mol %),
**118** (10 mol %),
toluene, 0°

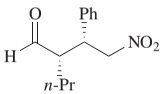


| R | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| Ph | 20 | (86) | 84:16 | 95.5:4.5 | 95.0:5.0 |
| 4-$BrC_6H_4$ | 18 | (98) | 77:23 | 90.5:9.5 | 93.0:7.0 |
| 4-$ClC_6H_4$ | 18 | (95) | 78:22 | 91.0:9.0 | 91.5:8.5 |
| 4-$MeOC_6H_4$ | 28 | (84) | 84:16 | 93.0:7.0 | 92.5:7.5 |
| 4-$MeC_6H_4$ | 28 | (91) | 87:13 | 94.5:5.5 | 93.0:7.0 |

343

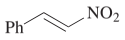


**6** (15 mol %),
$CHCl_3$, –25°, 15 h

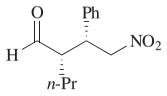


(83) *syn*/*anti* = 94:6
er 78.0:22.0

251

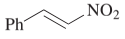


**25** (10 mol %),
$Me_2PEG$ (10 mol %),
$H_2O$, rt, 24 h

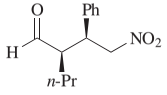


(90) *syn/anti* = 87:13
er 74.0:26.0

264

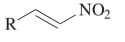


**81** (5 mol %),
2-$MeC_6H_4CO_2H$ (5 mol %),
*n*-hexane, rt, 12 h

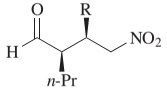


(84) *syn/anti* = 97.5:2.5
er 71.0:29.0

319

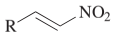


**168a** (3 mol %),
**211** (21 mol %),
$H_2O$, rt

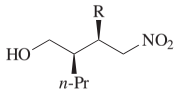


482

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 5 | (91) | 99:1 | 99.5:0.5 |
| Ph | 5 | (88) | 96:4 | 99.5:0.5 |
| 4-$BrC_6H_4$ | 24 | (85) | 95:5 | 99.5:0.5 |
| 3-$MeOC_6H_4$ | 10 | (93) | 94:6 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 24 | (81) | 96:4 | 99.5:0.5 |



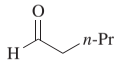
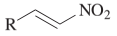
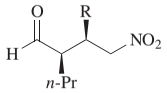
1. Catalyst (20 mol %),
$PhCO_2H$ (20 mol %), $H_2O$, rt
2. $NaBH_4$, EtOH, 0°



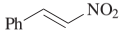
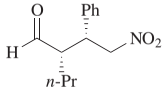
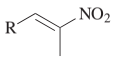
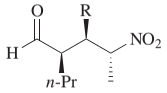
167

| R | Catalyst | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Ph | **172** | 72 | (55) | >98:2 | 98.5:1.5 |
| Ph | **207b** | 48 | (68) | >98:2 | 92.5:7.5 |
| 4-$MeOC_6H_4$ | **207b** | 72 | (42) | >98:2 | 99.0:1.0 |

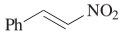
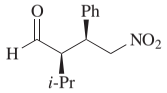
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

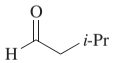
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **185** (10 mol %), $CHCl_3$, –45 to 0° |  | 448 |

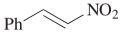
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 20 | (96) | — | 97.5:2.5 |
| Bn | 48 | (72) | 95:5 | 96.5:3.5 |

| | | | | |
|---|---|---|---|---|
| |  | **196** (10 mol %), DMAP (10 mol %), MeOH, rt, 72 h |  | (74) *syn*/*anti* = 59:41 er 95.0:5.0 | 458 |
| |  | **145b** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt |  | | 463 |

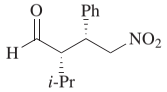
| R | Time (h) | | dr | er |
|---|---|---|---|---|
| Ph | 48 | (74) | 94:4:2 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 48 | (60) | 91:5:4 | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | 10 | (90) | 92:5:2:1 | >99.5:0.5 |
| 2-Np | 24 | (88) | 96:3:1 | 97.5:2.5 |

| | | | | |
|---|---|---|---|---|
| |  | **1** (15 mol %), [bmim][$BF_4$], rt, 24 h |  | (80) *syn*/*anti* = 94:6 er 60.0:40.0 | 433 |

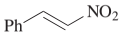


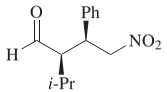

**3** (15 mol %), microwaves (15 W), 27°, 1 h



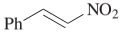

(97) *syn*/*anti* = 90:10, er 89.0:11.0 — 310



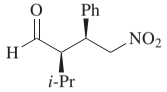

**6** (20 mol %), THF, rt, 22 h




(80) *syn*/*anti* = 80:20, er 87.5:12.5 — 253

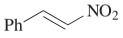



Catalyst (15 mol %), TFA (5 mol %), rt, 60 h

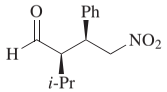



255

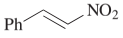
| Catalyst | | dr | er |
|---|---|---|---|
| **12** | (73) | 90:10 | 88.5:11.5 |
| **13** | (100) | 90:10 | 86.0:14.0 |



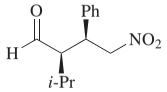

**13** (10 mol %), TFA (2 mol %), neat, 27 h



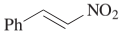

(87) dr 95:5, er 68.0:32.0 — 275



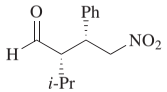

**15** (10 mol %), TFA (2.5 mol %), rt, 36 h




(80) *syn*/*anti* = 97:3, er 70.0:30.0 — 326

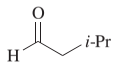
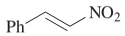
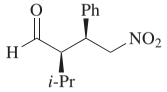
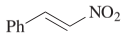
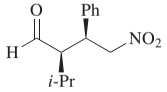
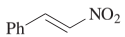
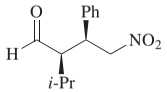
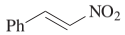
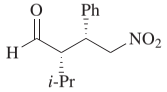
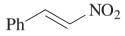
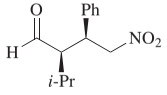
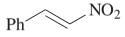
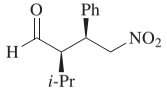
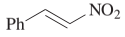
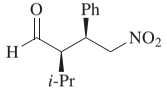


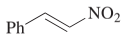

**22** (15 mol %), TFA (5 mol %), rt, 60 h



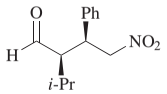

(82) *syn*/*anti* = 98:2, er 79.0:21.0 — 262

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **34** (20 mol %), 2-$HOC_6H_4CO_2H$ (20 mol %), *i*-PrOH, rt |  | (85) *syn*/*anti* = 80:20 er 78.0:22.0 | 273 |
| |  | **34** (5 mol %), **35** (5 mol %), cyclohexane/*n*-butanol (1:1), rt, 12 h |  | (90)[b] *syn*/*anti* = 79:21 er 85.0:15.0 | 274 |
| |  | **39** (15 mol %), TFA (5 mol %), neat, rt, 144 h |  | (46) *syn*/*anti* = 93:7 er 71.0:29.0 | 276 |
| |  | **68** (30 mol %), $PhCO_2H$ (20 mol %), toluene, rt, 4 d |  | (23) *syn*/*anti* = 99:1 er 90.5:9.5 | 279 |
| |  | **84** (5 mol %), $CHCl_3$/MeOH (1:1), rt, 48 h |  | (94) *syn*/*anti* > 98:2 er 53.5:46.5 | 323 |
| |  | **86** (20 mol %), $CH_2Cl_2$, 0°, 59 h |  | (70) *syn*/*anti* = 96:4 er 92.5:7.5 | 327 |
| |  | **103** (20 mol %), $H_2O$, rt, 24 h |  | (80) *syn*/*anti* = 97:3 er 80.5:19.5 | 348 |

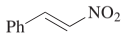


**195** (5 mol %),
$PhCO_2H$ (5 mol %),
$CH_2Cl_2/H_2O$ (2.5:1), rt, 24 h

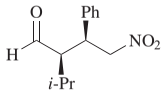


(33) *syn/anti* = 87:13
er 92.0:8.0

457

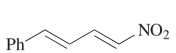


**212** (10 mol %),
$2,4\text{-}(O_2N)_2C_6H_3SO_3H$
(5 mol %), $CHCl_3$, 0°

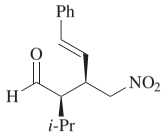


(93) *syn/anti* = 98:2
er 61.0:39.0

347

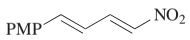


**34** (5 mol %),
**85** (5 mol %),
$CH_2Cl_2$, rt, 48 h

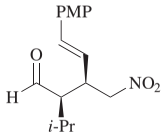


(76) *syn/anti* = 59:41
er 91.5:8.5

325

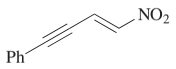


**145b** (5 mol %),
$CHCl_3$, rt, 4 d

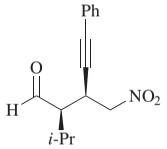


(94) *syn/anti* = 95:5
er 99.0:1.0

121



**145b** (*x* mol %), $CHCl_3$



| *x* | Temp (°) | | *syn/anti* | er | |
|---|---|---|---|---|---|
| 5 | –25 | (83) | 94:6 | 97.0:3.0 | 121 |
| 10 | –10 | (83) | 96:4 | 99.5:0.5 | 483 |

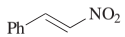
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

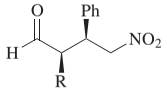
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5–6}$





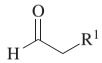
**1** (10 mol %), **118** (10 mol %), toluene, 0°

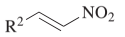


343

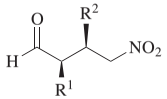
| R | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| *n*-Pr | 20 | (86) | 84:16 | 95.5:4.5 | 95.0:5.0 |
| *i*-Pr | 45 | (64) | 95:5 | 95.5:4.5 | — |
| *n*-Bu | 20 | (80) | 86:14 | 95.5:4.5 | 95.5:4.5 |

$C_5$





**1** (20 mol %), **169b** (5 mol %), benzene, rt

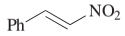


434

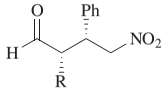
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| *n*-Pr | Ph | (86) | 15:1 | 88.0:12.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | (50) | 14:1 | 72.0:28.0 |
| *n*-Pr | 4-$MeC_6H_4$ | (65) | 15:1 | 75.0:25.0 |
| *i*-Pr | Ph | (88) | 38:1 | 87.5:12.5 |
| *i*-Pr | 4-$BrC_6H_4$ | (80) | 35:1 | 80.0:20.0 |

$C_{5–8}$





**3** (15 mol %), $CHCl_3$

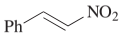


251

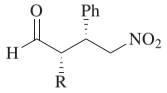
| R | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | –25° | 96 | (98) | 96:4 | 86.5:15.5 |
| *n*-Pr | rt | 15 | (99) | 72:28 | 81.0:19.0 |
| *i*-Pr | rt | 48 | (99) | 87:13 | 80.5:19.5 |
| Ph | rt | 48 | (19) | 72:28 | 63.0:37.0 |

$C_5$





**3** (15 mol %),
HCl (*x* mol %), $CHCl_3$

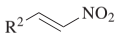


250

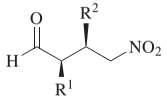
| R | *x* | Temp | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | 0 | –25° | 96 | (98) | 96:4 | 86.5:14.5 |
| *n*-Pr | 0 | rt | 15 | (99) | 72:28 | 81.0:19.0 |
| *n*-Pr | 15 | 0° | 48 | (82) | 96:4 | 86.0:14.0 |
| *n*-Pr | 15 | rt | 15 | (99) | 85:15 | 83.5:16.5 |
| *i*-Pr | 0 | rt | 48 | (99) | 87:13 | 80.5:19.5 |
| *i*-Pr | 15 | rt | 120 | (95) | 95:5 | 84.0:16.0 |

$C_{5–7}$





**16b** (20 mol %), *i*-PrOH, 0°

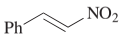


73

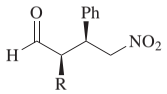
| $R^1$ | $R^2$ | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | Ph | 20 | (99) | 50:1 | 98.0:2.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | 24 | (86) | 20:1 | 99.5:0.5 |
| *n*-Pr | 2-$CF_3C_6H_4$ | 28 | (63) | 22:1 | 97.0:3.0 |
| *n*-Bu | Ph | 24 | (94) | 30:1 | 99.5:0.5 |
| *n*-Bu | $BnCH_2$ | 24 | (76) | 50:1 | 61.0:39.0 |
| *n*-$C_5H_{11}$ | Ph | 24 | (91) | 50:1 | 98.5:1.5 |

$C_{5–8}$





**51** (10 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
$H_2O$, rt



288

| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| *n*-Pr | 19 | (95) | 97:3 | 87.0:13.0 |
| *n*-$C_6H_{13}$ | 19 | (94) | 88:12 | 87.0:13.0 |

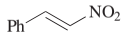
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

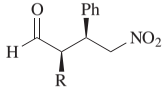
*Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.*

$C_{5–9}$





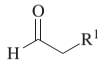
**79** (5 mol %), benzene, 2°

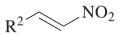


267

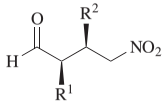
| R | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| *i*-Pr | 48 | (86) | 83:17 | 96.5:3.5 | — |
| *n*-$C_4H_9$ | 72 | (84) | 79:21 | 95.0:5.0 | — |
| *n*-$C_5H_{11}$ | 72 | (85) | 90:10 | 97.5:2.5 | — |
| Bn | 48 | (78) | 76:24 | 91.5:8.5 | 92.0:8.0 |

$C_{5–6}$





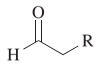
**107** (20 mol %), $Et_2O$, 4°, 6 d

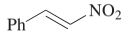


351

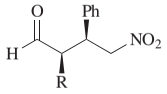
| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | Ph | (49) | 89:11 | 82.0:18.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | (29) | 92:8 | 83.5:16.5 |
| *n*-Pr | 4-$MeC_6H_4$ | (60) | 96:4 | 83.5:16.5 |
| *i*-Pr | Ph | (53) | 96:4 | 83.0:17.0 |
| *i*-Pr | 4-$MeC_6H_4$ | (64) | 97:3 | 86.5:13.5 |
| *n*-Bu | Ph | (64) | 97:3 | 84.0:16.0 |
| *n*-Bu | 4-$MeC_6H_4$ | (60) | 96:4 | 83.5:16.5 |

$C_5$





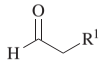
Catalyst ($x$ mol %), $CHCl_3$

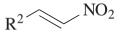


355

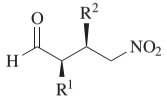
| R | Catalyst | $x$ | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|---|
| *n*-Pr | **113** | 10 | –25° | 40 | (94) | 95:5 | 92.0:8.0 |
| *n*-Pr | **113** | 15 | –40° | 96 | (89) | 95:5 | 94.0:6.0 |
| *n*-Pr | **113** | 20 | rt | 4 | (100) | 73:27 | 89.0:11.0 |
| *i*-Pr | **113** | 20 | rt | 72 | (86) | 67:33 | 83.5:16.5 |
| *i*-Pr | **114** | 20 | rt | 18 | (99) | >99.5:0.5 | 83.5:16.5 |

$C_{5\text{-}6}$





Catalyst ($x$ mol %),
additive (5 mol %), solvent



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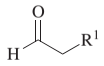
| $R^1$ | $R^2$ | Catalyst | $x$ | Additive | Solvent | Temp | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|---|---|---|---|
| *n*-Pr | Ph | **115a** | 2 | none | $Et_2O$ | 0° | 6 | (49) | 89:11 | 82.0:18.0 |
| *n*-Pr | Ph | **115b** | 20 | TFA | MeOH | rt | 2 | (99) | 97:3 | 72.5:27.5 |
| *n*-Pr | 4-$BrC_6H_4$ | **115a** | 2 | none | $Et_2O$ | 0° | 6 | (<5) | — | — |
| *n*-Pr | 4-$BrC_6H_4$ | **115b** | 20 | TFA | MeOH | rt | 2 | (91) | 92:8 | 70.5:29.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | **115a** | 2 | none | $Et_2O$ | 0° | 6 | (29) | 92:8 | 83.5:16.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | **115b** | 20 | TFA | MeOH | rt | 2 | (91) | 92:8 | 72.0:28.0 |
| *n*-Pr | 4-$MeC_6H_4$ | **115a** | 2 | none | $Et_2O$ | 0° | 6 | (38) | 96:4 | 84.0:16.0 |
| *n*-Pr | 4-$MeC_6H_4$ | **115b** | 20 | TFA | MeOH | rt | 2 | (98) | 93:7 | 72.0:28.0 |
| *n*-Pr | 2-$CF_3C_6H_4$ | **115a** | 2 | none | $Et_2O$ | 0° | 6 | (<5) | — | — |
| *n*-Pr | 2-$CF_3C_6H_4$ | **115b** | 20 | TFA | MeOH | rt | 2 | (98) | 93:7 | 70.5:29.5 |
| *i*-Pr | Ph | **115a** | 2 | none | $Et_2O$ | 0° | 6 | (53) | 96:4 | 83.0:17.0 |
| *i*-Pr | Ph | **115b** | 20 | TFA | MeOH | rt | 2 | (99) | 91:9 | 66.5:33.5 |
| *n*-Bu | Ph | **115a** | 2 | none | $Et_2O$ | 0° | 6 | (64) | 97:3 | 84.0:16.0 |
| *n*-Bu | Ph | **115b** | 20 | TFA | MeOH | rt | 2 | (99) | 78:22 | 73.0:27.0 |

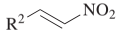
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

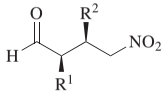
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_5$



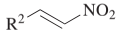


Catalyst (5 mol %), $CH_2Cl_2$, rt, 48 h

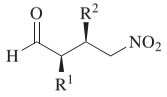


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| $R^1$ | $R^2$ | Catalyst | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | Ph | **123** | (98) | 98:2 | 99.0:1.0 |
| *n*-Pr | Ph | **124** | (98) | 99:1 | 99.0:1.0 |
| *n*-Pr | 4-$ClC_6H_4$ | **123** | (98) | 98:2 | 99.0:1.0 |
| *n*-Pr | 4-$ClC_6H_4$ | **124** | (98) | 99:1 | 99.0:1.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | **123** | (98) | 78:22 | 85.5:14.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | **124** | (98) | 91:9 | 91.0:9.0 |
| *n*-Pr | 4-$MeC_6H_4$ | **123** | (38) | 53:47 | 68.5:31.5 |
| *n*-Pr | 4-$MeC_6H_4$ | **124** | (34) | 52:48 | 60.5:39.5 |
| *i*-Pr | Ph | **123** | (98) | 68:32 | 63.0:37.0 |
| *i*-Pr | Ph | **124** | (98) | 54:46 | 79.0:21.0 |



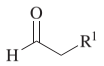
**145b** (*x* mol %), hexane

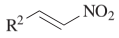


60

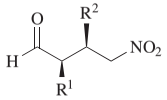
| $R^1$ | $R^2$ | *x* | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|---|
| *n*-Pr | Ph | 10 | 0° | 48 | (74) | 95:5 | 99.5:0.5 |
| *i*-Pr | Ph | 20 | rt | 46 | (72) | 93:7 | 99.5:0.5 |
| *i*-Pr | 2-Np | 20 | rt | 24 | (77) | 94:6 | 99.5:0.5 |

$C_{5-6}$





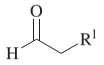
**145b** (2 mol %),
$PhCO_2H$ (20 mol %),
$H_2O$, 0°

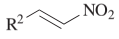


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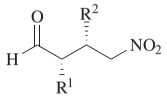
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| allyl | $EtO_2C$ | (94) | 85:15 | 99.5:0.5 |
| allyl | 2-$C_4H_3O$ | (70) | 82:18 | 86.5:13.5 |
| allyl | *n*-$C_5H_{11}$ | (69) | 86:14 | 99.5:0.5 |
| allyl | Ph | (98) | 96:4 | 99.5:0.5 |
| allyl | 4-$FC_6H_4$ | (91) | 92:8 | 99.0:1.0 |
| propargyl | Ph | (91) | 93:7 | 97.5:2.5 |
| $CH_2$=$CH(CH_2)_2$ | Ph | (93) | 97:3 | >99.5:0.5 |

$C_{5-11}$





**145b** (*x* mol %),
$PhCO_2H$ (5–20 mol %),
$H_2O$, 0°, 1 h; then rt



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| $R^1$ | $R^2$ | *x* | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | *n*-Bu | 2 | 2 | (83) | 94:6 | >99.5:0.5 |
| *n*-Pr | 2-$C_4H_3O$ | 0.5 | 6 | (96) | 98:2 | >99.5:0.5 |
| *n*-Pr | 2-$C_4H_3O$ | 1 | 2 | (95) | 98:2 | >99.5:0.5 |
| *n*-Pr | *c*-$C_6H_{11}$ | 2 | 12 | (88) | 94:6 | >99.5:0.5 |
| *n*-Pr | *c*-$C_6H_{11}$ | 2 | 44 | (78) | 94:6 | >99.5:0.5 |
| *n*-Pr | Ph | 1 | 6 | (96) | 98:2 | >99.5:0.5 |
| *n*-Pr | 2-$BrC_6H_4$ | 1 | 4 | (98) | 95:5 | >99.5:0.5 |
| *n*-Pr | 2-$BrC_6H_4$ | 1 | 24 | (95) | 92:8 | >99.5:0.5 |
| *n*-Pr | 4-$BrC_6H_4$ | 1 | 13 | (87) | 96:4 | >99.5:0.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | 1 | 12 | (86) | 97:3 | >99.5:0.5 |
| *i*-Pr | *n*-Bu | 1 | 7 | (96) | 97:3 | >99.5:0.5 |
| Bn | *n*-Bu | 2 | 2.5 | (81) | 96:4 | >99.5:0.5 |
| $CH_2$=$CH(CH_2)_7$ | *n*-Bu | 2 | 5 | (85) | 94:6 | >99.5:0.5 |
| $CH_2$=$CH(CH_2)_7$ | Ph | 1 | 5 | (86) | 96:4 | >99.5:0.5 |

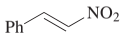
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

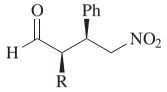
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-7}$





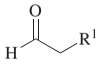
**166** (10 mol %), $CH_2Cl_2$, rt, times

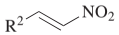


435, 421

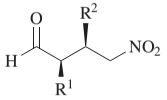
| R | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| *n*-Pr | 27 | (98) | 82:18 | 99.5:0.5 |
| *n*-$C_5H_{11}$ | 48 | (91) | 75:25 | 99.0:1.0 |

$C_{5-9}$





**168a** (3 mol %), $PhCO_2H$ (30 mol %), $H_2O$, rt



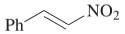
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Catalyst Recycling ($R^1$ = *n*-Pr; $R^2$ = Ph)

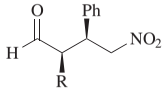
| Run | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|
| 1 | 5 | (97) | 97:3 | 99.5:0.5 |
| 2 | 5 | (96) | 97:3 | 99.5:0.5 |
| 3 | 5 | (97) | 96:4 | 99.5:0.5 |
| 4 | 5 | (97) | 97:3 | 99.5:0.5 |
| 5 | 6 | (93) | 96:4 | 99.5:0.5 |
| 6 | 8 | (95) | 97:3 | 99.5:0.5 |
| 7 | 12 | (68) | 97:3 | 99.5:0.5 |
| 8 | 24 | (15) | 97:3 | 99.5:0.5 |

| $R^1$ | $R^2$ | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | 2-$C_4H_3O$ | 5 | (93) | 97:3 | >99.5:0.5 |
| *n*-Pr | Ph | 5 | (97) | 97:3 | >99.5:0.5 |
| *n*-Pr | 4-$BrC_6H_4$ | 24 | (86) | 96:4 | >99.5:0.5 |
| *n*-Pr | 2-$ClC_6H_4$ | 24 | (74) | 97:3 | 99.0:1.0 |
| *n*-Pr | 3-$MeOC_6H_4$ | 12 | (96) | 95:5 | 99.5:0.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | 22 | (83) | 95:5 | 99.0:1.0 |
| *n*-Pr | 2-$CF_3C_6H_4$ | 72 | (78) | 96:4 | >99.5:0.5 |
| *i*-Pr | Ph | 21 | (84) | 97:3 | >99.5:0.5 |
| *n*-Bu | Ph | 5 | (94) | 97:3 | 99.5:0.5 |
| *n*-$C_5H_{11}$ | Ph | 8 | (99) | 98:2 | 99.5:0.5 |
| *n*-$C_7H_{15}$ | Ph | 22 | (99) | 97:3 | 99.5:0.5 |
| Bn | *n*-Bu | 5 | (76) | 98:2 | 99.5:0.5 |





**168a** (3 mol %), **211** (21 mol %), $H_2O$, rt

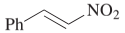


482

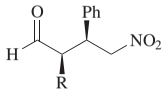
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Pr | 20 | (85) | 95:5 | >99.5:0.5 |
| *n*-Bu | 5 | (96) | 96:4 | 99.5:0.5 |
| *n*-$C_5H_{11}$ | 8 | (95) | 96:4 | 99.5:0.5 |
| *n*-$C_7H_{15}$ | 20 | (99) | 97:3 | 99.5:0.5 |
| Bn | 5 | (74) | 95:5 | 99.5:0.5 |

$C_5$





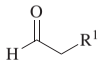
**168b** (10 mol %), $PhCF_3$, rt

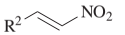


436

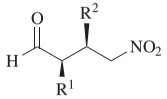
| R | Time (h) | | dr | er |
|---|---|---|---|---|
| *n*-Pr | 26 | (92) | 25:1 | 99.0:1.0 |
| *i*-Pr | 36 | (86) | 16:1 | >99.5:0.5 |

$C_{5–6}$





**170** (20 mol %), THF, rt



139, 253

| $R^1$ | $R^2$ | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *i*-Pr | 2-$C_4H_3S$ | 2 | (82) | 86:14 | 85.5:14.5 |
| *i*-Pr | *n*-$C_5H_{11}$ | 3 | (42) | 89:11 | — |
| *i*-Pr | Ph | 3 | (78) | 92:8 | 86.0:14.0 |
| *i*-Pr | 2-$CF_3C_6H_4$ | 3 | (77) | 98:2 | 89.0:11.0 |
| *i*-Pr | 1-Np | 3 | (67) | 96:4 | 87.5:12.5 |
| *i*-Pr | 2-Np | 3 | (96) | 89:11 | 84.5:15.5 |
| *n*-Bu | Ph | 1 | (87) | 85:15 | 84.5:15.5 |

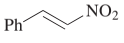
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

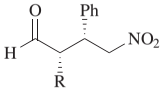
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-8}$





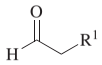
**171** (15 mol %), $CHCl_3$, rt

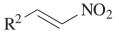


437

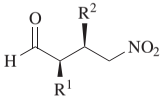
| R | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | 3 | (88) | 87:13 | 94.5:5.5 |
| *i*-Pr | 3 | (85) | 94:6 | 94.0:6.0 |
| *c*-$C_6H_{11}$ | 13 | (88) | 95:5 | 95.0:5.0 |

$C_{5-7}$





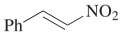
**173** (20 mol %), DMAP (20 mol %), *i*-PrOH, 0°



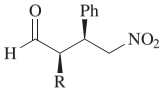
438

| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | Ph | 24 | (66) | 98:2 | 95.0:5.0 |
| *i*-Pr | Ph | 72 | (87) | 89:11 | 95.0:5.0 |
| *i*-Pr | 4-$BrC_6H_4$ | 72 | (75) | 88:12 | 95.5:4.5 |
| *i*-Pr | 1-Np | 72 | (89) | 90:10 | 93.5:6.5 |
| *n*-Bu | Ph | 24 | (74) | 98:2 | 92.0:8.0 |
| *n*-$C_5H_{11}$ | Ph | 24 | (79) | 89:11 | 97.0:3.0 |





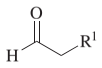
**174** (10 mol %), $CH_2Cl_2$/hexane, 0°

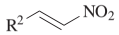


439

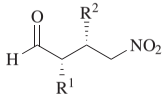
| R | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Pr | 6 | (66) | 89:11 | 84.0:16.0 |
| *n*-$C_5H_{11}$ | 5 | (—) | 96:4 | 87.5:12.5 |

$C_{5-9}$





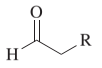
**175** (*x* mol %),
NMM (1–5 mol %),
$CHCl_3$/*i*-PrOH (9:1)

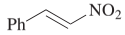


130

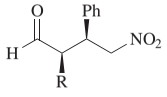
| $R^1$ | $R^2$ | *x* | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|---|
| *n*-Pr | Ph | 1 | rt | 12 | (94) | 15:1 | 96.0:4.0 |
| *n*-Pr | Ph | 3 | –15° | 48 | (90) | 90:1 | 98.0:2.0 |
| *i*-Pr | Ph | 3 | rt | 24 | (88) | 50:1 | 96.0:4.0 |
| *i*-Pr | Ph | 5 | –15° | 48 | (99) | >99:1 | 98.0:2.0 |
| *n*-Bu | Ph | 1 | rt | 12 | (99) | 15:1 | 96.0:4.0 |
| *n*-Bu | Ph | 5 | –15° | 48 | (96) | >99:1 | 98.0:2.0 |
| Bn | Ph | 1 | rt | 12 | (89) | 15:1 | 97.5:2.5 |
| Bn | Ph | 3 | –15° | 48 | (95) | 80:1 | 99.0:1.0 |
| Bn | 2-$CF_3C_6H_4$ | 1 | –15° | 24 | (84) | >99:1 | >99.5:0.5 |
| Bn | 2-$CF_3C_6H_4$ | 1 | rt | 12 | (93) | 60:1 | 99.0:1.0 |

$C_5$





**176** (10 mol %),
hexane/benzene, 5°, 7 d



| R | |
|---|---|
| *n*-Pr | (80) |
| *i*-Pr | (83) |

dr >99:1, er >99.5:0.5

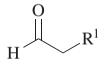
440

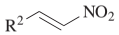
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

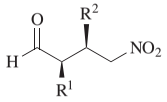
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-7}$





**178** (10 mol %), $CCl_4$, rt

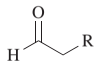


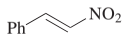
441

Catalyst Recycling ($R^1$ = *i*-Pr; $R^2$ = Ph)

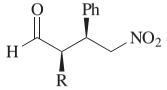
| Run | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 5 | (81) | 81:19 | 99.5:0.5 |
| 2 | 5 | (70) | 80:20 | 99.5:0.5 |
| 3 | 5 | (72) | 81:19 | 99.5:0.5 |
| 4 | 5 | (74) | 79:21 | 99.0:1.0 |
| 5 | 5 | (65) | 75:25 | 99.5:0.5 |

| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | Ph | 30 | (75) | 93:7 | 98.5:1.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | 48 | (78) | 90:10 | 99.5:0.5 |
| *i*-Pr | Ph | 72 | (81) | 81:19 | 99.5:0.5 |
| *i*-Pr | 4-$BrC_6H_4$ | 96 | (60) | 85:15 | 99.5:0.5 |
| *i*-Pr | 1-Np | 50 | (71) | 89:11 | 99.5:0.5 |
| *n*-Bu | Ph | 48 | (73) | 92:8 | 99.5:0.5 |
| *n*-$C_5H_{11}$ | Ph | 36 | (82) | 95:5 | 99.5:0.5 |





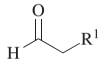
**179** (*x* mol %), $CH_2Cl_2$

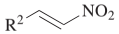


442

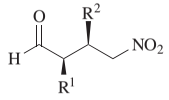
| R | *x* | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | 10 | 0 | 18 | (87) | 96:4 | 99.5:0.5 |
| *n*-Pr | 10 | 20 | 12 | (90) | 83:17 | 99.5:0.5 |
| *i*-Pr | 20 | 20 | 48 | (91) | 98:2 | 99.5:0.5 |
| *n*-Bu | 10 | 20 | 17 | (89) | 97:3 | 99.5:0.5 |
| *n*-$C_5H_{11}$ | 10 | 0 | 20 | (83) | 98:2 | 99.5:0.5 |

$C_5$



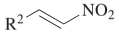


**180** (1–2 mol %),
additive, $H_2O$, rt

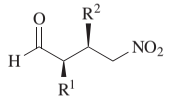


443

| $R^1$ | $R^2$ | Additive | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *n*-Pr | *c*-$C_6H_{11}$ | $PhCO_2H$ | 9 | (99) | 92:8 | >99.8:0.2 |
| *n*-Pr | Ph | none | 4 | (99) | 95:5 | >99.8:0.2 |
| *n*-Pr | 4-$BrC_6H_4$ | none | 4 | (99) | 95:5 | >99.8:0.2 |
| *n*-Pr | 4-$MeOC_6H_4$ | none | 4 | (98) | 93:7 | >99.8:0.2 |
| *i*-Pr | Ph | $PhCO_2H$ | 7 | (65) | 98:2 | >99.5:0.5 |



**182** (10 mol %),
$CHCl_3$/MeOH (9:1)



445

| $R^1$ | $R^2$ | Temp | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | Ph | 0° | 5 | (78) | 99:1 | 95.5:4.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | 0° | 5 | (84) | 95:5 | 93.5:6.5 |
| *i*-Pr | 2-$C_4H_3S$ | rt | 5 | (76) | 93:7 | 89.5:10.5 |
| *i*-Pr | Ph | rt | 3.5 | (85) | 91:9 | 92.0:8.0 |

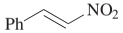
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

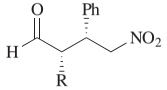
*Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.*

$C_{5-8}$





**183** (15 mol %), $CHCl_3$, rt

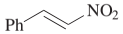


446

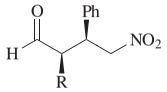
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | 8 | (96) | 89:11 | 94.0:6.0 |
| *i*-Pr | 8 | (85) | 96:4 | 94.5:5.5 |
| Ph | 3 | (76) | 62:38 | 68.5:31.5 |

$C_{5-6}$





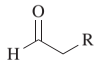
**187** (*x* mol %),
$PhCO_2H$ (5 mol %),
$CH_2Cl_2$

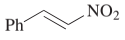


449

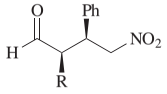
| R | *x* | Temp | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *n*-Pr | 1.5 | rt | 48 | (85) | 92:8 | 89.0:11.0 |
| *n*-Pr | 5 | –20° | 48 | (83) | 99:1 | 96.5:3.5 |
| *i*-Pr | 3 | rt | 60 | (82) | 97:3 | 91.0:9.0 |
| *i*-Pr | 5 | –20° | 60 | (78) | 99:1 | 96.5:3.5 |
| *n*-Bu | 1.5 | rt | 60 | (83) | 96:4 | 88.5:11.5 |
| *n*-Bu | 5 | –20° | 48 | (84) | 99:1 | 96.5:3.5 |

$C_{5-11}$





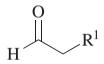
**189** (20 mol %),
solvent, rt, 72 h

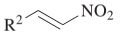


451

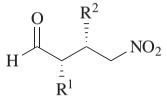
| R | Solvent | | dr | er |
|---|---|---|---|---|
| *n*-Pr | $H_2O$ | (57) | 92:8 | 91.0:9.0 |
| $CH_2{=}CH(CH_2)_7$ | $H_2O$ | (54) | >99:1 | 90.5:9.5 |
| $CH_2{=}CH(CH_2)_7$ | EtOH/$H_2O$ (1:1) | (70) | >99:1 | 93.0:7.0 |

$C_5$



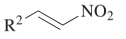


**191** (*x* mol %),
DMAP (5–10 mol %),
MeOH, rt

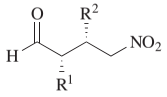


454

| $R^1$ | $R^2$ | *x* | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | Ph | 5 | 48 | (81) | 67:33 | 97.5:2.5 |
| *i*-Pr | 4-$BrC_6H_4$ | 10 | 72 | (86) | 99:1 | >99.5:0.5 |
| *i*-Pr | 1-Np | 10 | 72 | (87) | 96:4 | 99.5:0.5 |



Catalyst (5 mol %),
$CH_2Cl_2$, rt, 72 h



455

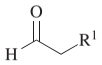
| $R^1$ | $R^2$ | Catalyst | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | Ph | **192** | (98) | 67:33 | 18.5:81.5 |
| *n*-Pr | Ph | **213** | (90) | 73:27 | 90.0:10.0 |
| *n*-Pr | 4-$ClC_6H_4$ | **192** | (92) | 62:38 | 13.5:86.5 |
| *n*-Pr | 4-$ClC_6H_4$ | **213** | (90) | 55:45 | 75.5:24.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | **192** | (82) | 57:43 | 48.0:52.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | **213** | (86) | 56:44 | 89.0:11.0 |
| *n*-Pr | 4-$MeC_6H_4$ | **192** | (90) | 63:37 | 19.0:81.0 |
| *n*-Pr | 4-$MeC_6H_4$ | **213** | (94) | 60:40 | 77.0:23.0 |
| *i*-Pr | Ph | **213** | (22) | 89:11 | 91.0:9.0 |

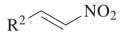
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

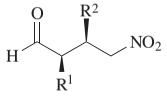
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-6}$





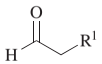
Catalyst (10 mol %), TFA (5 mol %), rt

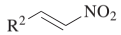


456

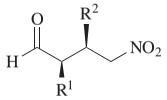
| $R^1$ | $R^2$ | Catalyst | Solvent | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|---|---|
| *n*-Pr | Ph | **194a** | THF | 24 | (96) | 80:20 | 87:5:12.5 | 85.5:14.5 |
| *n*-Pr | Ph | **194b** | $CH_2Cl_2$ | 24 | (98) | 87:13 | 90.5:9.5 | 89.0:11.0 |
| *n*-Pr | 4-$BrC_6H_4$ | **194b** | $CH_2Cl_2$ | 24 | (96) | 78:22 | 86.5:13.5 | 88.0:12.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | **194b** | $CH_2Cl_2$ | 36 | (94) | 86:14 | 90.0:10.0 | 87.5:12.5 |
| *n*-Pr | 2-$MeC_6H_4$ | **194b** | $CH_2Cl_2$ | 36 | (85) | 90:10 | 89.5:10.5 | 90.0:10.0 |
| *n*-Pr | 4-$MeC_6H_4$ | **194b** | $CH_2Cl_2$ | 36 | (97) | 82:18 | 91.0:9.0 | 92.0:8.0 |
| *i*-Pr | Ph | **194a** | THF | 60 | (37) | 97:3 | 88.5:11.5 | — |
| *i*-Pr | Ph | **194b** | $CH_2Cl_2$ | 60 | (84) | 99:1 | 91.0:9.0 | — |
| *n*-Bu | Ph | **194a** | THF | 36 | (97) | 73:27 | 86.0:14.0 | 86.5:13.5 |
| *n*-Bu | Ph | **194b** | $CH_2Cl_2$ | 36 | (99) | 90:10 | 90.0:10.0 | 88.5:11.5 |

$C_5$





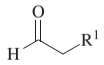
**197a** (10 mol %), **202a** (10 mol %), toluene, rt

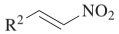


459

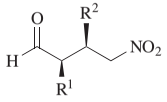
| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | Ph | 3 | (70) | 83:17 | 87.0:13.0 |
| *n*-Pr | 4-$BrC_6H_4$ | 1 | (87) | 99:1 | 92.5:7.5 |
| *n*-Pr | 3-$MeOC_6H_4$ | 1 | (83) | 96:4 | 91.0:9.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | 1 | (85) | 89:11 | 98.0:2.0 |
| *n*-Pr | 4-$MeC_6H_4$ | 1 | (80) | 100:0 | 99.5:0.5 |
| *i*-Pr | Ph | 2 | (90) | 99:1 | 93.5:6.5 |

$C_{5-7}$





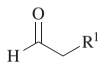
**197b** (*x* mol %), $CH_2Cl_2$

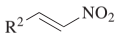


132

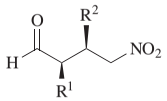
| $R^1$ | $R^2$ | *x* | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|---|
| *n*-Pr | 2-$C_4H_3S$ | 5 | 0° | 20 | (70) | >99:1 | 97.0:3.0 |
| *n*-Pr | *c*-$C_6H_{11}$ | 5 | 0° | 20 | (75) | >99:1 | >99.5:0.5 |
| *n*-Pr | Ph | 5 | 0° | 20 | (72) | 95:5 | 98.0:2.0 |
| *n*-Pr | Ph | 10 | rt | 2.5 | (67) | 90:10 | 97.0:3.0 |
| *n*-Pr | 4-$MeOC_6H_4$ | 5 | 0° | 20 | (72) | 96:4 | >99.5:0.5 |
| *n*-Pr | $PhCH_2CH_2$ | 5 | 0° | 20 | (72) | >99:1 | >99.5:0.5 |
| *i*-Pr | 2-$C_4H_3S$ | 10 | rt | 14 | (76) | 94:6 | 96.0:4.0 |
| *i*-Pr | Ph | 10 | rt | 20 | (75) | 95:5 | 95.5:4.5 |
| *n*-$C_5H_{11}$ | Ph | 5 | 0° | 20 | (70) | 99:1 | 98.0:2.0 |
| *n*-$C_5H_{11}$ | 4-$BrC_6H_4$ | 5 | 0° | 20 | (70) | 97:3 | 99.0:1.0 |

$C_{5-6}$





**198** (5 mol %), DIPEA (5 mol %), $CH_2Cl_2$, 0°, times



460

| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *i*-Pr | Ph | 72 | (96) | 97:3 | 97.5:2.5 |
| *i*-Pr | 4-$ClC_6H_4$ | 90 | (98) | 98:2 | 98.5:1.5 |
| *i*-Pr | 2-$MeOC_6H_4$ | 168 | (94) | 99:1 | 98.0:2.0 |
| *n*-Bu | Ph | 12 | (98) | 95:5 | 97.5:2.5 |

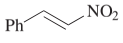
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

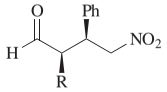
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-11}$





**199** (10 mol %),
$PhCO_2H$ (1 eq)
$EtOH/H_2O$ (1:1), rt

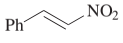


461

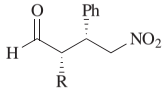
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | 6 | (86) | 95:5 | 98.5:1.5 |
| $CH_2$=$CH(CH_2)_7$ | 12 | (85) | 97:3 | 98.5:1.5 |

$C_{5-6}$



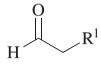


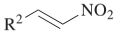
**200** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt



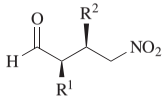
462

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | 40 | (85) | 92:8 | 93.5:6.5 |
| *i*-Pr | 120 | (30) | 97:3 | 97.0:3.0 |
| *n*-Bu | 40 | (95) | 99:1 | 97.5:2.5 |





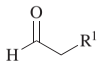
**201** (1 mol %),
**202a** (1 mol %),
$CH_2Cl_2$, 0°, 24 h

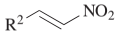


470

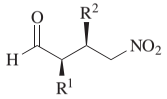
| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | $BnCH_2$ | (93) | >99:1 | 99.5:0.5 |
| *i*-Pr | Ph | (96) | 98:2 | 99.0:1.0 |
| *n*-Bu | Ph | (93) | 95:5 | 98.0:2.0 |

$C_{5-8}$





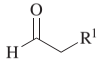
**203** (2 mol %),
$HCO_2H$ (20 mol %),
$H_2O$, rt, 12–18 h

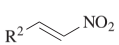


471

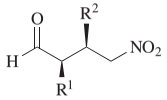
| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | Ph | (93) | 96:4 | 98.0:2.0 |
| *i*-Pr | Ph | (95) | 96:4 | 99.0:1.0 |
| *i*-Pr | 4-$FC_6H_4$ | (92) | 97:3 | 97.5:2.5 |
| *i*-Pr | 3-$MeOC_6H_4$ | (90) | 95:5 | 99.5:0.5 |
| *i*-Pr | 4-$MeOC_6H_4$ | (94) | 94:6 | 98.0:2.0 |
| *i*-Pr | 1-Np | (92) | 96:4 | >99.5:0.5 |
| *n*-Bu | Ph | (93) | 96:4 | 98.0:2.0 |
| *n*-Bu | 4-$MeC_6H_4$ | (90) | 90:10 | 97.5:2.5 |
| *n*-Bu | 1-Np | (94) | 92:8 | 99.0:1.0 |
| *n*-$C_6H_{13}$ | Ph | (91) | 93:7 | 97.0:3.0 |
| *n*-$C_6H_{13}$ | 4-$MeOC_6H_4$ | (93) | 95:5 | 98.0:2.0 |

$C_{5-9}$





**207a** (10 mol %),
$NaHCO_3$ (20 mol %),
brine, rt



486

| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | Ph | 48 | (90) | 91:9 | 99.5:0.5 |
| *n*-Pr | 4-$BrC_6H_4$ | 34 | (89) | 92:8 | 99.5:0.5 |
| *n*-Pr | 2-$ClC_6H_4$ | 72 | (69) | 93:7 | 98.5:1.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | 34 | (91) | 90:10 | 93.0:7.0 |
| *n*-Pr | 4-$MeC_6H_4$ | 96 | (72) | 97:3 | 98.5:1.5 |
| *n*-Pr | 2-$CF_3C_6H_4$ | 40 | (55) | 91:9 | 99.0:1.0 |
| *i*-Pr | Ph | 72 | (32) | 98:2 | 99.5:0.5 |
| *n*-Bu | Ph | 16 | (77) | 96:4 | 99.0:1.0 |
| *n*-$C_5H_{11}$ | Ph | 48 | (78) | 96:4 | 98.0:2.0 |
| *n*-$C_7H_{15}$ | Ph | 48 | (59) | 96:4 | 96.5:3.5 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

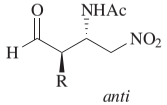
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-9}$



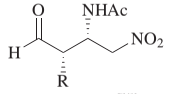


**145b** (20 mol %), AcOH (20 mol %), $CHCl_3$, –10°



*anti*

+

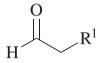


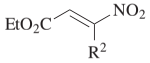
*syn*

468

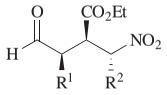
| R | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|
| *i*-Pr | 9 | (98) | 7:1 | 99.0:1.0 |
| $Cl(CH_2)_3$ | 3 | (80) | 4:1 | 97.0:3.0 |
| Bn | 1.5 | (93) | 6:1 | 96.5:3.5 |

$C_{5-11}$





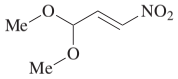
**145b** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 12–24 h



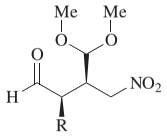
463

| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| *n*-Pr | Et | (79) | 92:7:1 | >99.5:0.5 |
| *i*-Pr | Me | (82) | 93:5:2 | >99.5:0.5 |
| $Cl(CH_2)_3$ | Me | (65) | 84:9:7 | >99.5:0.5 |
| Bn | Me | (82) | 93:6:1 | >99.5:0.5 |
| Bn | Et | (83) | 93:7<1 | 99.0:1.0 |
| $CH_2{=}CH(CH_2)_7$ | Me | (75) | 90:7:3 | >99.5:0.5 |



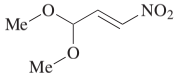


**16a** (10 mol %), *i*-PrOH, rt

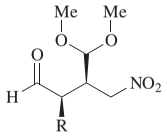


430

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Pr | 70 | (46) | 9:1 | 94.0:6.0 |
| *n*-$C_6H_{13}$ | 72 | (65) | 1.7:1 | 90.0:10.0 |
| Ph | 36 | (99) | 3:1 | 70.0:30.0 |
| *n*-$C_5H_{11}CH{=}CHCH_2$ | 72 | (63) | 3:1:1 | 91.0:9.0 |
| *n*-$C_9H_{19}$ | 72 | (63) | 9:1 | 91.5:8.5 |



**145b** (10 mol %),
DMF, $H_2O$ (2 eq), rt



116

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Pr | 72 | (75) | >20:1 | >99.5:0.5 |
| *n*-$C_6H_{13}$ | 72 | (85) | >20:1 | >99.5:0.5 |
| Ph | 48 | (85) | 1.5:1 | >99.5:0.5 |
| *n*-$C_5H_{11}CH{=}CHCH_2$ | 72 | (81) | 3:1 | >99.5:0.5 |
| *n*-$C_9H_{19}$ | 72 | (61) | >20:1 | 96.0:4.0 |

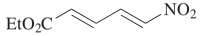
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

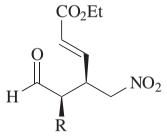
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-9}$





**145b** (5 mol %), toluene, 1–2.5 d

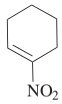


466

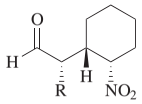
| R | Temp | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | 0° to rt | (81) | 95:5 | 99.0:1.0 |
| *i*-Pr | rt to 45° | (78) | 92:8 | 99.0:1.0 |
| *n*-Bu | rt | (76) | 94:6 | 99.5:0.5[c] |
| *c*-$C_6H_{11}CH_2$ | rt | (74) | >98:2 | 99.5:0.5 |
| Bn | 0° | (74) | 90:10 | >99.5:0.5[c] |
| 4-$MeOC_6H_4CH_2$ | 0° to rt | (61) | 87:13 | 98.5:1.5 |

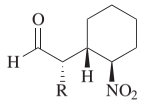
$C_{5-10}$





*ent*-**145b** (20 mol %), 3-$O_2NC_6H_4CO_2H$ (10 mol %), $CHCl_3$, rt

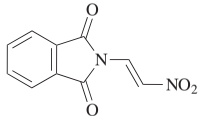


**I** +  **II** 467

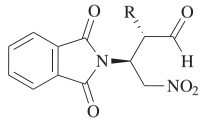
| R | Time (h) | | dr **I**/**II** | er |
|---|---|---|---|---|
| *n*-Pr | 40 | (86) | 16:1 | 99.5:0.5 |
| *i*-Pr | 54 | (79) | 10:1 | >99.5:0.5 |
| *n*-Bu | 40 | (85) | 16:1 | 99.5:0.5 |
| $(Boc)_2N(CH_2)_4$ | 42 | (73) | 13:1 | 98.0:2.0 |
| *n*-$C_6H_{13}$ | 42 | (81) | 15:1 | >99.5:0.5 |
| *c*-$C_6H_{11}$ | 54 | (70) | 15:1 | >99.5:0.5 |
| $BnCH_2$ | 40 | (75) | 9:1 | 99.0:1.0 |

$C_{5-9}$





**186** (*x* mol %),
AcOH (25 mol %),
MeCN, 0°

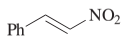


468

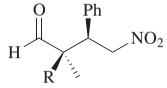
| R | *x* | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| $BnO(CH_2)_3$ | 5 | 4 | (99) | 12:1 | 99.5:0.5 |
| $4\text{-}ClC_6H_4$ | 20 | 2.5 | (93) | 11:1 | 96.0:4.0 |
| $3,4\text{-}Cl_2C_6H_3$ | 20 | 6 | (92) | 9:1 | 94.0:6.0 |
| $4\text{-}FC_6H_4$ | 20 | 4.5 | (87) | 12:1 | 96.5:3.5 |
| Bn | 5 | 7 | (99) | 14:1 | 99.5:0.5 |

$C_{5-6}$





**5** (10 mol %),
TFA (10 mol %),
brine, rt



252

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Et | 72 | (74) | 59:41 | 87.0:13.0 |
| *n*-Pr | 96 | (97) | 61:39 | 82.0:18.0 |

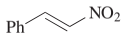
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

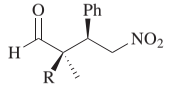
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-14}$





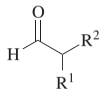
**6** (15 mol %), TFA (15 mol %), *i*-PrOH, 4°

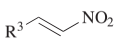


472

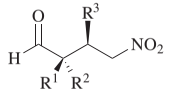
| R | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|
| Et | (94) | 74:26 | 90.5:9.5 | 87.5:12.5 |
| *n*-Pr | (95) | 74:26 | 93.0:7.0 | 83.5:16.5 |
| $Me_2C{=}CH(CH_2)_2$ | (93) | 84:16 | 87.5:12.5 | 72.5:27.5 |
| Ph | (87) | 89:11 | 59.0:41.0 | 89.5:10.5 |
| 3,4-$(OCH_2O)C_6H_3CH_2$ | (75) | 67:33 | 87.0:13.0 | 71.5:28.5 |
| *n*-$C_9H_{19}$ | (96) | 70:30 | 92.5:7.5 | 79.0:21.0 |
| 4-*i*-$PrC_6H_4CH_2$ | (75) | 55:45 | 82.5:17.5 | 82.5:17.5 |
| 4-*t*-$BuC_6H_4CH_2$ | (64) | 54:46 | 85.0:15.0 | 82.0:18.0 |

$C_{5-7}$





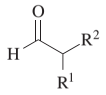
**16b** (20 mol %), *i*-PrOH, 0°

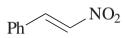


258

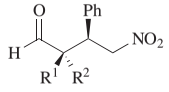
| $R^1$ | $R^2$ | $R^3$ | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | H | Ph | 0.83 | (99) | 50:1 | 98.0:2.0 |
| *n*-Pr | H | 4-$MeOC_6H_4$ | 1 | (86) | 20:1 | 99.5:0.5 |
| *n*-Pr | H | 2-$CF_3C_6H_4$ | 1.16 | (63) | 22:1 | 97.0:3.0 |
| *n*-Pr | Me | Ph | 3 | (72) | 1.3:1 | 80.0:20.0 |
| *n*-Bu | H | Ph | 1 | (94) | 30:1 | 99.5:0.5 |
| *n*-Bu | H | $BnCH_2$ | 1 | (76) | 50:1 | 61.0:39.0 |
| *n*-$C_5H_{11}$ | H | Ph | 1.08 | (91) | 50:1 | 98.5:1.5 |

$C_{5-9}$



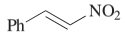


Catalyst (20 mol %), solvent, rt

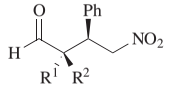


315

| $R^1$ | $R^2$ | Catalyst | Solvent | Time (d) | | dr | er |
|---|---|---|---|---|---|---|---|
| *i*-Pr | H | **74** | MeOH | 2 | (86) | 91:9 | 86.0:14.0 |
| Ph | Me | **74** | MeOH | 4 | (92) | 93:7 | 56.0:44.0 |
| Ph | Me | **214** | toluene | 7 | (45) | 93:7 | 75.0:25.0 |



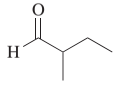
**80a** (10 mol %),
$PhCO_2H$ (10 mol %),
$H_2O$, neat, rt

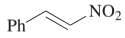


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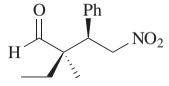
| $R^1$ | $R^2$ | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| H | *i*-Pr | 3.8 | (76) | 6.7:1 | 97.5:2.5 |
| H | *n*-Bu | 4.2 | (91) | 12.5:1 | 91.5:8.5 |
| Me | Et | 2.3 | (95) | 2:1 | 96.0:4.0 |
| Me | Ph | 3.3 | (93) | >20:1 | 83.0:17.0 |

$C_5$





**115b** (20 mol %),
TFA (5 mol %),
MeOH, rt, 6 d



(54) *syn*/*anti* = 56:44
er (*syn*) 81.5:18.5
er (*anti*) 85.5:14.5

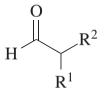
356

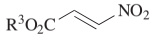
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

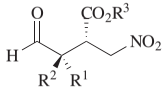
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_{5-11}$





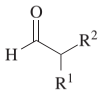
*ent*-**145b** (5 mol %), $PhCO_2H$ (50 mol %), $H_2O$, 0°, 1 h; then rt

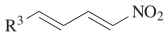


118

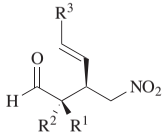
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | H | Me | 2 | (90) | 97:3 | >99.5:0.5 |
| *n*-Pr | H | *t*-Bu | 6 | (90) | 97:3 | >99.5:0.5 |
| *n*-Pr | H | Bn | 2 | (86) | 98:2 | >99.5:0.5 |
| *i*-Bu | H | Me | 2.5 | (83) | 98:2 | >99.5:0.5 |
| Ph | Me | Me | 15 | (81) | 81:19 | 98.0:2.0 |
| $CH_2$=$CH(CH_2)_7$ | H | Me | 2 | (81) | 96:4 | >99.5:0.5 |

$C_{5-9}$



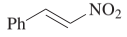


**145b** (5 mol %), $H_2O$/EtOH (5 %), rt

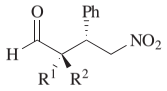


121

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | H | Ph | 10 | (91) | 93:7 | 99.5:0.5 |
| *i*-Pr | H | Et | 8 | (81) | 90:10 | 92.5:7.5 |
| *i*-Pr | H | *c*-$C_6H_{11}$ | 48 | (62) | 94:6 | 97.5:2.5 |
| *i*-Pr | H | Ph | 14 | (91) | 94:6 | >99.5:0.5 |
| *i*-Pr | H | 4-$ClC_6H_4$ | 36 | (93) | 92:8 | 99.0:1.0 |
| *i*-Pr | H | 4-$MeOC_6H_4$ | 48 | (94) | 66:34 | 94.5:5.5 |
| allyl | H | Ph | 35 | (84) | 52:48 | 96.5:3.5 |
| $CH_2$=$CH(CH_2)_2$ | H | Et | — | (99) | 82:18 | 97.5:2.5 |
| Me | Ph | Ph | 96 | (78) | 95:5 | 58.0:42.0 |



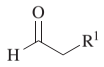
**204b** (10 mol %),
$CH_2Cl_2$, rt, 48 h

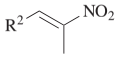


477

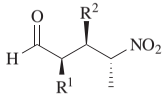
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| *n*-Pr | H | (59) | 2:1 | 89.0:11.0 |
| *i*-Pr | H | (41) | 6.1:1 | 94.5:5.5 |
| Me | *n*-Pr | (60) | 3.5:1 | 61.0:39.0 |
| Me | Ph | (84) | 2:1 | 55.0:45.0 |
| Bn | H | (61) | 2:1 | 94.5:5.5 |

$C_{6–10}$





**145b** (10 mol %),
4-$O_2NC_6H_4OH$ (40 mol %),
$CHCl_3$, rt



464

| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| *n*-Bu | Ph | 25 | (94) | 90:6:4:<1 | >99.5:0.5 |
| *n*-Bu | 4-$ClC_6H_4$ | 17 | (94) | 91:6:3:<1 | >99.5:0.5 |
| *n*-Bu | 4-$FC_6H_4$ | 21 | (93) | 92:6:2:<1 | >99.5:0.5 |
| *n*-Bu | 4-$MeC_6H_4$ | 27 | (84) | 90:6:4:<1 | >99.5:0.5 |
| *n*-$C_6H_{13}$ | 4-$ClC_6H_4$ | 18 | (93) | 91:6:3:<1 | >99.5:0.5 |
| *n*-$C_8H_{19}$ | Ph | 24 | (94) | 89:7:4:<1 | >99.5:0.5 |
| *n*-$C_8H_{19}$ | 4-$FC_6H_4$ | 18 | (85) | 89:10:1:<1 | >99.5:0.5 |
| *n*-$C_8H_{19}$ | 4-$MeC_6H_4$ | 25 | (87) | 90:6:4:<1 | >99.5:0.5 |

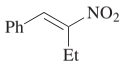
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

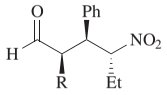
*Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.*

$C_{6-10}$





**145b** (10 mol %),
4-$O_2NC_6H_4OH$ (80 mol %),
$CHCl_3$, rt

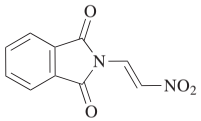


464

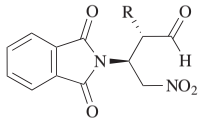
| R | Time (h) | | dr | er |
|---|---|---|---|---|
| *n*-Bu | 61 | (92) | 85:15:<1:<1 | >99.5:0.5 |
| *n*-$C_8H_{19}$ | 65 | (89) | 83:17:<1:<1 | >99.5:0.5 |

$C_{6-8}$





*ent*-**145c** (*x* mol %),
AcOH (25 mol %),
MeCN, 0°

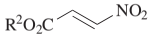


468

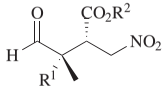
| R | *x* | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| $Me_2C$=CH | 20 | 2 | (98) | 9:1 | 98.5:1.5 |
| Ph | 10 | 1.5 | (99) | 26:1 | 98.5:1.5 |

$C_{6-9}$





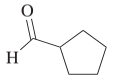
**204a** (16 mol %),
**204b** (4 mol %),
$CH_2Cl_2$, rt

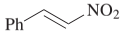


481

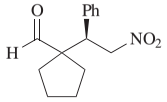
| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| *n*-Pr | Bn | 48 | (75) | 4:1 | 97.5:2.5 |
| Ph | Me | 38 | (84) | >20:1 | 99.0:1.0 |
| Ph | Bn | 48 | (85) | >20:1 | 98.5:1.5 |

$C_6$



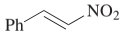


**6** (15 mol %), TFA (15 mol %), *i*-PrOH, 4°, 24 h

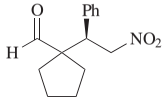


(93) er 95.5:4.5

472

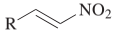


**16b** (20 mol %), *i*-PrOH, 0°, 42 h

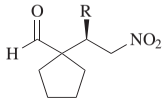


(89) er 96.5:3.5

73, 258



**74** (20 mol %), toluene, 0°



315

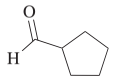
| R | Time (d) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 1 | (92) | 96.0:4.0 |
| 2-$C_4H_3S$ | 1 | (91) | 94.0:6.0 |
| Ph | 1 | (88) | 97.0:3.0 |
| 2-$BrC_6H_4$ | 5 | (88) | 96.0:4.0 |
| 3-$BrC_6H_4$ | 2 | (86) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 1.5 | (90) | 95.5:4.5 |
| 3-$ClC_6H_4$ | 1 | (90) | 97.5:2.5 |
| 4-$ClC_6H_4$ | 1 | (95) | 97.5:2.5 |
| 2-$MeOC_6H_4$ | 5 | (68) | 84.5:15.5 |
| 3-$MeOC_6H_4$ | 1 | (80) | 89.5:10.5 |
| 4-$MeOC_6H_4$ | 2 | (85) | 87.5:12.5 |
| 4-$MeC_6H_4$ | 1 | (96) | 96.5:3.5 |
| 3-$CF_3C_6H_4$ | 1 | (92) | 97.5:2.5 |
| $BnCH_2$ | 5 | (54) | 99.5:0.5 |

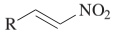
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

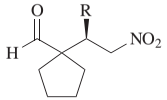
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_6$



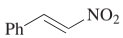


**75** (20 mol %), $PhCO_2H$ (20 mol %), neat, 0°

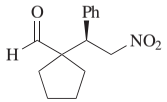


474

| R | Time (d) | | er |
|---|---|---|---|
| 2-$C_4H_3S$ | 1 | (95) | 94.5:5.5 |
| Ph | 1 | (95) | 96.5:3.5 |
| 2-$BrC_6H_4$ | 1 | (85) | 90.0:10.0 |
| 3-$BrC_6H_4$ | 0.5 | (84) | 96.0:4.0 |
| 4-$BrC_6H_4$ | 1 | (86) | 96.0:4.0 |
| 3-$ClC_6H_4$ | 0.5 | (87) | 96.0:4.0 |
| 4-$ClC_6H_4$ | 1 | (97) | 96.0:4.0 |
| 2-$MeOC_6H_4$ | 0.5 | (99) | 90.5:9.5 |
| 3-$MeOC_6H_4$ | 0.5 | (99) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 0.5 | (94) | 94.0:6.0 |
| 4-$MeC_6H_4$ | 1 | (95) | 96.5:3.5 |
| 2-$CF_3C_6H_4$ | 3 | (80) | 88.5:11.5 |
| 3-$CF_3C_6H_4$ | 1.5 | (90) | 97.0:3.0 |
| $BnCH_2$ | 1 | (85) | 97.5:2.5 |



**115b** (20 mol %), TFA (5 mol %), MeOH, rt, 6 d



(82) er 92.5:7.5

356

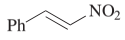
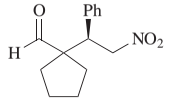
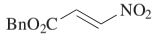
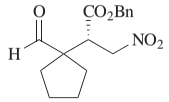
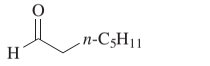
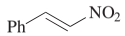
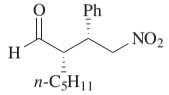
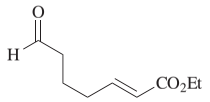
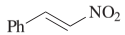
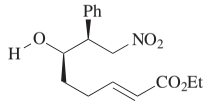
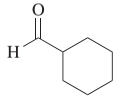
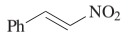
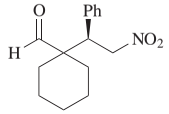
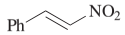
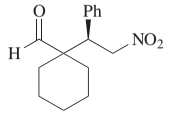
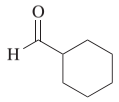
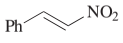
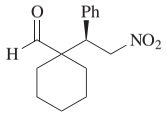
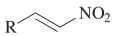
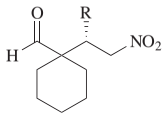
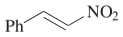
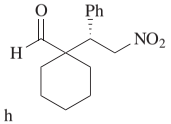
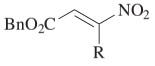
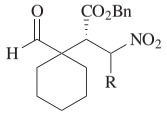
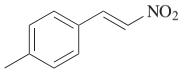
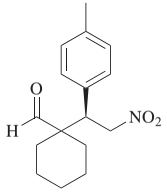
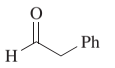
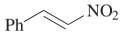
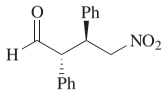
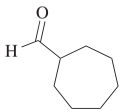
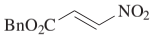
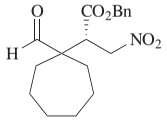
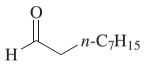
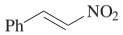
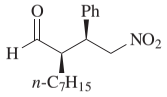
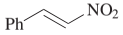
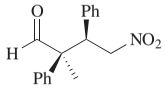
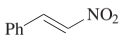
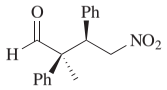
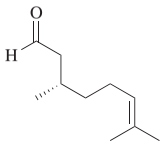
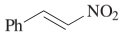
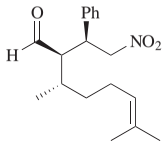
| | | | | | |
|---|---|---|---|---|---|
| |  | **181** (20 mol %), DMAP (20 mol %), $CHCl_3$, rt, 23 h |  | (41) er 95.5:4.5 | 444 |
| |  | **204a** (16 mol %), **204b** (4 mol %), $CH_2Cl_2$, rt, 9 h |  | (68) er 94.0:6.0 | 481 |
| $C_7$ | | | | | |
|  |  | **106a** (20 mol %), toluene, rt, 24 h |  | (50) *syn*/*anti* = 95:5 er 87.5:12.5 | 350 |
|  |  | 1. **145b** (20 mol %), AcOH (20 mol %), $CH_2Cl_2$, 0°, 18 h<br>2. $NaBH_4$, $CH_2Cl_2$, –20°, 24 h |  | (82) *syn*/*anti* = 21:1 er > 99.5:0.5 | 487 |
|  |  | **6** (15 mol %), TFA (15 mol %), *i*-PrOH, 4°, 96 h |  | (90) er 79.5:20.5 | 472 |
| |  | **16b** (20 mol %), *i*-PrOH, 0°, 4 d |  | (42) er 82.0:18.0 | 258 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_7$ | | | | |
|  |  | **52** (20 mol %), $CH_2Cl_2$, rt, 72 h |  (51) er 90.0:10.0 | 473 |
| |  | **68** (30 mol %), $PhCO_2H$ (20 mol %), toluene, rt, 4 d |  | 279 |
| | | | R — er: 2-$C_4H_3O$ (57) 99.5:0.5; Ph (42) 77.5:22.5 | |
| |  | **93** (10 mol %), 2,4-$(O_2N)_2C_6H_3SO_3H$ (2.5 mol %), 4-*n*-$C_{12}H_{25}C_6H_4SO_3Na$ (10 mol %), 2 M in $CHCl_3$, rt, 70 h |  (31) er 96.0:4.0 | 333 |
| |  | **204a** (24 mol %), **204b** (6 mol %), $CH_2Cl_2$, rt, time |  | 481 |
| | | | R — Time (h) — *syn*/*anti* — er: H 72 (72) — 93.5:6.5; Et 96 (84) >20:1 96.0:4.0 | |
| |  | **210** (20 mol %), [bmim][$BF_4$], rt, 36 h |  (90) er 73.0:27.0 | 480 |

| | | | | | |
|---|---|---|---|---|---|
| $C_8$ |  |  | **181** (20 mol %), imidazole (20 mol %), $CH_2Cl_2$, rt, 21 h |  | (90) dr 4:1<br>er (major) 91.0:9.0<br>er (minor) 90.0:10.0 | 444 |
| |  |  | **204a** (24 mol %), **204b** (6 mol %), $CH_2Cl_2$, rt, 9 h |  | (70) er 97.5:2.5 | 481 |
| $C_9$ |  |  | **95e** (10 mol %), $H_2O$, rt, 12 h |  | (98) dr 4:1<br>er 90.5:9.5 | 337 |
| |  |  | **205b** (10 mol %), DABCO (40 mol %), $CHCl_3$, –30°, 5 h |  | (82) *syn*/*anti* = 97:3<br>er 73.5:26.5 | 478 |
| | |  | **215** (20 mol %), $H_2O$ (5 eq), $CH_2Cl_2$, rt, 24 h |  | (84) *syn*/*anti* = 11.9:1<br>er (*syn*) 98.5:1.5<br>er (*anti*) 66.0:34.0 | 72 |
| $C_{10}$ |  |  | **74** (10 mol %), neat, rt |  | (93) dr 91:9 | 315 |

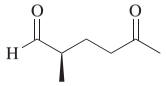
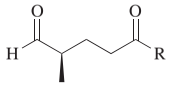
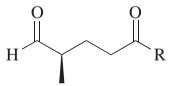
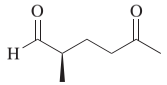
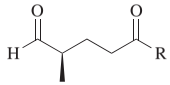
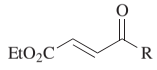
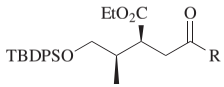
[a] The opposite enantiomer was obtained.

[b] The yield was determined by GC with an internal standard.

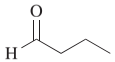
[c] Using the catalyst with the opposite configuration, the opposite enantiomer was obtained.

TABLE 2. ALDEHYDES AS DONORS (*Continued*)

B. ENONES AS ACCEPTORS

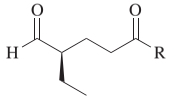
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **145a** (20 mol %), 3,4-$(HO)_2C_6H_3CO_2Et$ (20 mol %), 5° |  (58) er >95.0:5.0 | 227 |
| |  | **145a** (5 mol %), 3,4-$(HO)_2C_6H_3CO_2Et$ (20 mol %), neat, 4° |  R Time (h) er<br>Me 36 (82) 98.5:1.5<br>Et 48 (70) 99.5:0.5 | 488 |
| |  | **162a** (20 mol %), HFIP (1 eq), THF, rt |  R Time (h) er<br>Me 30 (83) 82.0:18.0<br>Et 40 (85) 77.0:23.0 | 489 |
| |  | **207c** (10 mol %), EtOH, 40°, 64 h |  (80) er 96.0:4.0 | 61 |
| |  | **216** (5 mol %), 3,4-$(HO)_2C_6H_3CO_2Et$ (20 mol %), neat, rt, 20 h |  R er<br>Me (84) 95.0:5.0<br>Et (79) 96.0:4.0 | 133 |
|  | | 1. **145b** (5 mol %), AcOH (5 mol %), MeOH, 0° to rt, 1 h<br>2. $NaBH_4$, EtOH, $CH_2Cl_2$, –78°; then TBDPSCl, imidazole |  R *syn*/*anti* er<br>Me (64) 9:1 98.0:2.0<br>Et (63) 6:1 96.5:3.5 | 490 |

$C_4$





**145a** (5 mol %),
3,4-$(HO)_2C_6H_3CO_2Et$
(*x* mol %), neat, 4°

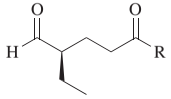


| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| Me | 0 | 36 | (75) | 98.5:1.5 |
| Et | 20 | 48 | (68) | 97.5:2.5 |

488



**162a** (20 mol %),
HFIP (1 eq), THF, rt

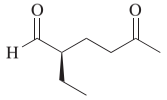


| R | Time (h) | | er |
|---|---|---|---|
| Me | 30 | (86) | 89.5:10.5 |
| Et | 40 | (80) | 86.5:13.5 |

489

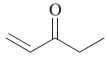


**207c** (10 mol %),
EtOH, 40°, 64 h

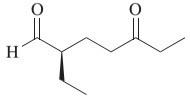


(83) er 96.5:3.5

61



**216** (5 mol %),
3,4-$(HO)_2C_6H_3CO_2Et$
(20 mol %), neat, rt, 20 h



(68) er 96.0:4.0

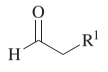
133

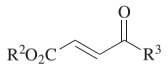
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

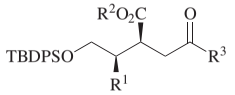
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{4-5}$





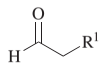
1. **145b** (5 mol %), AcOH (5 mol %), MeOH, 0° to rt, 1 h
2. $NaBH_4$, EtOH, $CH_2Cl_2$, –78°; then TBDPSCl, imidazole

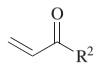


490

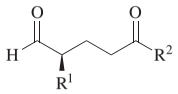
| $R^1$ | $R^2$ | $R^3$ | | *syn/anti* | er |
|---|---|---|---|---|---|
| Et | Et | Me | (71) | 11:1 | 98.5:1.5 |
| $BnO(CH_2)_2$ | Et | Me | (63) | 7:1 | 99.0:1.0 |
| *i*-Pr | Et | Me | (71) | 10:1 | 98.5:1.5 |
| *i*-Pr | Et | $BnO(CH_2)_3$ | (50) | 7:1 | >99.5:0.5 |
| *i*-Pr | Et | $CH_2{=}CH(CH_2)_2$ | (55) | 9:1 | 98.0:2.0 |
| *i*-Pr | Bn | Me | (74) | 11:1 | 99.0:1.0 |

$C_{5-9}$



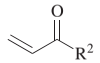


**145a** (5 mol %), 3,4-$(HO)_2C_6H_3CO_2Et$ (*x* mol %), neat

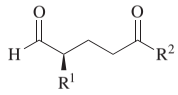


488

| $R^1$ | $R^2$ | *x* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|
| *n*-Pr | Me | 0 | 4 | 36 | (69) | >97.5:2.5 |
| *n*-Pr | Et | 20 | 4 | 48 | (69) | >97.5:2.5 |
| *i*-Pr | Me | 0 | 4 | 36 | (65) | 99.0:1.0 |
| *i*-Pr | Et | 20 | rt | 48 | (60) | 99.5:0.5 |
| *n*-$C_6H_{13}$ | Me | 0 | 4 | 24 | (85) | >97.5:2.5 |
| *n*-$C_6H_{13}$ | Et | 20 | 4 | 24 | (87) | >97.5:2.5 |
| Bn | Me | 0 | 4 | 24 | (82) | >97.5:2.5 |
| Bn | Et | 20 | 4 | 24 | (69) | >97.5:2.5 |



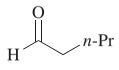
**162a** (20 mol %), HFIP (1 eq), solvent, rt



| $R^1$ | $R^2$ | Solvent | Time (h) | | er |
|---|---|---|---|---|---|
| *i*-Pr | Me | THF | 80 | (91) | 91.0:9.0 |
| *i*-Pr | Et | THF | 96 | (93) | 87.5:12.5 |
| *i*-Pr | *t*-Bu | neat | 96 | (30) | 75.0:25.0 |
| *n*-$C_7H_{15}$ | Me | THF | 30 | (82) | 88.0:12.0 |
| Bn | Me | THF | 30 | (78) | 82.5:17.5 |
| Bn | Et | THF | 40 | (72) | 79.0:21.0 |

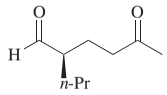
489

$C_5$





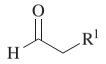
**207c** (10 mol %), EtOH, 40°, 64 h

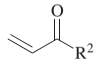


(82) er 97.5:2.5

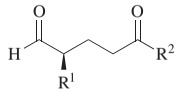
61

$C_{5-9}$





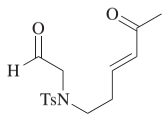
**216** (5 mol %), 3,4-$(HO)_2C_6H_3CO_2Et$ (20 mol %), neat, rt, 20 h



| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| *i*-Pr | Me | (55) | 91.0:9.0 |
| Bn | Me | (62) | 94.5:5.5 |
| Bn | Et | (54) | 96.0:4.0 |

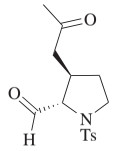
133

$C_8$



Intramolecular

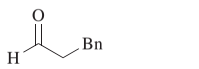
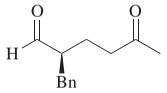
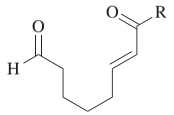
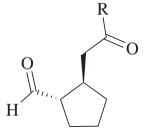
**217** (10 mol %) THF, rt, 15–24 h



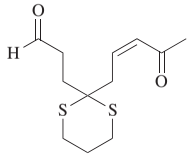
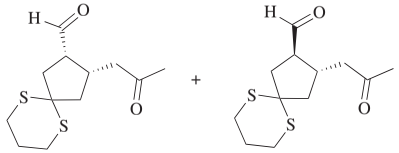
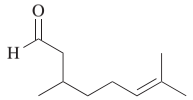
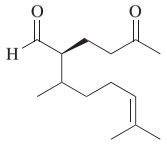
(90) *antilsyn* = 8:1 er 96.5:3.5

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TABLE 2. ALDEHYDES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_9$  |  | **145b** (30 mol %), neat |  (52) er 98.5:1.5 | 60 |
| $C_{9-18}$  | Intramolecular | **217** (10 mol %) THF, rt, 15–24 h |  | 135 |

| R | | *anti*/*syn* | er |
|---|---|---|---|
| Me | (99) | 12:1 | 96.5:3.5 |
| Et | (99) | 21:1 | 97.0:3.0 |
| Ph | (99) | 24:1 | 98.5:1.5 |
| 2-Np | 99) | 17:1 | 98.5:1.5 |

| | | | |
|---|---|---|---|
| $C_9$  | Intramolecular | **218** (10 mol %), acetone, –20° |  (93) *cis*/*trans* > 95:5, er >99.5:0.5 | 134 |
| $C_{10}$  |  | **145a** (20 mol %), 3,4-$(HO)_2C_6H_3CO_2Et$ (20 mol %), 3° |  | 491 |

| Donor | Product | | dr |
|---|---|---|---|
| (*S*)-enantiomer | (2*S*,3*S*)-enantiomer | (90) | 18:1 |
| (*R*)-enantiomer | (2*S*,3*R*)-enantiomer | (87) | 14:1 |

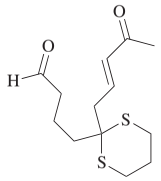
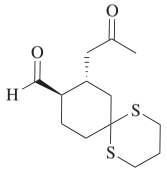
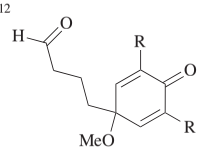
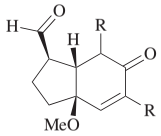
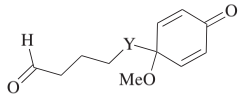
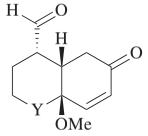
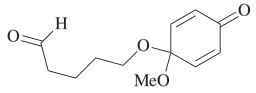
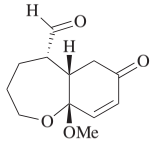
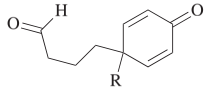
| | | | | | |
|---|---|---|---|---|---|
|  | Intramolecular | **145c** (5 mol %), THF, rt |  | (99) dr 20:1<br>er 99.5:0.5 | 492 |
| $C_{10–12}$<br>  | Intramolecular | *ent*-**186** (10 mol %),<br>$PhI(OAc)_2$ (1 eq),<br>MeOH, 0° |  | R (70)[a] dr 15:1 er 98.5:1.5<br>H<br>Me (75)[a] 2:1 70.0:30.0 | 493 |
| $C_{10–11}$<br>  | Intramolecular | *ent*-**186** (10 mol %),<br>$PhI(OAc)_2$ (1 eq),<br>MeOH, 0° |  | Y (84)[a] dr >20:1 er 99.5:0.5<br>O<br>TsN (68)[a] >20:1 99.5:0.5<br>$CH_2$ (75)[a] >20:1 99.5:0.5 | 493 |
| $C_{11}$<br>  | Intramolecular | *ent*-**186** (10 mol %),<br>$PhI(OAc)_2$ (1 eq),<br>MeOH, 0° |  | (74) dr 6.7:1<br>er 98.5:1.5 | 493 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

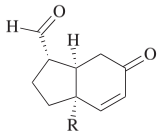
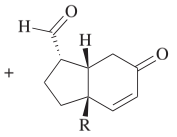
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{11-17}$



Intramolecular

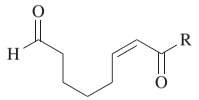
**218** (10 mol %), MeCN, 0°, 3–5 h

 **I** +  **II**

134

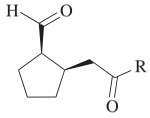
| R | | I/II | er |
|---|---|---|---|
| Me | (93) | 96:4 | 95.5:4.5 |
| allyl | (96) | 92:8 | 97.5:2.5 |
| *n*-Bu | (100) | 91:9 | 95.0:5.0 |
| Bn | (89) | 95:5 | 95.0:5.0 |

$C_{14}$



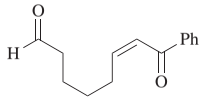
Intramolecular

**142** (0.05–1 mg/mL), pH 7.4 phosphate buffer saline, 5% of MeCN, rt



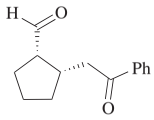
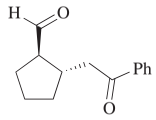
387

| R | | *cis*/*trans* | er |
|---|---|---|---|
| Ph | (—) | 12:1 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | (—) | 3:1 | 94.0:6.0 |
| 4-$O_2NC_6H_4$ | (—) | 2:1 | 98.0:2.0 |



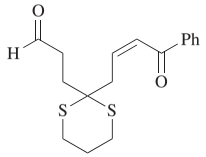
Intramolecular

**218** (10 mol %), acetone, 0°

 + 

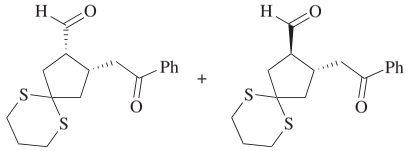
134

(100) *cis*/*trans* = 89:11, er 99.5:0.5



Intramolecular

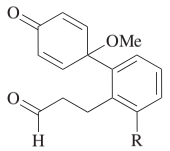
**218** (10 mol %), acetone, 0°



134

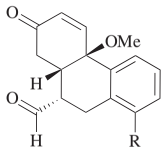
(93) *cis*/*trans* > 95:5, er 99.5:0.5

$C_{15}$



Intramolecular

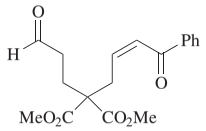
*ent*-**186** (10 mol %),
$PhI(OAc)_2$ (1 eq),
MeOH, 0°



| R | | dr | er |
|---|---|---|---|
| H | (75)[a] | >20:1 | 99.5:0.5 |
| Cl | (52)[a] | >20:1 | 99.5:0.5 |

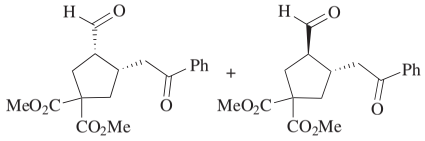
493

$C_{16}$



Intramolecular

**218** (10 mol %), acetone, 0°



134

(95) *cis*/*trans* = 91:9, er 98.5:1.5

[a] The enone was generated in situ after MeOH/$PhI(OAc)_2$ mediated dearomatization.

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS

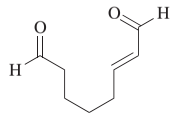
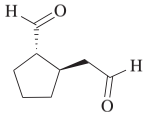
| Donor/Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | |
| $C_8$  | **217** (10 mol %), THF, rt, 15–24 h |  (85) *anti*/*syn* = 49:1 er 90.0:10.0 | 135 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)

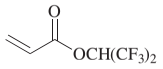
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

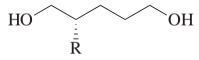
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{3-9}$





1. **219** (10 mol %), $Et_2O$, 15°
2. $NaBH_4$, MeOH

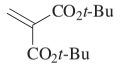


| R | Time (h) | | er |
|---|---|---|---|
| Me | 72 | (80) | 98.0:2.0 |
| $BnOCH_2$ | 72 | (46) | 97.0:3.0 |
| $BnO(CH_2)_3$ | 24 | (70) | 98.0:2.0 |
| *i*-Pr | 72 | (57) | 97.5:2.5 |
| *n*-Bu | 24 | (70) | 96.0:4.0 |
| *c*-$C_6H_{11}$ | 24 | (86) | 98.5:1.5 |
| *c*-$C_6H_{11}CH_2$ | 24 | (60) | 94.0:6.0 |
| Bn | 24 | (76) | 97.0:3.0 |

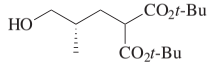
494

$C_3$





1. **219** (*x* mol %), $Et_2O$, 0°, 4 h
2. $NaBH_4$, MeOH

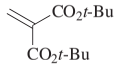


| *x* | | er |
|---|---|---|
| 3 | (79) | 98.0:2.0 |
| 10 | (80) | 98.0:2.0 |

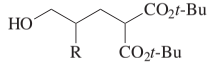
495, 494

$C_{3-9}$





1. **219** (*x* mol %), solvent
2. $NaBH_4$, MeOH



| R | *x* | Solvent | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|
| $BnOCH_2$ | 10 | $Et_2O$ | 0 | 4 | (69) | 96.5:3.5 |
| $CbzHNCH_2$ | 10 | THF | 0 | 40 | (82) | 92.0:8.0 |
| $MeO_2CCH_2$ | 10 | THF | 0 | 40 | (65) | 93.5:6.5 |
| $BnO(CH_2)_3$ | 10 | $Et_2O$ | 0 | 4 | (94) | 97.5:2.5 |
| *i*-Pr | 10 | $Et_2O$ | rt | 24 | (80) | 98.5:1.5 |

495, 494

TABLE 2. ALDEHYDES AS DONORS (*Continued*)

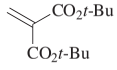
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

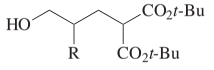
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{3-9}$





1. **219** (*x* mol %), solvent
2. $NaBH_4$, MeOH

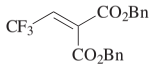


| R | *x* | Solvent | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|
| *n*-Bu | 10 | $Et_2O$ | 0 | 4 | (83) | 97.0:3.0 |
| *n*-$C_6H_{13}$ | 10 | $Et_2O$ | 0 | 4 | (83) | 97.0:3.0 |
| *c*-$C_6H_{11}$ | 10 | $Et_2O$ | rt | 72 | (89) | 97.0:3.0 |
| (3-$C_5H_4N$)$CH_2$ | 10 | $Et_2O$ | 0 | 4 | (87) | 96.5:3.5 |
| *c*-$C_6H_{11}CH_2$ | 10 | $Et_2O$ | 0 | 4 | (70) | 93.0:7.0 |
| Bn | 3 | $Et_2O$ | 0 | 4 | (83) | 97.5:2.5 |
| Bn | 10 | $Et_2O$ | 0 | 4 | (94) | 97.0:3.0 |

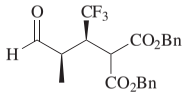
495, 494

$C_3$



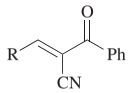


**145b** (10 mol %), $CHCl_3$, 0°, 24 h

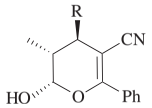


(94) dr 6.5:1, er 95.5:4.5

127

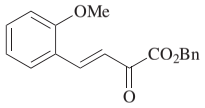


**145b** (20 mol %), 2-$FC_6H_4CO_2H$ (20 mol %), $CH_2Cl_2$, rt, 1.5 d

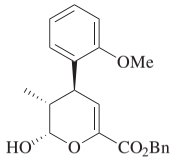


| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| 4-$BrC_6H_4$ | (81) | 3:1 | 97.5:2.5 | 77.5:22.5 |
| 4-$NCC_6H_4$ | (79) | 3:1 | 93.5:6.5 | 80.5:19.5 |

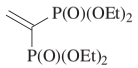
406



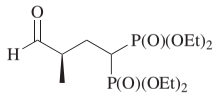
**198** (10 mol %), 2-$ClC_6H_4CO_2H$ (10 mol %), *i*-PrOH, rt, 1 d



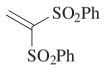
(93) dr 99.5:0.5 er 98.5:1.5 — 496



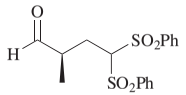
**145b** (25 mol %), $CHCl_3$, rt, 12 h



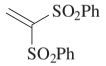
(75) er 87.5:12.5 — 125



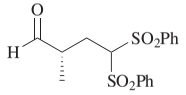
**145b** (25 mol %), $CHCl_3$



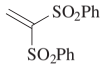
(75) er 87.5:12.5 — 125



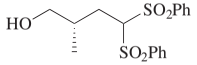
**207c** (10 mol %), $CH_2Cl_2$, 0°, 2 h



(93) er 98.5:1.5 — 497

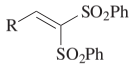


1. **220** (*x* mol %), $CH_2Cl_2$, rt, 4–8 h
2. $NaBH_4$, MeOH

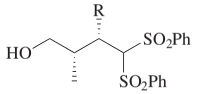


| *x* | | er |
|---|---|---|
| 5 | (82) | 96.0:4.0 |
| 10 | (59) | 98.0:2.0 |

498



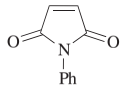
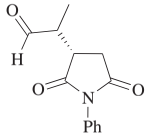
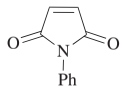
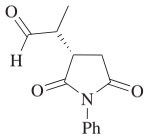
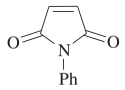
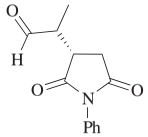
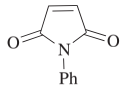
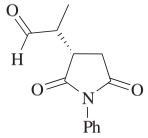
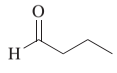
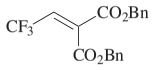
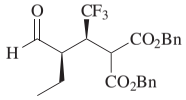
1. **207c** (10 mol %), $CHCl_3$, 0°
2. $NaBH_4$, MeOH

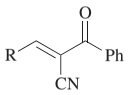


497

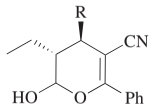
| R | Time (h) | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 14 | (86) | 4:1 | 99.0:1.0 |
| 2-$C_4H_3S$ | 16 | (90) | 3:1 | 99.0:1.0 |
| Ph | 12 | (91) | 15:1 | 99.0:1.0 |
| 4-$BrC_6H_4$ | 15 | (92) | 12:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 20 | (94) | 10:1 | >99.5:0.5 |
| 4-$MeC_6H_4$ | 12 | (88) | 10:1 | 97.5:2.5 |
| 2-Np | 24 | (82) | 10:1 | 99.5:0.5 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **208** (0.5 mol %), $PhCO_2H$ (5 mol %), $CHCl_3$, rt, 6–36 h |  (96) dr 2.4:1 er (major) 99.5:0.5 er (minor) 98.5:1.5 | 499 |
| |  | **209** (0.5 mol %), $PhCO_2H$ (5 mol %), $CHCl_3$, rt, 6–36 h |  (97) dr 2.1:1 er (major) 99.5:0.5 er (minor) 99.5:0.5 | 499 |
| |  | **221a** (5 mol %), $CH_2Cl_2$, rt, 6 h |  (98) dr 1.3:1 er (major) 98.0:2.0 er (minor) 98.5:1.5 | 500 |
| |  | **221b** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 96 h |  (43) *syn*/*anti* = 58:42 er (*syn*) 99.5:0.5 er (*anti*) 99.5:0.5 | 501 |
| $C_4$ | | | | |
|  |  | **145b** (10 mol %), $CHCl_3$, 0°, 24 h |  (84) dr 6.1:1 er 98.5:1.5 | 127 |

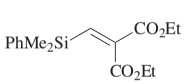


**145b** (20 mol %),
2-$FC_6H_4CO_2H$ (20 mol %),
$CH_2Cl_2$, rt

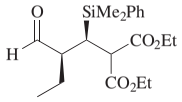


406

| R | Time (d) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| $4\text{-}BrC_6H_4$ | 2.5 | (87) | 1.6:1 | 91.5:8.5 | 94.5:5.5 |
| $4\text{-}O_2NC_6H_4$ | 3 | (84) | 1.6:1 | 93.5:6.5 | 94.0:6.0 |
| $4\text{-}NCC_6H_4$ | 2.5 | (75) | 1.3:1 | 93.5:6.5 | 95.0:5.0 |

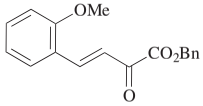


**145b** (15 mol %),
AcOH (15 mol %),
$CH_2Cl_2$, rt, 4 d

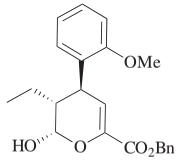


(79) dr 86:14
er 99.0:1.0

502, 503

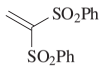


**198** (10 mol %),
2-$ClC_6H_4CO_2H$ (10 mol %),
*i*-PrOH, rt, 1 d

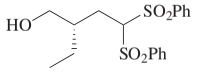


(92) dr 99.5:0.5
er 98.5:1.5

496



1. **220** (*x* mol %),
$CH_2Cl_2$, rt, 4–8 h
2. $NaBH_4$, MeOH



| *x* | | er |
|---|---|---|
| 5 | (66) | 96.5:3.5 |
| 10 | (71) | 97.0:3.0 |

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TABLE 2. ALDEHYDES AS DONORS (*Continued*)

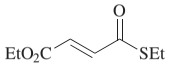
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

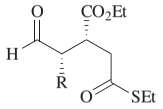
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{4–11}$





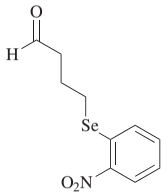
*ent*-**145b** (*x* mol %),
AcOH (*y* mol %),
MeOH, 0°, 1 h; then rt

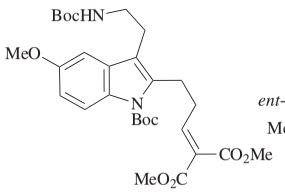


504

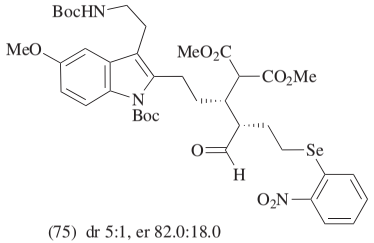
| R | *x* | *y* | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| $BnOCH_2CH_2$ | 10 | 50 | 27 | (90) | 6:1 | >99.5:0.5 |
| *i*-Pr | 20 | 100 | 38 | (69) | 9:1 | >99.5:0.5 |
| $HC{\equiv}C(CH_2)_2$ | 10 | 50 | 26 | (95) | 8:1 | >99.5:0.5 |
| Bn | 10 | 50 | 48 | (94) | 7:1 | >99.5:0.5 |
| $CH_2{=}CH(CH_2)_7$ | 10 | 50 | 36 | (100) | 8:1 | >99.5:0.5 |

$C_4$



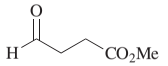


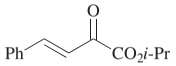
*ent*-**145b** (10 mol %),
MeCN, 0°, 3 d



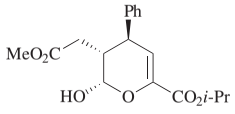
(75) dr 5:1, er 82.0:18.0

505





**198** (10 mol %),
2-$ClC_6H_4CO_2H$ (10 mol %),
*i*-PrOH, rt, 3 h

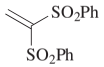


(96) dr 99.5:0.5
er 95.0:5.0

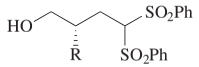
496

$C_{4–9}$





1. **220** (*x* mol %), $CH_2Cl_2$, rt, 4–8 h
2. $NaBH_4$, MeOH

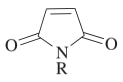


498

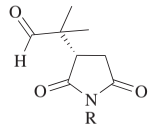
| R | *x* | | er |
|---|---|---|---|
| $BnO(CH_2)_2$ | 10 | (66) | 98.5:1.5 |
| *n*-Pr | 5 | (56) | 97.0:3.0 |
| *n*-Pr | 10 | (88) | 97.5:2.5 |
| *i*-Pr | 10 | (99) | 99.5:0.5 |
| *n*-Bu | 5 | (49) | 96.0:4.0 |
| *n*-Bu | 10 | (93) | 96.0:4.0 |
| *n*-$C_6H_{13}$ | 5 | (55) | 95.0:5.0 |
| *n*-$C_6H_{13}$ | 10 | (60) | 96.5:3.5 |
| *n*-$C_7H_{15}$ | 10 | (71) | 95.5:4.5 |
| Bn | 10 | (95) | 96.5:3.5 |

$C_4$





**208** (0.5 mol %), $PhCO_2H$ (5 mol %), $CHCl_3$, rt, 6–36 h



| R | | er |
|---|---|---|
| Ph | (97) | 99.5:0.5 |
| 3-$BrC_6H_4$ | (72) | 98.5:1.5 |
| 4-$BrC_6H_4$ | (66) | 97.0:3.0 |
| 3-$ClC_6H_4$ | (77) | 97.0:3.0 |
| 4-$ClC_6H_4$ | (79) | 98.0:2.0 |
| 4-$FC_6H_4$ | (91) | 99.0:1.0 |
| 2-$MeOC_6H_4$ | (94) | 99.0:1.0 |
| 3-$O_2NC_6H_4$ | (59) | 97.5:2.5 |
| 4-$O_2NC_6H_4$ | (75) | 97.5:2.5 |
| 4-$MeC_6H_4$ | (94) | 99.0:1.0 |
| 2,6-$Me_2C_6H_3$ | (80) | 97.5:2.5 |
| Bn | (95) | 99.5:0.5 |

499

TABLE 2. ALDEHYDES AS DONORS (*Continued*)

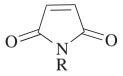
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

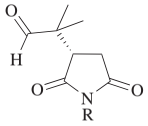
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_4$

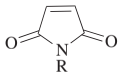




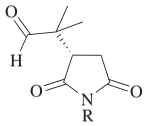
**209** (0.5 mol %), $PhCO_2H$ (5 mol %), $CHCl_3$, rt, 6–36 h



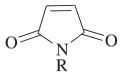
| R | | er | |
|---|---|---|---|
| Ph | (98) | 98.0:2.0 | |
| 3-$BrC_6H_4$ | (75) | 97.0:3.0 | 499 |
| 4-$BrC_6H_4$ | (64) | 95.0:5.0 | |
| 3-$ClC_6H_4$ | (77) | 97.5:2.5 | |
| 4-$ClC_6H_4$ | (81) | 97.5:2.5 | |
| 4-$FC_6H_4$ | (88) | 96.5:3.5 | |
| 2-$MeOC_6H_4$ | (93) | 99.0:1.0 | |
| 3-$O_2NC_6H_4$ | (62) | 96.5:3.5 | |
| 4-$O_2NC_6H_4$ | (70) | 98.5:1.5 | |
| 4-$MeC_6H_4$ | (92) | 98.5:1.5 | |
| 2,6-$Me_2C_6H_3$ | (82) | 99.0:1.0 | |
| Bn | (96) | 99.0:1.0 | |



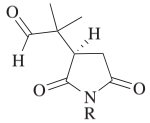
**221a** (5 mol %), $CH_2Cl_2$, rt, 6 h



| R | | er | |
|---|---|---|---|
| Me | (94) | 99.5:0.5 | |
| Ph | (98) | 99.5:0.5 | 500 |
| 4-$ClC_6H_4$ | (93) | 99.5:0.5 | |
| 2-$FC_6H_4$ | (93) | 99.5:0.5 | |
| 3-$FC_6H_4$ | (93) | 99.5:0.5 | |
| 4-$FC_6H_4$ | (94) | 99.5:0.5 | |
| 4-$MeOC_6H_4$ | (82) | 99.5:0.5 | |
| 3-$O_2NC_6H_4$ | (93) | 99.5:0.5 | |
| 4-$MeC_6H_4$ | (94) | 99.5:0.5 | |
| Bn | (98) | 99.5:0.5 | |

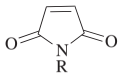


**221a** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt

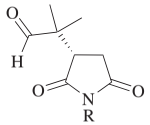


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| R | Time (h) | | er |
|---|---|---|---|
| *n*-Pr | 1 | (97) | 99.5:0.5 |
| *i*-Pr | 3 | (96) | 99.5:0.5 |
| Ph | 1 | (96) | 99.5:0.5 |
| 4-$BrC_6H_4$ | 1 | (98) | >99.5:0.5 |
| 4-$ClC_6H_4$ | 1 | (98) | >99.5:0.5 |
| 4-$MeOC_6H_4$ | 2 | (97) | >99.5:0.5 |
| 4-$MeC_6H_4$ | 1 | (93) | 99.5:0.5 |
| 3-$CF_3C_6H_4$ | 1 | (96) | >99.5:0.5 |
| Bn | 1 | (97) | >99.5:0.5 |



**221b** (10 mol %), $CH_2Cl_2$, rt



501

| R | Time (h) | | er |
|---|---|---|---|
| 4-$ClC_6H_4$ | 48 | (89) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 69 | (93) | 99.5:0.5 |
| 4-$O_2NC_6H_4$ | 48 | (86) | >99.5:0.5 |
| 4-$MeC_6H_4$ | 34 | (78) | >99.5:0.5 |
| Bn | 24 | (85) | >99.5:0.5 |

TABLE 2. ALDEHYDES AS DONORS (*Continued*)

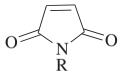
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

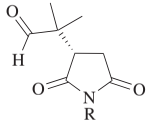
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_4$



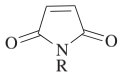


**222** (5 mol %), $CH_2Cl_2$, rt

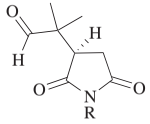


507

| R | Time (h) | | er |
|---|---|---|---|
| Ph | 24 | (96) | 94.0:6.0 |
| 4-$ClC_6H_4$ | 46 | (81) | 91.0:9.0 |
| 4-$MeOC_6H_4$ | 48 | (96) | 91.5:8.5 |
| 4-$O_2NC_6H_4$ | 48 | (87) | 88.5:11.5 |
| 4-$MeC_6H_4$ | 48 | (85) | 87.5:12.5 |
| Bn | 48 | (96) | 95.5:4.5 |

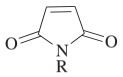


**223** (20 mol %),
DMF/$H_2O$ (2:1), rt

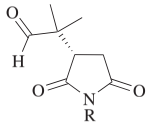


508

| R | Time (d) | | er |
|---|---|---|---|
| H | 1.5 | (94) | 91.5:8.5 |
| Me | 1.5 | (84) | 87.5:12.5 |
| Ph | 2 | (99) | 94.0:6.0 |
| 4-$AcOC_6H_4$ | 1.5 | (92) | 89.5:10.5 |
| 4-$BrC_6H_4$ | 2 | (94) | 96.5:3.5 |
| Bn | 2 | (99) | 88.0:12.0 |



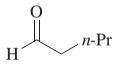
**224** (5 mol %),
$PhSO_2NH_2$ (*x* mol %),
base (5 mol %),
2 M in $CH_2Cl_2$, rt

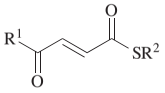


509

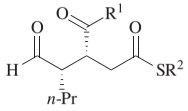
| R | *x* | Base | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | — | KOH | 4 | (96) | >99.5:0.5 |
| Ph | 5 | DMAP | 6 | (91) | 98.0:2.0 |
| Bn | 5 | DMAP | 5 | (94) | 98.5:1.5 |

$C_5$





*ent*-**145b** (*x* mol %),
AcOH (50 mol %),
MeOH, 0°, 1 h; then rt



504

| $R^1$ | $R^2$ | *x* | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| EtO | Et | 10 | 22 | (100) | 7:1 | >99.5:0.5 |
| EtO | $CF_3CH_2$ | 2 | 7 | (92) | 8:1 | >99.5:0.5 |
| EtO | Ph | 5 | 4 | (99) | 12:1 | >99.5:0.5 |
| EtO | 4-$BrC_6H_4$ | 2 | 7 | (91) | 8:1 | 96.0:4.0 |
| EtO | 4-$BrC_6H_4$ | 5 | 2 | (93) | 12:1 | >99.5:0.5 |
| EtO | Bn | 10 | 23 | (100) | 12:1 | >99.5:0.5 |
| *t*-BuO | Et | 10 | 21 | (100) | 9:1 | >99.5:0.5 |
| *t*-BuO | Ph | 5 | 5 | (90) | 9:1 | >99.5:0.5 |
| BnO | Et | 10 | 19 | (99) | 12:1 | >99.5:0.5 |
| BnO | Ph | 5 | 3.5 | (94) | 9.1 | >99.5:0.5 |
| $C_4H_8N$ | Ph | 5 | 5 | (92) | 8:1 | 91.0:9.0 |

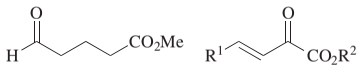
TABLE 2. ALDEHYDES AS DONORS (*Continued*)

D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

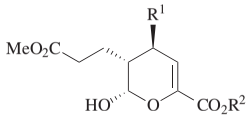
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_5$





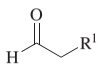
**198** (10 mol %), 2-$ClC_6H_4CO_2H$ (10 mol %), *i*-PrOH, rt

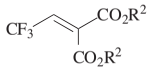


dr 99.5:0.5 496

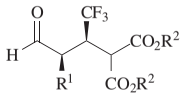
| $R^1$ | $R^2$ | Time (d) | | er |
|---|---|---|---|---|
| Et | Et | 5 | (87) | 97.5:2.5 |
| 2-$C_4H_3O$ | *i*-Pr | 3 | (92) | 95.5:4.5 |
| *n*-$C_5H_{11}$ | Et | 5 | (73) | 96.0:4.0 |
| Ph | Et | 3 | (90) | 95.5:4.5 |
| Ph | *i*-Pr | 3 | (95) | 95.5:4.5 |
| Ph | Bn | 3 | (98) | 97.5:2.5 |
| 2-$BrC_6H_4$ | *i*-Pr | 3 | (82) | 96.5:3.5 |
| 3-$BrC_6H_4$ | *i*-Pr | 3 | (94) | 95.5:4.5 |
| 4-$BrC_6H_4$ | *i*-Pr | 3 | (94) | 95.0:5.0 |
| 2-$ClC_6H_4$ | *i*-Pr | 3 | (92) | 96.5:3.5 |
| 4-$ClC_6H_4$ | *i*-Pr | 3 | (99) | 96.5:3.5 |
| 2,6-$Cl_2C_6H_3$ | *i*-Pr | 3 | (89) | 96.5:3.5 |
| 2-$FC_6H_4$ | *i*-Pr | 3 | (99) | 95.5:4.5 |
| 4-$FC_6H_4$ | *i*-Pr | 3 | (93) | 95.5:4.5 |
| 2-$MeOC_6H_4$ | *i*-Pr | 5 | (72) | 99.0:1.0 |
| 2-$MeOC_6H_4$ | Bn | 4 | (87) | 99.5:0.5 |
| 3-$MeOC_6H_4$ | *i*-Pr | 3 | (90) | 96.5:3.5 |
| 4-$MeOC_6H_4$ | *i*-Pr | 7 | (66) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | Bn | 6 | (76) | 98.0:2.0 |
| 4-$MeC_6H_4$ | *i*-Pr | 5 | (74) | 95.5:4.5 |
| 2-Np | *i*-Pr | 3 | (93) | 96.0:4.0 |

$C_{5-9}$





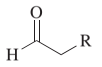
**145b** (10 mol %), $CHCl_3$, 0°, 24 h

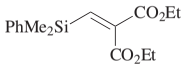


127

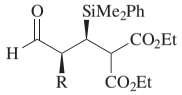
| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| *n*-Pr | Bn | (91) | 5.9:1 | 99.0:1.0 |
| *i*-Pr | Bn | (91) | 14:1 | 98.0:2.0 |
| Bn | Me | (94) | 5.7:1 | 99.0:1.0 |
| Bn | Et | (91) | 5.2:1 | 99.5:0.5 |
| Bn | Bn | (90) | 5.1:1 | 98.0:2.0 |

$C_{5-7}$





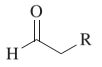
**145b** (15 mol %), AcOH (15 mol %), $CH_2Cl_2$, rt, 4 d

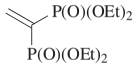


503

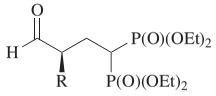
| R | | *syn*/*anti* | er |
|---|---|---|---|
| *n*-Pr | (70) | 86:14 | 99.4:0.6 |
| *n*-Bu | (73) | 84:16 | >99.5:0.5 |
| *n*-$C_5H_{11}$ | (75) | 81:19 | 98.9:1.1 |

$C_{5-9}$





**145b** (25 mol %), $CHCl_3$, rt, 12 h



| R | | er | |
|---|---|---|---|
| *n*-Pr | (75) | 93.0:7.0 | 128, 125 |
| *i*-Pr | (80) | 95.0:5.0 | |
| allyl | (65) | 73.0:27.0 | |
| *t*-Bu | (85) | 98.5:1.5 | |
| Bn | (81) | 92.5:7.5 | |

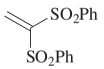
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

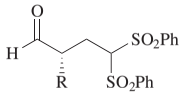
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{5-11}$



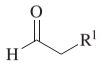


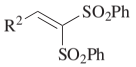
**207c** (10 mol %), $CH_2Cl_2$, 0°, 2 h



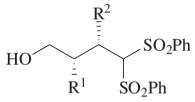
| R | | er | |
|---|---|---|---|
| *n*-Pr | (93) | 98.5:1.5 | 497 |
| *n*-Bu | (94) | 99.5:0.5 | |
| *t*-Bu | (93) | 97.0:3.0 | |
| *n*-$C_5H_{11}$ | (94) | >99.5:0.5 | |
| Bn | (94) | 97.0:2.0 | |
| *n*-$C_9H_{19}$ | (97) | >99.5:0.5 | |

$C_{5-9}$





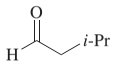
1. **207c** (10 mol %), $CHCl_3$, 0°
2. $NaBH_4$, MeOH

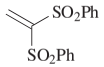


497

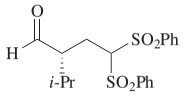
| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| *n*-Pr | Ph | 12 | (94) | 6:1 | 99.5:0.5 |
| Bn | 4-$MeOC_6H_4$ | 16 | (91) | 17:1 | 99.5:0.5 |

$C_5$

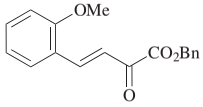




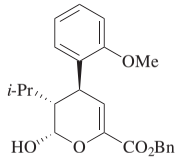
**171** (25 mol %), $CHCl_3$, –60°, 2 h



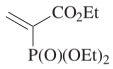
(79) er 77.5:22.5 437



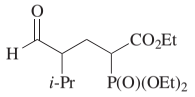
**198** (10 mol %), 2-$ClC_6H_4CO_2H$ (10 mol %), *i*-PrOH, rt, 10 h



(42) dr 99.5:0.5
er 99.0:1.0 496



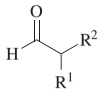
**207c** (10 mol %), $CH_2Cl_2$, rt, 24 h

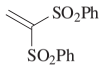


100% conv.
dr 4:1, er 98.0:2.0

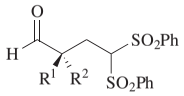
129

$C_{5-9}$



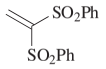


*ent*-**3** (25 mol %), $CHCl_3$

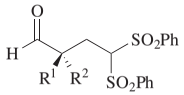


125, 510

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Et | Me | rt | 4 | (59) | 56.0:44.0 |
| *n*-Pr | H | –60 | 2 | (76) | 76.5:23.5 |
| *i*-Pr | H | –60 | 2 | (71) | 87.5:12.5 |
| *t*-Bu | H | –60 | 2 | (78) | 90.0:10.0 |
| *c*-$C_6H_{11}$ | H | –60 | 2 | (71) | 85.0:15.0 |
| Ph | Me | rt | 7 | (14) | 50.0:50.0 |



**113** (*x* mol %), $CHCl_3$



355

| $R^1$ | $R^2$ | *x* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|
| *n*-Pr | H | 10 | –60 | 2 | (87) | 87.0:13.0 |
| *i*-Pr | H | 5 | –60 | 3 | (86) | 92.5:7.5 |
| *i*-Pr | H | 10 | –60 | 2 | (90) | 92.5:7.5 |
| allyl | H | 10 | –60 | 2 | (84) | 88.5:11.5 |
| *t*-Bu | H | 10 | –60 | 4 | (96) | 87.5:12.5 |
| *c*-$C_6H_{11}$ | H | 1 | –60 | 3 | (82) | 95.5:4.5 |
| Ph | Me | 10 | rt | 4 | (84) | 58.0:42.0 |

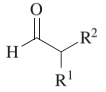
TABLE 2. ALDEHYDES AS DONORS (*Continued*)

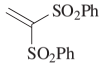
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

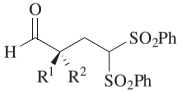
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{5-13}$





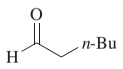
**145b** (25 mol %), $CHCl_3$

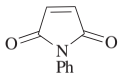


125

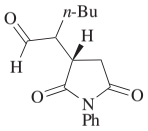
| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Et | Me | rt | 24 | (75) | 56.0:44.0 |
| *n*-Pr | H | –60° | 2 | (87) | 92.5:7.5 |
| *i*-Pr | H | –60° | 2 | (90) | 96.0:4.0 |
| allyl | H | –60° | 2 | (88) | 96.0:4.0 |
| *t*-Bu | H | –60° | 2 | (90) | 99.0:1.0 |
| *c*-$C_6H_{11}$ | H | –60° | 2 | (86) | 91.5:8.5 |
| *c*-$C_6H_{11}$ | Me | rt | 24 | (71) | 82.0:18.0 |
| Ph | Me | rt | 24 | (78) | 73.5:26.5 |
| (*Z*)-dec-4-ene | H | –60° | 2 | (77) | 96.5:3.5 |
| 1-Np | Me | rt | 24 | (76) | 95.5:4.5 |

$C_6$



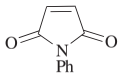


**208** (0.5 mol %), $PhCO_2H$ (5 mol %), $CHCl_3$, rt, 6–36 h

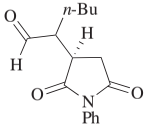


(66) dr 1.9:1
er (major) 98.5:1.5
er (minor) 97.0:3.0

499



**209** (0.5 mol %), $PhCO_2H$ (5 mol %), $CHCl_3$, rt, 6–36 h

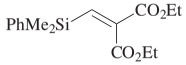


(71) dr 1.7:1
er (major) 97.5:2.5
er (minor) 98.0:2.0

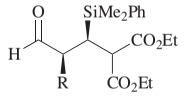
499

$C_{6-7}$





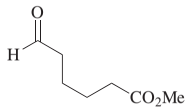
**145b** (15 mol %), AcOH (15 mol %), $CH_2Cl_2$, rt, 4 d

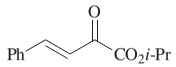


502

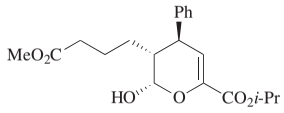
| R | | *syn*/*anti* | er |
|---|---|---|---|
| *n*-Bu | (73) | 84:16 | >99.5:0.5 |
| *n*-$C_5H_{11}$ | (75) | 81:19 | 99.0:1.0 |

$C_6$

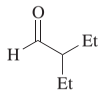


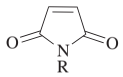


**198** (10 mol %), 2-$ClC_6H_4CO_2H$ (10 mol %), *i*-PrOH, rt, 3 d

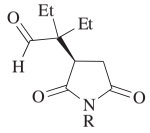


(95) dr 99.5:0.5 er 95.0:5.0 496



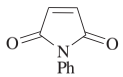


**221a** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 3 h

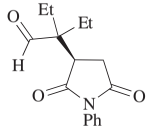


| R | | er |
|---|---|---|
| *n*-Pr | (97) | 99.5:0.5 |
| Ph | (95) | 99.0:1.0 |

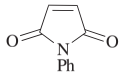
506



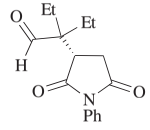
**221b** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 168 h



(99) er 99.5:0.5 501

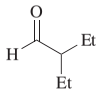
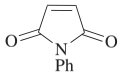
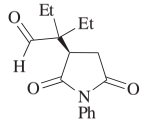
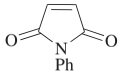
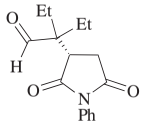
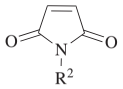
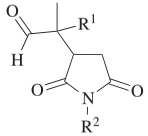


**222** (5 mol %), $CH_2Cl_2$, rt, 144 h



(79) er 80.0:20.0 507

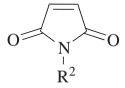
TABLE 2. ALDEHYDES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_6$ | | | | |
|  |  | **223** (20 mol %), DMF/$H_2O$ (2:1), rt, 4 d |  (79) er 80.0:20.0 | 508 |
| |  | **224** (5 mol %), KOH (5 mol %), 2 M in $CH_2Cl_2$, rt, 6 h |  (96) er >99.5:0.5 | 509 |
| $C_{6-14}$ | | | | |
|  |  | **221a** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt |  | 506 |

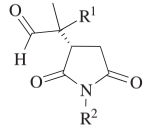
| $R^1$ | $R^2$ | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| *n*-Pr | Ph | 1 | (95) | 1:1 | 99.0:1.0 | 98.0:2.0 |
| 4-*t*-Bu$C_6H_4CH_2$ | Ph | 4 | (96) | 2:1 | 99.5:0.5 | 98.0:2.0 |
| 4-*t*-Bu$C_6H_4CH_2$ | 4-Cl$C_6H_4$ | 4 | (98) | 2:1 | 99.5:0.5 | 99.5:0.5 |

$C_{6-10}$





**224** (5 mol %),
$PhSO_2NH_2$ (*x* mol %),
base (5 mol %),
2 M in $CH_2Cl_2$, rt



| $R^1$ | $R^2$ | *x* | Base | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|---|---|
| *n*-Pr | Ph | 5 | DMAP | 16 | (88) | 74:26 | 99.0:1.0 | 93.0:7.0 |
| $Me_2C{=}CH(CH_2)_2$ | Ph | 0 | KOH | 4 | (94) | 92:8 | >99.5:0.5 | >99.5:0.5 |
| $Me_2C{=}CH(CH_2)_2$ | Ph | 5 | DMAP | 5 | (98) | 90:10 | >99.5:0.5 | >99.5:0.5 |
| Ph | Ph | 0 | KOH | 24 | (82) | >99:1 | 96.0:4.0 | 96.0:4.0 |
| Ph | Ph | 5 | DMAP | 24 | (81) | >99:1 | 96.0:4.0 | 96.0:4.0 |
| 3,4-$(OCH_2O)C_6H_3CH_2$ | Ph | 0 | KOH | 4 | (87) | 97:3 | 99.0:1.0 | — |
| 3,4-$(OCH_2O)C_6H_3CH_2$ | Ph | 5 | DMAP | 16 | (89) | 97:3 | 97.0:3.0 | — |
| 3,4-$(OCH_2O)C_6H_3CH_2$ | Bn | 0 | KOH | 4 | (89) | 96:4 | >99.5:0.5 | — |
| 3,4-$(OCH_2O)C_6H_3CH_2$ | Bn | 5 | DMAP | 20 | (84) | 93:7 | 99.0:1.0 | — |

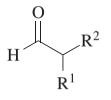
TABLE 2. ALDEHYDES AS DONORS (*Continued*)

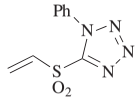
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

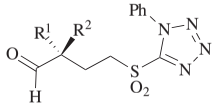
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{6-13}$





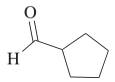
**225c** (20 mol %),
4-$O_2NC_6H_4CO_2H$ (*x* mol %),
$CHCl_3$, rt

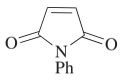


511

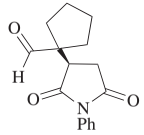
| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Me | *n*-Pr | 50 | 96 | (48) | 70.0:30.0 |
| Me | 2-$C_4H_3S$ | 20 | 72 | (68) | 79.0:21.0 |
| Me | $Me_2C{=}CH(CH_2)_2$ | 50 | 96 | (46) | 71.0:29.0 |
| Me | Ph | 20 | 48 | (76) | 97.0:3.0 |
| Me | 4-$BrC_6H_4$ | 20 | 48 | (71) | 96.5:3.5 |
| Me | 2-$FC_6H_4$ | 20 | 72 | (30) | 96.0:4.0 |
| Me | 4-$MeC_6H_4$ | 20 | 48 | (60) | 96.5:3.5 |
| Me | 4-$NCC_6H_4$ | 20 | 48 | (65) | 93.0:7.0 |
| Me | Bn | 50 | 96 | (62) | 85.5:14.5 |
| Me | 2-Np | 20 | 48 | (83) | 94.5:5.5 |
| Et | Ph | 50 | 120 | (50) | 87.5:12.5 |

$C_6$



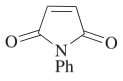


**221b** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt, 76 h

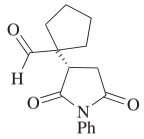


(92) er 95.5:4.5

501



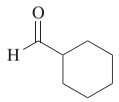
**222** (5 mol %),
$CH_2Cl_2$, rt, 25 h

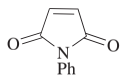


(98) er 89.5:10.5

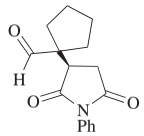
507

$C_7$

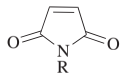




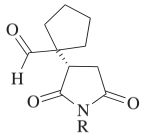
**223** (20 mol %),
$DMF/H_2O$ (2:1), rt, 4 d



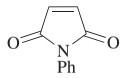
(99) er 93.0:7.0 508



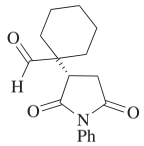
**224** (5 mol %),
$PhSO_2NH_2$ (5 mol %),
DMAP (5 mol %),
2 M in $CH_2Cl_2$, rt, 20 h



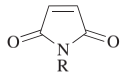
| R | Time (h) | | er | |
|---|---|---|---|---|
| Ph | 16 | (93) | 98.5:1.5 | 509 |
| Bn | 11 | (86) | 99.5:0.5 | |



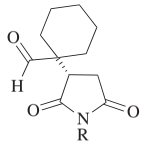
**147** (5 mol %),
$CH_2Cl_2$, rt, 168 h



(90) er 82.5:17.5 507



**208** (0.5 mol %),
$PhCO_2H$ (5 mol %),
$CHCl_3$, rt, 6–36 h



| R | | er | |
|---|---|---|---|
| Ph | (92) | 97.5:2.5 | |
| 4-$FC_6H_4$ | (96) | 98.5:1.5 | 499 |
| 2-$MeOC_6H_4$ | (97) | 96.5:3.5 | |
| 4-$MeC_6H_4$ | (85) | 96.0:4.0 | |
| 2,6-$Me_2C_6H_3$ | (70) | 96.0:4.0 | |
| Bn | (96) | 95.0:5.0 | |

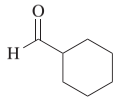
TABLE 2. ALDEHYDES AS DONORS (*Continued*)

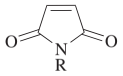
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

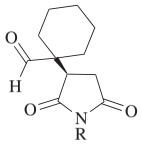
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_7$

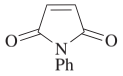




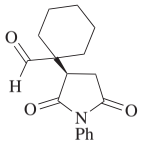
**209** (0.5 mol %), $PhCO_2H$ (5 mol %), $CHCl_3$, rt, 6–36 h



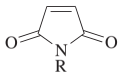
| R | | er | |
|---|---|---|---|
| Ph | (93) | 95.0:5.0 | |
| 4-$FC_6H_4$ | (96) | 98.5:1.5 | 499 |
| 2-$MeOC_6H_4$ | (97) | 96.5:3.5 | |
| 4-$MeC_6H_4$ | (80) | 95.0:5.0 | |
| 2,6-$Me_2C_6H_3$ | (75) | 95.0:5.0 | |
| Bn | (95) | 95.0:5.0 | |



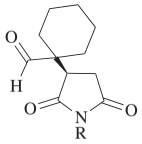
**221a** (5 mol %), $CH_2Cl_2$, rt, 6 h



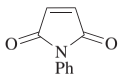
(55) er 99.0:1.0 — 500



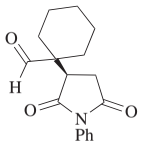
**221a** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 5 h



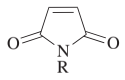
| R | | er | |
|---|---|---|---|
| Ph | (97) | 99.0:1.0 | |
| 3-$ClC_6H_4$ | (98) | 99.0:1.0 | 506 |
| 4-$MeC_6H_4$ | (97) | 98.5:1.5 | |
| 4-$CF_3C_6H_4$ | (95) | 98.5:1.5 | |



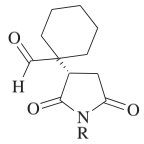
**223** (20 mol %), $DMF/H_2O$ (2:1), rt, 4 d



(99) er 92.0:8.0 — 508



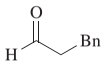
**224** (5 mol %),
$PhSO_2NH_2$ (5 mol %),
DMAP (5 mol %),
2 M in $CH_2Cl_2$, rt, 20 h

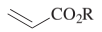


| R | | er |
|---|---|---|
| Ph | (77) | 98.5:1.5 |
| Bn | (80) | 98.0:2.0 |

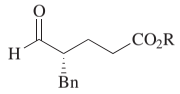
509

$C_9$



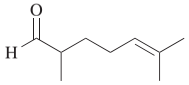


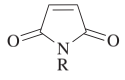
**219** (10 mol %),
$Et_2O$, 0°, 72 h



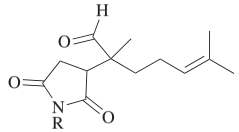
| R | | er |
|---|---|---|
| $(CF_3)_2CH$ | (63) | 96.0:4.0 |
| $(CF_3)_2(Me)C$ | (38) | 96.5:3.5 |

494





**221a** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, rt, 1 h



| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| Ph | (99) | 2:1 | 99.5:0.5 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | (99) | 2:1 | 99.5:0.5 | 99.5:0.5 |

506

TABLE 2. ALDEHYDES AS DONORS (*Continued*)

D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

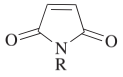
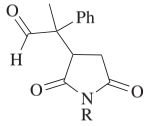
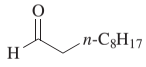
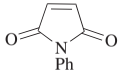
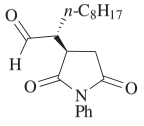
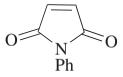
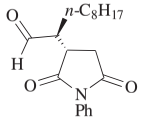
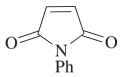
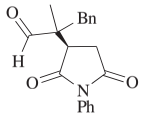
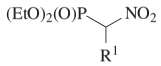
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_9$ | | | | |
|  |  | **221a** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, 35° |  dr 8:1 | 506 |
| | | | R / Time (h) / er: Ph 36 (90) 95.5:4.5; 4-$BrC_6H_4$ 36 (92) 97.5:2.5; 3-$ClC_6H_4$ 24 (93) 97.0:3.0; 4-$MeOC_6H_4$ 60 (85) 96.5:3.5 | |
| $C_{10}$ | | | | |
|  |  | **221b** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, rt, 24 h |  (63) *syn*/*anti* 73:27; er (*syn*) 99.5:0.5; er (*anti*) 99.0:1.0 | 501 |
| |  | **222** (5 mol %), $CH_2Cl_2$, rt, 168 h |  (87) dr 56:44; er (major) 71.0:29.0; er (minor) 64.0:36.0 | 507 |
|  |  | **221a** (5 mol %), $CH_2Cl_2$, rt, 6 h |  (85) dr 1:1; er 96.5:3.5; er 97.0:3.0 | 500 |

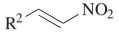
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS
A. NITROALKENES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

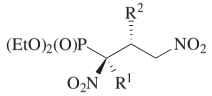
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{2-3}$





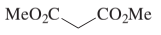
**69b** (10 mol %), 0.5 M in $C_6H_5CF_3$

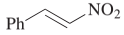


512

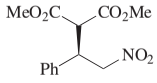
| $R^1$ | $R^2$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| Me | Me | –10 | 60 | (80) | 12:1 | 97.0:3.0 |
| Me | *i*-Bu | –10 | 60 | (82) | 13:1 | 99.0:1.0 |
| Me | 2-$C_4H_3O$ | –10 | 70 | (70) | 11:1 | 94.5:5.5 |
| Me | 2-$C_4H_3S$ | 0 | 26 | (76) | 5:1 | 96.5:3.5 |
| Me | *n*-$C_5H_{11}$ | –10 | 40 | (79) | 20:1 | >99.0:1.0 |
| Me | Ph | –10 | 45 | (74) | 12:1 | 96.5:3.5 |
| Me | 3-$ClC_6H_4$ | –10 | 26 | (64) | 10:1 | 96.0:4.0 |
| Me | 4-$ClC_6H_4$ | –10 | 62 | (64) | 10:1 | 96.5:3.5 |
| Me | 4-$FC_6H_4$ | –10 | 80 | (60) | 10:1 | 97.0:3.0 |
| Me | 4-$MeOC_6H_4$ | –10 | 32 | (65) | 10:1 | 96.0:4.0 |
| Me | 3-$O_2NC_6H_4$ | 0 | 70 | (64) | 10:1 | 94.5:5.5 |
| Me | 4-$MeC_6H_4$ | –10 | 90 | (82) | 10:1 | 96.5:3.5 |
| Me | 4-$CF_3C_6H_4$ | –10 | 36 | (70) | 12:1 | 96.0:4.0 |
| Me | PhCH=CH | –10 | 88 | (70) | 6:1 | 95.5:4.5 |
| Me | 2-Np | 0 | 32 | (38) | 10:1 | 93.0:7.0 |
| Et | *i*-Bu | –10 | 60 | (85) | >20:1 | 96.5:3.5 |
| Et | *n*-$C_5H_{11}$ | –10 | 60 | (70) | >20:1 | 96.0:4.0 |

$C_3$





**68** (30 mol %), $PhCO_2H$ (20 mol %), toluene, rt, 4 d



(14) er 63.5:36.5

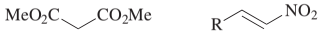
279

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

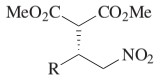
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





**226a** (*x* mol %), 1 M in THF

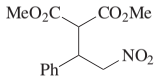


195

| R | *x* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| *i*-Bu | 10 | –20 | 72 | (86) | 97.0:3.0 |
| 2-$C_4H_3O$ | 10 | –20 | 36 | (97) | 99.0:1.0 |
| 2-$C_4H_3S$ | 10 | –20 | 36 | (99) | 99.0:1.0 |
| *n*-$C_5H_{11}$ | 10 | –20 | 72 | (81) | 97.0:3.0 |
| 3-$C_5H_4N$ | 10 | –20 | 36 | (98) | 98.0:2.0 |
| *c*-$C_6H_{11}$ | 20 | –20 | 109 | (71) | 97.0:3.0 |
| Ph | 10 | –20 | 36 | (97) | 98.0:2.0 |
| 4-$BrC_6H_4$ | 10 | –20 | 36 | (99) | 98.0:2.0 |
| 4-$ClC_6H_4$ | 10 | –20 | 36 | (97) | 98.5:1.5 |
| 2-$FC_6H_4$ | 10 | –20 | 36 | (97) | 98.5:1.5 |
| 4-$FC_6H_4$ | 10 | –20 | 36 | (97) | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 10 | –20 | 44 | (90) | 98.5:1.5 |
| 2-$O_2NC_6H_4$ | 10 | –50 | 69 | (90) | 98.5:1.5 |
| 2-$MeC_6H_4$ | 10 | –20 | 36 | (95) | 99.0:1.0 |
| 3-$MeC_6H_4$ | 10 | –20 | 36 | (97) | 98.5:1.5 |
| 4-$MeC_6H_4$ | 10 | –20 | 36 | (97) | 99.0:1.0 |
| 4-*i*-$PrC_6H_4$ | 10 | –20 | 36 | (95) | 98.5:1.5 |
| 1-Np | 10 | –20 | 36 | (99) | 99.0:1.0 |

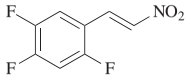


**227** (10 mol %), $Cs_2CO_3$, THF

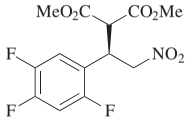


(60) er 52.5:47.5

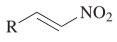
513



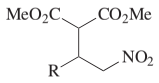
**228** (1 mol %), THF, –20°, 15 h



(88) er 97.5:2.5 514



**229a** (10 mol %), toluene, –20°



515

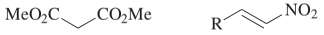
| R | Time (h) | | er |
|---|---|---|---|
| *n*-Pr | 36 | (97) | 95.0:5.0 |
| *i*-Bu | 48 | (89) | 95.0:5.0 |
| 2-$C_4H_3O$ | 36 | (99) | 96.5:3.5 |
| Ph | 36 | (99) | 97.0:3.0 |
| 2-$BrC_6H_4$ | 20 | (99) | 98.5:1.5 |
| 4-$BrC_6H_4$ | 36 | (99) | 97.0:3.0 |
| 2-$ClC_6H_4$ | 36 | (99) | 97.5:2.5 |
| 4-$ClC_6H_4$ | 20 | (98) | 96.5:3.5 |
| 4-$FC_6H_4$ | 36 | (97) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 36 | (99) | 97.5:2.5 |
| 4-$PhOC_6H_4$ | 36 | (99) | 95.5:4.5 |
| 4-$O_2NC_6H_4$ | 16 | (99) | 95.0:5.0 |
| 4-$MeC_6H_4$ | 36 | (99) | 96.0:4.0 |
| PhCH=CH | 84 | (92) | 96.0:4.0 |
| 4-$MeOC_6H_4CH$=CH | 72 | (91) | 95.0:5.0 |
| 4-$O_2NC_6H_4CH$=CH | 72 | (91) | 95.0:5.0 |
| 2-Np | 36 | (99) | 98.0:2.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

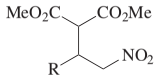
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



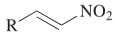


**229b** (10 mol %), toluene, rt

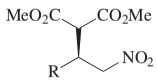


515

| R | Time (h) | | er |
|---|---|---|---|
| Ph | 144 | (99) | 99.5:0.5 |
| 2-$BrC_6H_4$ | 60 | (99) | 99.0:1.0 |
| 4-$BrC_6H_4$ | 108 | (99) | 95.0:5.0 |
| 2-$ClC_6H_4$ | 60 | (99) | 98.5:1.5 |
| 4-$ClC_6H_4$ | 108 | (99) | 95.0:5.0 |
| 4-$FC_6H_4$ | 60 | (99) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | 60 | (99) | 95.5:4.5 |

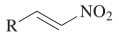


**230a** (10 mol %), solvent

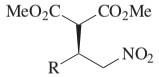


179

| R | Solvent | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | $CH_2Cl_2$ | –20 | 30 | (93) | 97.5:2.5 |
| 2-$C_4H_3S$ | $CH_2Cl_2$ | –20 | 30 | (87) | 97.0:3.0 |
| *n*-$C_5H_{11}$ | $CH_2Cl_2$ | –20 | 72 | (81) | 93.5:6.4 |
| *c*-$C_6H_{11}$ | — | rt | 31 | (82) | 91.0:9.0 |
| Ph | $CH_2Cl_2$ | –20 | 30 | (95) | 97.0:3.0 |
| 2-$BrC_6H_4$ | $CH_2Cl_2$ | –20 | 30 | (95) | 96.0:4.0 |
| 3-$BrC_6H_4$ | $CH_2Cl_2$ | –20 | 30 | (85) | 95.0:5.0 |
| 4-$BrC_6H_4$ | $CH_2Cl_2$ | –20 | 48 | (87) | 95.0:5.0 |
| 2-$ClC_6H_4$ | $CH_2Cl_2$ | –20 | 30 | (99) | 97.0:3.0 |
| 2-$MeOC_6H_4$ | $CH_2Cl_2$ | –20 | 30 | (96) | 98.5:1.5 |
| 3-$MeOC_6H_4$ | $CH_2Cl_2$ | –20 | 30 | (96) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | $CH_2Cl_2$ | –20 | 30 | (96) | 96.0:4.0 |
| 3-$MeC_6H_4$ | $CH_2Cl_2$ | –20 | 52 | (92) | 95.5:4.5 |
| 4-$MeC_6H_4$ | $CH_2Cl_2$ | –20 | 48 | (82) | 96.0:4.0 |
| 2-Np | $CH_2Cl_2$ | –20 | 48 | (83) | 94.5:5.5 |

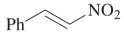


**230a** (10 mol %), $CH_2Cl_2$

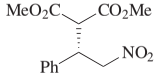


| R | Temp (°) | Time (h) | | er |
|---|---|---|---|---|
| 4-$FC_6H_4$ | –20 to 0 | 96 | (96) | 97.0:3.0 |
| 3-(*c*-$C_5H_9$)-4-$MeOC_6H_3$ | –20 | — | (92) | 96.0:4.0 |

516

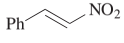


**231** (10 mol %), toluene, rt, 16 h

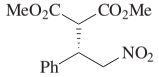


(81) er 92.0:8.0

517

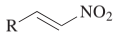


**232b** (5 mol %), solvent, rt

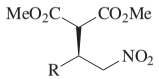


| Solvent | Time (h) | | er |
|---|---|---|---|
| $CH_2Cl_2$ | 168 | (65) | 96.5:3.5 |
| brine | 22 | (92) | 95.0:5.0 |

518



**233** (*x* mol %), 1 M in THF, rt



| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 1 | 36 | (96) | 97.5:2.5 |
| Ph | 1 | 24 | (98) | 96.0:4.0 |
| 2-$BrC_6H_4$ | 1 | 24 | (97) | 96.0:4.0 |
| 4-$BrC_6H_4$ | 1 | 24 | (99) | 96.0:4.0 |
| 2-$ClC_6H_4$ | 1 | 24 | (98) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 1 | 24 | (98) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 1 | 48 | (98) | 95.5:4.5 |
| 4-$MeC_6H_4$ | 1 | 36 | (97) | 96.5:3.5 |
| PhCH=CH | 3 | 72 | (91) | 92.0:8.0 |
| 1-Np | 1 | 24 | (>99) | 96.5:3.5 |

519

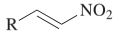
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

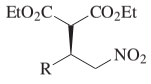
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



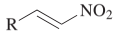


*ent*-**164b** (10 mol %), neat, –20°, 24 h

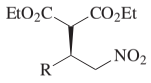


| R | | er |
|---|---|---|
| Et | (78) | 89.0:11.0 |
| *n*-Pr | (77) | 93.5:6.5 |
| *n*-Bu | (74) | 93.5:6.5 |
| 2-$C_4H_3S$ | (91) | 96.5:3.5 |
| *n*-$C_5H_{11}$ | (71) | 94.5:5.5 |
| *c*-$C_6H_{11}$ | (76) | 93.0:7.0 |
| Ph | (88) | 95.0:5.0 |
| 4-$FC_6H_4$ | (92) | 94.0:6.0 |
| 4-$MeC_6H_4$ | (67) | 92.5:7.5 |
| 4-$MeOC_6H_4$ | (86) | 94.5:5.5 |
| *n*-$C_{10}H_{21}$ | (61) | 91.5:8.5 |

520

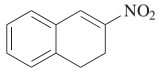


*ent*-**164b** (10 mol %), toluene, rt

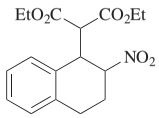


| R | Time (h) | | er |
|---|---|---|---|
| *i*-Bu | 48 | (88) | 90.5:9.5 |
| 2-$C_4H_3S$ | 48 | (74) | 95.0:5.0 |
| *n*-$C_5H_{11}$ | 48 | (78) | 90.5:9.5 |
| Ph | 24 | (86) | 96.5:3.5 |
| 4-$FC_6H_4$ | 12 | (87) | 96.0:4.0 |
| 2,6-$(MeO)_2C_6H_3$ | 72 | (87) | 96.5:3.5 |
| 1-Np | 24 | (95) | 96.0:4.0 |

86

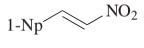


*ent*-**164b** (10 mol %), toluene, rt, 5 d

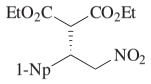


(68) dr 93:7
er 77.5:22.5
er 80.0:20.0

87



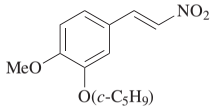
**226b** (1 mol %),
$H_2O$, rt, 10 h



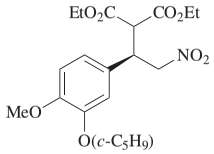
Catalyst Recycling

| Run | | er |
|---|---|---|
| 1 | (94) | 94.5:5.5 |
| 2 | (89) | 94.5:5.5 |
| 3 | (87) | 95.0:5.0 |
| 4 | (89) | 94.0:6.0 |
| 5 | (85) | 92.5:7.5 |
| 6 | (79) | 93.5:6.5 |
| 7 | (77) | 94.0:6.0 |
| 8 | (74) | 88.0:12.0 |

521

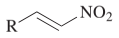


**234** (5.5 mol %),
$Mg(OTf)_2$ (5 mol %),
NMM (6 mol %),
$CHCl_3$, MS, rt

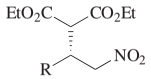


(95) er 98.0:2.0

103



**235b** (2 mol %), solvent



| R | Solvent | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| *i*-Bu | toluene | 50° | 15 | (92) | 95.0:5.0 |
| *n*-$C_5H_{11}$ | neat | 50° | 9 | (93) | 94.0:6.0 |
| Ph | toluene | rt | 24 | (99) | 97.5:2.5 |
| $PhCH_2CH_2$ | toluene | rt | 28 | (95) | 95.5:4.5 |
| PhCH=CH | toluene | rt | 72 | (99) | 97.5:2.5 |

33

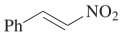
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

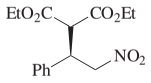
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



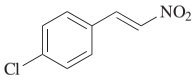


**236** (10 mol %), $CH_2Cl_2$

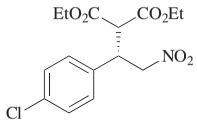


| Temp (°) | Time (h) | | er |
|---|---|---|---|
| –40 | 96 | (87) | 99.0:1.0 |
| –20 | 72 | (96) | 97.5:2.5 |
| 0 | 24 | (99) | 96.5:3.5 |

522

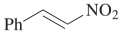


**238b** (10 mol %), toluene, –18°, 27 h

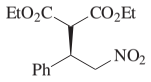


(98) er 96.5:3.5

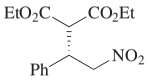
523



Catalyst (5 mol %), $Et_3N$ (10 mol %), MeCN, rt, 24 h



**I** +

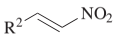


**II**

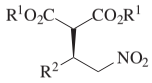
| Catalyst | | er **I/II** |
|---|---|---|
| $Cu^{I}$(**239**)$PF_6$ | (55) | 86.0:14.0 |
| $Cu^{II}$(**239**)$(ClO_4)_2$ | (40) | 15.0:85.0 |

524





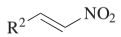
*ent*-**164b** (10 mol %), toluene, rt



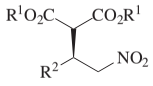
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Ph | 9 | (89) | 93.0:7.0 |
| Et | *i*-Bu | 24 | (88) | 90.5:9.5 |
| Et | 2-$C_4H_3S$ | 24 | (74) | 95.0:5.0 |
| Et | *n*-$C_5H_{11}$ | 24 | (78) | 90.5:9.5 |

87

| | | | | |
|---|---|---|---|---|
| Et | Ph | 24 | (86) | 96.5:3.5 |
| Et | 2-$BrC_6H_4$ | 24 | (96) | 97.0:3.0 |
| Et | 4-$ClC_6H_4$ | 24 | (80) | 97.0:3.0 |
| Et | 4-$FC_6H_4$ | 24 | (87) | 96.0:4.0 |
| Et | 4-$MeOC_6H_4$ | 24 | (85) | 95.5:4.5 |
| Et | 2,6-$(MeO)_2C_6H_3$ | 24 | (87) | 96.5:3.5 |
| Et | 3,4-$(OCH_2O)C_6H_3$ | 24 | (71) | 93.0:7.0 |
| Et | *N*-Ts-3-indolyl | 24 | (64) | 94.0:6.0 |
| Et | 1-Np | 24 | (95) | 96.0:4.0 |
| *i*-Pr | Ph | 48 | (70) | 94.0:6.0 |



*ent*-**164b** (5 mol %),
$CO_2$ (1), 100 bar, rt



| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | *i*-Bu | 60 | (55) | 91.0:9.0 |
| Me | Ph | 8 | (86) | 94.0:6.0 |
| Me | 4-$ClC_6H_4$ | 4 | (95) | 94.0:6.0 |
| Me | 4-$MeOC_6H_4$ | 12 | (83) | 92.5:7.5 |
| Me | 2,4-$MeO_2C_6H_3$ | 48 | (48) | 93.5:6.5 |
| Et | Ph | 4 | (59) | 93.5:6.5 |
| Et | 4-$ClC_6H_4$ | 4 | (95) | 94.0:6.0 |
| Et | 4-$MeOC_6H_4$ | 12 | (83) | 92.5:7.5 |
| Et | 2,4-$MeO_2C_6H_3$ | 48 | (48) | 93.5:6.5 |
| *i*-Pr | Ph | 12 | (30) | 83.5:16.5 |

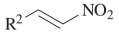
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

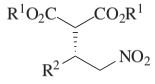
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



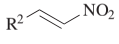


**226b** (1 mol %), $H_2O$, rt, 6–10 h

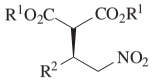


521

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | 2-$C_4H_3O$ | (93) | 87.0:13.0 |
| Me | Ph | (91) | 83.0:17.0 |
| Me | 3-$BrC_6H_4$ | (86) | 81.0:19.0 |
| Me | 4-$BrC_6H_4$ | (75) | 92.0:8.0 |
| Me | 2-$ClC_6H_4$ | (93) | 85.0:15.0 |
| Me | 4-$ClC_6H_4$ | (78) | 87.5:12.5 |
| Me | 4-$FC_6H_4$ | (76) | 74.5:25.5 |
| Me | 4-$HOC_6H_4$ | (55) | 64.0:36.0 |
| Me | 3-$MeOC_6H_4$ | (82) | 82.0:18.0 |
| Me | 4-$MeOC_6H_4$ | (71) | 93.0:7.0 |
| Me | 4-$AcOC_6H_4$ | (62) | 79.5:20.5 |
| Me | 4-$TBSOC_6H_4$ | (88) | 95.0:5.0 |
| Me | 4-$MeC_6H_4$ | (74) | 78.0:22.0 |
| Me | 1-Np | (76) | 91.0:9.0 |
| Me | 2-Np | (78) | 83.0:17.0 |
| Et | 1-Np | (93) | 92.5:7.5 |
| Et | 2-Np | (90) | 89.5:10.5 |
| *i*-Pr | Ph | (49) | 87.0:13.0 |
| Bn | Ph | (85) | 80.0:20.0 |



**228** (*x* mol %), 1 M in THF



| $R^1$ | $R^2$ | *x* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|
| Me | *i*-Bu | 10 | –20 | 72 | (84) | 96.0:4.0 |
| Me | 2-$C_4H_3O$ | 10 | –20 | 36 | (95) | 98.0:2.0 |
| Me | 2-$C_4H_3S$ | 10 | –20 | 44 | (96) | 97.5:2.5 |
| Me | *n*-$C_5H_{11}$ | 10 | –20 | 72 | (82) | 95.5:4.5 |
| Me | 3-$C_5H_4N$ | 10 | –20 | 36 | (99) | 96.0:4.0 |
| Me | *c*-$C_6H_{11}$ | 20 | –20 | 108 | (80) | 95.5:4.5 |
| Me | Ph | 10 | –20 | 36 | (99) | 96.5:3.5 |
| Me | 4-$BrC_6H_4$ | 10 | –20 | 36 | (98) | 97.0:3.0 |
| Me | 4-$ClC_6H_4$ | 10 | –20 | 36 | (97) | 97.0:3.0 |
| Me | 2-$FC_6H_4$ | 10 | –20 | 36 | (94) | 97.5:2.5 |
| Me | 4-$FC_6H_4$ | 10 | –20 | 36 | (97) | 97.0:3.0 |
| Me | 4-$MeOC_6H_4$ | 10 | –20 | 47 | (94) | 97.5:2.5 |
| Me | 2-$O_2NC_6H_4$ | 10 | –50 | 72 | (88) | 96.0:4.0 |
| Me | 2-$MeC_6H_4$ | 10 | –20 | 36 | (97) | 98.0:2.0 |
| Me | 3-$MeC_6H_4$ | 10 | –20 | 36 | (99) | 96.5:3.5 |
| Me | 4-$MeC_6H_4$ | 10 | –20 | 44 | (97) | 97.0:3.0 |
| Me | 4-*i*-$PrC_6H_4$ | 10 | –20 | 39 | (96) | 96.5:3.5 |
| Me | 1-Np | 10 | –20 | 36 | (99) | 96.0:4.0 |
| Et | Ph | 10 | –20 | 36 | (86) | 95.0:5.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

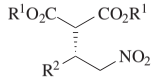
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



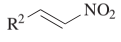


**233** (*x* mol %), 1 M in THF, rt

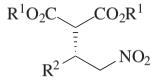


519

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Me | *i*-Bu | 3 | 72 | (79) | 94.5:5.5 |
| Me | 2-$C_4H_3O$ | 1 | 36 | (98) | 98.5:1.5 |
| Me | *c*-$C_6H_{11}$ | 5 | 60 | (92) | 94.5:5.5 |
| Me | Ph | 1 | 24 | (97) | 97.0:3.0 |
| Me | 2-$BrC_6H_4$ | 1 | 18 | (97) | 97.5:2.5 |
| Me | 4-$BrC_6H_4$ | 1 | 18 | (97) | 97.0:3.0 |
| Me | 2-$ClC_6H_4$ | 1 | 18 | (>99) | 98.0:2.0 |
| Me | 4-$ClC_6H_4$ | 1 | 18 | (97) | 97.5:2.5 |
| Me | 4-$MeOC_6H_4$ | 1 | 48 | (99) | 97.0:3.0 |
| Me | 4-$MeC_6H_4$ | 1 | 36 | (97) | 96.5:3.5 |
| Me | $PhCH_2CH_2$ | 1 | 60 | (83) | 93.0:7.0 |
| Me | PhCH=CH | 3 | 60 | (90) | 95.0:5.0 |
| Me | 1-Np | 1 | 18 | (98) | 98.0:2.0 |
| Et | Ph | 5 | 18 | (99) | 81.5:18.5 |
| *i*-Pr | Ph | 5 | 72 | (90) | 78.5:21.5 |



*ent*-**234** (5.5 mol %),
$Mg(OTf)_2$ (5 mol %),
NMM (6 mol %),
MS, solvent, rt



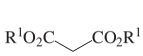
| $R^1$ | $R^2$ | Solvent | | er | |
|---|---|---|---|---|---|
| Me | Ph | $CHCl_3$ | (93) | 98.0:2.0 | 102,103 |
| Et | *i*-Bu | $CHCl_3$ | (90) | 94.0:6.0 | 102,103 |
| Et | 2-$C_4H_3O$ | $CHCl_3$ | (89) | 96.0:4.0 | 103 |
| Et | *n*-$C_5H_{11}$ | $CHCl_3$ | (89) | 96.5:3.5 | 102,103 |
| Et | Ph | $CHCl_3$ | (95) | 96.0:4.0 | 102,103 |
| Et | Ph | toluene | (93) | 96.5:3.5 | 102 |
| Et | 4-$FC_6H_4$ | $CHCl_3$ | (90) | 96.5:3.5 | 102,103 |
| Et | 2,6-$(MeO)_2C_6H_3$ | $CHCl_3$ | (97) | 96.5:3.5 | 102,103 |
| Et | 2,6-$(MeO)_2C_6H_3$ | toluene | (97) | 97.5:2.5 | 102,103 |
| Et | 3-MeO-4,5-$(OCH_2O)C_6H_2$ | $CHCl_3$ | (92) | 95.0:5.0 | 103 |
| Et | 3,4-$(OCH_2O)C_6H_3$ | $CHCl_3$ | (93) | 99.0:1.0 | 103 |
| *i*-Pr | Ph | $CHCl_3$ | (94) | 96.0:4.0 | 102,103 |
| *t*-Bu | Ph | $CHCl_3$ | (33) | 94.0:6.0 | 102,103 |
| Bn | Ph | $CHCl_3$ | (89) | 96.5:3.5 | 103 |

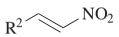
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

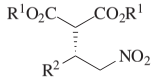
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



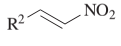


**235a** (2 mol %), solvent, rt

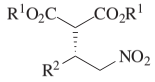


33

| $R^1$ | $R^2$ | Solvent | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Ph | toluene | 4 | (99) | 97.0:3.0 |
| Et | *i*-Pr | neat | 96 | (82) | 95.0:5.0 |
| Et | *i*-Bu | neat | 120 | (94) | 94.0:6.0 |
| Et | 2-$C_4H_3O$ | toluene | 14 | (98) | 97.5:2.5 |
| Et | *n*-$C_5H_{11}$ | neat | 48 | (84) | 94.5:5.5 |
| Et | Ph | toluene | 5 | (99) | 97.5:2.5 |
| Et | 4-$BrC_6H_4$ | toluene | 8 | (99) | 97.5:2.5 |
| Et | 2-$ClC_6H_4$ | toluene | 6 | (98) | 96.0:4.0 |
| Et | 4-$MeOC_6H_4$ | toluene | 7 | (99) | 97.5:2.5 |
| Et | 2,3-$(MeO)_2C_6H_3$ | toluene | 15 | (99) | 96.5:3.5 |
| Et | 2,4-$(MeO)_2C_6H_3$ | toluene | 72 | (98) | 97.0:3.0 |
| Et | 3,4-$(OCH_2O)C_6H_3$ | toluene | 46 | (97) | 97.5:2.5 |
| Et | 4-$MeC_6H_4$ | toluene | 7 | (99) | 97.5:2.5 |
| Et | $PhCH_2CH_2$ | toluene | 48 | (94) | 94.5:5.5 |
| Et | PhCH=CH | toluene | 30 | (95) | 97.5:2.5 |
| *i*-Pr | Ph | toluene | 10 | (96) | 97.5:2.5 |
| *t*-Bu | Ph | toluene | 36 | (97) | 97.5:2.5 |
| Bn | Ph | toluene | 6 | (99) | 97.5:2.5 |



**235a** (10 mol %), solvent, rt



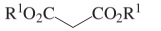
| $R^1$ | $R^2$ | Solvent | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Ph | — | 4 | (99) | 97.0:3.0 |
| Et | *i*-Pr | — | 96 | (82) | 95.0:5.0 |
| Et | *i*-Bu | — | 120 | (94) | 94.0:6.0 |
| Et | 2-$C_4H_3O$ | toluene | 14 | (98) | 97.5:2.5 |
| Et | *n*-$C_5H_{11}$ | toluene | 48 | (84) | 94.5:5.5 |
| Et | Ph | toluene | 5 | (99) | 97.5:2.5 |
| Et | 4-$BrC_6H_4$ | toluene | 8 | (99) | 97.5:2.5 |
| Et | 2-$ClC_6H_4$ | toluene | 6 | (98) | 96.0:4.0 |
| Et | 4-$MeOC_6H_4$ | toluene | 7 | (99) | 97.5:2.5 |
| Et | 2,3-$(MeO)_2C_6H_3$ | toluene | 15 | (99) | 96.5:3.5 |
| Et | 2,4-$(MeO)_2C_6H_3$ | toluene | 72 | (98) | 97.0:3.0 |
| Et | 3,4-$(OCH_2O)C_6H_3$ | toluene | 36 | (97) | 97.5:2.5 |
| Et | 4-$MeC_6H_4$ | toluene | 7 | (99) | 97.5:2.5 |
| *i*-Pr | Ph | toluene | 10 | (96) | 97.5:2.5 |
| *t*-Bu | Ph | toluene | 36 | (97) | 97.5:2.5 |
| Bn | Ph | toluene | 6 | (99) | 97.5:2.5 |

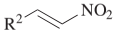
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

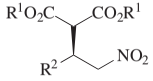
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



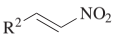


**237** (2 mol %), toluene, –20°, 48 h

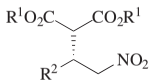


96

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | 2-$C_4H_3O$ | (91) | 99.0:1.0 |
| Me | 2-$C_4H_3S$ | (91) | 98.5:1.5 |
| Me | Ph | (97) | 97.5:2.5 |
| Me | 4-$ClC_6H_4$ | (93)[a] | 96.5:3.5 |
| Me | 4-$FC_6H_4$ | (98)[a] | 96.5:3.5 |
| Me | 3,4-$(OCH_2O)C_6H_3$ | (98) | 97.5:2.5 |
| Me | 4-$MeC_6H_4$ | (96)[a] | 96.0:4.0 |
| Et | Ph | (90) | 96.5:3.5 |

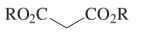


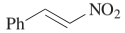
**238a** (10 mol %), toluene, –18°



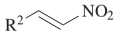
523

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Ph | 24 | (95) | 96.5:3.5 |
| Et | 2-$C_4H_3O$ | 46 | (94) | 97.5:2.5 |
| Et | Ph | 44 | (90) | 97.5:2.5 |
| Et | 4-$ClC_6H_4$ | 47 | (96) | 96.5:3.5 |
| Et | 4-$MeOC_6H_4$ | 72 | (94) | 97.0:3.0 |
| Et | 2-$O_2NC_6H_4$ | 48 | (>99) | 93.5:6.5 |
| Et | $PhCH_2CH_2$ | 144 | (69) | 90.5:9.5 |
| *i*-Pr | Ph | 96 | (64) | 95.5:4.5 |

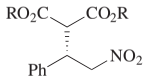




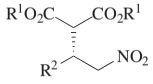




**241** (10 mol %),
toluene, –18°



**242** (10 mol %),
NMP (10 mol %),
toluene, rt



| R | Time (h) | | er | |
|---|---|---|---|---|
| Me | 24 | (94) | 67.5:32.5 | 526 |
| Et | 48 | (88) | 59.0:41.0 | |

527

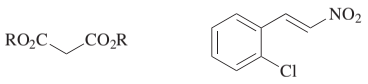
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | 2-$C_4H_3O$ | 77 | (85) | 97.0:3.0 |
| Me | *c*-$C_6H_{11}$ | 89 | (62) | 81.0:19.0 |
| Me | Ph | 80 | (86) | 97.5:2.5 |
| Me | 4-$BrC_6H_4$ | 90 | (94) | 97.5:2.5 |
| Me | 2-$ClC_6H_4$ | 92 | (93) | 98.5:1.5 |
| Me | 4-$ClC_6H_4$ | 90 | (91) | 97.0:3.0 |
| Me | 4-$FC_6H_4$ | 77 | (87) | 97.5:2.5 |
| Me | 4-$MeOC_6H_4$ | 74 | (79) | 91.5:8.5 |
| Me | 2-$O_2NC_6H_4$ | 90 | (84) | 94.0:6.0 |
| Me | 2-$MeC_6H_4$ | 70 | (89) | 98.0:2.0 |
| Me | 3-$MeC_6H_4$ | 95 | (79) | 97.5:2.5 |
| Me | 4-$MeC_6H_4$ | 72 | (84) | 98.0:2.0 |
| Me | 4-$CF_3C_6H_4$ | 95 | (86) | 96.0:4.0 |
| Me | 1-Np | 118 | (95) | 98.5:1.5 |
| Et | Ph | 132 | (81) | 97.0:3.0 |
| Et | 4-$BrC_6H_4$ | 88 | (83) | 96.5:3.5 |
| Et | 4-$ClC_6H_4$ | 82 | (75) | 96.5:3.5 |
| Et | 4-$MeOC_6H_4$ | 112 | (85) | 92.0:8.0 |
| Et | 4-$MeC_6H_4$ | 72 | (84) | 98.0:2.0 |
| Et | 1-Np | 94 | (87) | 91.5:8.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

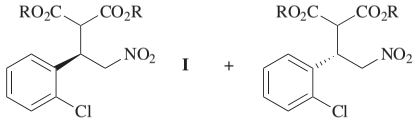
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$

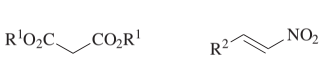


Catalyst (10 mol %), toluene, –15°, 48 h

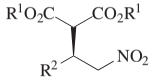


**I** +  **II** 528

| R | Catalyst | | er **I/II** |
|---|---|---|---|
| Me | **243** | (80) | 78.5:21.5 |
| Me | **244** | (81) | 12.5:87.5 |
| Et | **243** | (83) | 82.0:18.0 |
| Et | **244** | (81) | 19.0:81.0 |
| Bn | **243** | (85) | 79.5:20.5 |
| Bn | **244** | (80) | 16.5:83.5 |

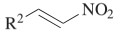


**246** (20 mol %), toluene, rt

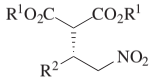


529

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | Et | 24 | (60) | 94.0:6.0 |
| *n*-$C_5H_{11}$ | Et | 96 | (88) | 94.0:6.0 |
| Ph | Me | 24 | (90) | 93.0:7.0 |
| Ph | Et | 24 | (94) | 92.0:8.0 |
| 2-$BrC_6H_4$ | Et | 24 | (76) | 94.5:5.5 |
| 4-$ClC_6H_4$ | Et | 24 | (41) | 94.0:6.0 |
| 4-$MeOC_6H_4$ | Et | 24 | (82) | 92.0:8.0 |
| 2.6-$(MeO)_2C_6H_3$ | Et | 24 | (57) | 94.0:6.0 |
| 2-Np | Et | 24 | (82) | 90.0:10.0 |

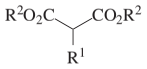


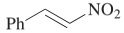
**247** (10 mol %), toluene



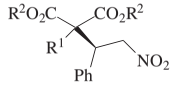
530

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Ph | 0 | 12 | (99) | 72.5:27.5 |
| Et | Ph | 0 | 12 | (99) | 75.0:25.0 |
| *i*-Pr | Ph | –15 | 20 | (99) | 86.5:13.5 |
| *i*-Pr | Ph | 0 | 12 | (99) | 84.0:16.0 |
| *i*-Pr | 4-$MeOC_6H_4$ | –15 | 20 | (85) | 98.5:1.5 |
| *i*-Pr | 4-$O_2NC_6H_4$ | –15 | 20 | (92) | 88.5:11.5 |
| *i*-Pr | 4-$MeC_6H_4$ | –15 | 20 | (94) | 96.0:4.0 |





*ent*-**164b** (10 mol %), toluene, rt



87

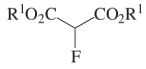
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Cl | Me | 1 | (>99) | 94.5:5.5 |
| MeO | Me | 28 | (89) | 97.0:3.0 |
| MsO | Me | 1 | (86) | 89.5:10.5 |
| AcHN | Et | 24 | (72) | 66.5:33.5 |
| BocHN | Et | 48 | (81) | 91.0:9.0 |

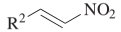
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

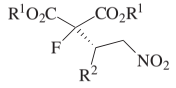
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



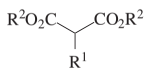


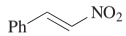
**231** (10 mol %), $CH_2Cl_2$



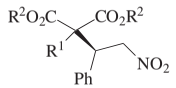
531

| $R^1$ | $R^2$ | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| Me | 2-$C_4H_3S$ | –20° | 4 | (96) | 98.5:1.5 |
| Me | 2-$O_2NC_6H_4$ | rt | 5 | (97) | 98.5:1.5 |
| Me | 1-Np | –20° | 5 | (92) | 95.5:4.5 |
| Et | 2-$C_4H_3O$ | –20° | 4 | (80) | 98.5:1.5 |
| Et | Ph | rt | 2 | (92) | 96.5:3.5 |
| Et | 4-$BrC_6H_4$ | –20° | 3 | (95) | 95.5:4.5 |
| Et | 4-$ClC_6H_4$ | rt | 5 | (91) | 97.5:2.5 |
| Et | 2-$FC_6H_4$ | –20° | 4 | (89) | 95.0:5.0 |
| Et | 4-$FC_6H_4$ | rt | 5 | (90) | 95.5:4.5 |
| Et | 4-$MeOC_6H_4$ | rt | 6 | (78) | 98.5:1.5 |
| Et | 4-$MeC_6H_4$ | –20° | 4 | (72) | 97.5:2.5 |



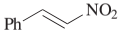


**234** (1.1 mol %), $Mg(OTf)_2$ (1 mol %), NMM (1.3 mol %), $CHCl_3$, $H_2O$, MS, rt

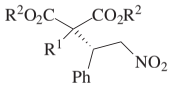


532

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Cl | Et | 64 | (84) | 99.5:0.5 |
| F | Et | 18 | (85) | 97.0:3.0 |
| MeO | Et | 24 | (88) | 95.0:5.0 |
| AcHN | Me | 17 | (75) | 72.0:28.0 |
| BocHN | Me | 19 | (90) | 82.5:17.5 |

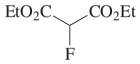


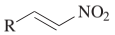
*ent*-**234** (5.5 mol %), $Mg(OTf)_2$ (5 mol %), morpholine (6 mol %), $CHCl_3$, MS, rt



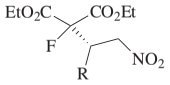
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| MeO | Me | (89) | 91.5:8.5 |
| AcHN | Et | (41) | 75.0:25.0 |
| BocHN | Et | (56) | 92.0:8.0 |

103



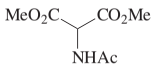


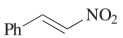
**235a** (5 mol %), toluene, rt



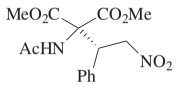
| R | Time (h) | | er |
|---|---|---|---|
| 4-$C_4H_3O$ | 19 | (89) | 95.0:5.0 |
| 4-$C_4H_3S$ | 10 | (90) | 95.5:4.5 |
| Ph | 20 | (97) | 98.5:1.5 |
| 2-$ClC_6H_4$ | 13 | (96) | 98.5:1.5 |
| 2-$FC_6H_4$ | 9 | (92) | 95.5:4.5 |
| 4-$FC_6H_4$ | 11 | (92) | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 10 | (91) | 97.5:2.5 |
| 4-$MeC_6H_4$ | 9 | (95) | 95.5:4.5 |

533





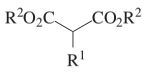
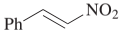
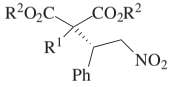
**235a** (10 mol %), toluene, rt, 72 h



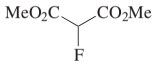
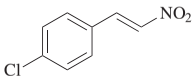
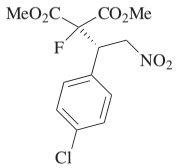
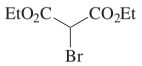
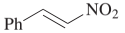
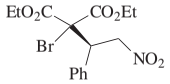
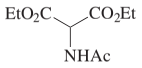
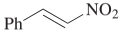
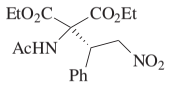
(92) er 97.0:3.0

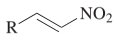
525, 33

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

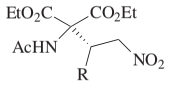
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **238a** (10 mol %), toluene, –18° |  | 523 |

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Cl | Me | 1 | (86) | 99.5:0.5 |
| BocHN | Et | 72 | (53) | 89.5:10.5 |

| | | | | |
|---|---|---|---|---|
|  |  | **240** (20 mol %), $CHCl_3$, rt |  (98) er 93.0:7.0 | 197 |
|  |  | **246** (20 mol %), toluene, rt, 24 h |  (62) er 92.5:7.5 | 529 |
|  |  | **248** (10 mol %), $Na_2CO_3$ (2.08 eq), THF, rt, 20 h |  (59) er 90.0:10.0 | 534 |

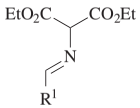


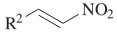
**420d** (15 mol %),
$Na_2CO_3$ (2.05 eq),
$Et_2O$/THF (4:1), rt



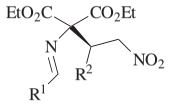
535

| R | Time (h) | | er |
|---|---|---|---|
| Ph | 3 | (60) | 99.5:0.5 |
| 2-$ClC_6H_4$ | 3.5 | (76) | 83.5:16.5 |
| 4-$ClC_6H_4$ | 4 | (45) | 99.5:0.5 |
| 3-$MeOC_6H_4$ | 2 | (51) | 80.0:20.0 |
| 4-$MeOC_6H_4$ | 4 | (39) | 67.0:33.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 7 | (52) | 86.0:14.0 |
| 4-$O_2NC_6H_4$ | 6 | (78) | 98.5:1.5 |





**245** (10 mol %),
4 Å MS, toluene



536

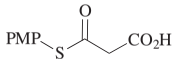
| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | *n*-Pr | rt | 72 | (56)[b] | 98.5:1.5 |
| Ph | *i*-Pr | rt | 72 | (60)[b] | 99.0:1.0 |
| Ph | 2-$C_4H_3O$ | 0 | 50 | (89)[b] | 99.0:1.0 |
| Ph | 2-$C_4H_3S$ | 0 | 50 | (90)[b] | 98.0:2.0 |
| Ph | *c*-$C_6H_{11}$ | rt | 72 | (48)[b] | 99.0:1.0 |
| Ph | Ph | 0 | 50 | (93)[b] | 98.0:2.0 |
| Ph | 4-$BrC_6H_4$ | 0 | 50 | (84)[b] | 98.0:2.0 |
| Ph | 2-$ClC_6H_4$ | 0 | 50 | (80)[b] | 97.0:3.0 |
| Ph | 3-$ClC_6H_4$ | 0 | 50 | (93)[b] | 99.0:1.0 |
| Ph | 4-$ClC_6H_4$ | 0 | 50 | (87)[b] | 99.0:1.0 |
| Ph | 4-$FC_6H_4$ | 0 | 50 | (83)[b] | 99.0:1.0 |
| Ph | 4-$MeOC_6H_4$ | 0 | 50 | (83)[b] | 97.5:2.5 |
| Ph | 4-$MeC_6H_4$ | 0 | 50 | (95)[b] | 98.0:2.0 |
| 4-$FC_6H_4$ | Ph | 0 | 50 | (93)[b] | 98.0:2.0 |
| 4-$MeC_6H_4$ | Ph | 0 | 50 | (86)[b] | 98.5:1.5 |

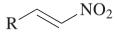
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

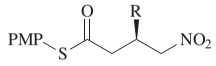
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



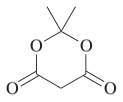



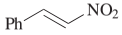

**232a** (*x* mol %), 0.1 M in MTBE



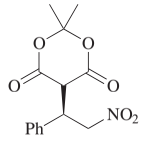

537

| R | *x* | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| *i*-Bu | 5 | 45° | 60 | (22) | 96.0:4.0 |
| 2-$C_4H_3O$ | 5 | 45° | 33 | (78) | 94.0:6.0 |
| 2-$C_4H_3O$ | 20 | rt | 72 | (88) | 94.0:6.0 |
| 2-$C_4H_3S$ | 5 | 45° | 24 | (79) | 95.5:4.5 |
| 2-$C_4H_3S$ | 20 | rt | 72 | (91) | 95.5:4.5 |
| *c*-$C_6H_{11}$ | 5 | 45° | 60 | (15) | >99.5:0.5 |
| Ph | 5 | 45° | 30 | (80) | 96.5:3.5 |
| Ph | 20 | rt | 72 | (96) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 5 | 45° | 22 | (83) | 95.5:4.5 |
| 4-$BrC_6H_4$ | 20 | rt | 72 | (86) | 95.5:4.5 |
| 4-$ClC_6H_4$ | 5 | 45° | 22 | (80) | 95.0:5.0 |
| 4-$ClC_6H_4$ | 20 | rt | 72 | (88) | 95.0:5.0 |
| 4-$FC_6H_4$ | 5 | 45° | 25 | (82) | 95.5:4.5 |
| 4-$FC_6H_4$ | 20 | rt | 72 | (86) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | 5 | 45° | 34 | (80) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 20 | rt | 72 | (94) | 96.0:4.0 |
| 4-$MeC_6H_4$ | 5 | 45° | 34 | (81) | 98.0:2.0 |
| 4-$MeC_6H_4$ | 20 | rt | 72 | (96) | 98.0:2.0 |




*ent*-**164b** (10 mol %), toluene, rt, 24 h




(88) er 73.0:27.0

87

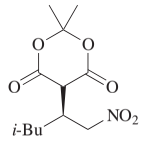








**230b** (10 mol %),
$CH_2Cl_2$, rt, 23 h

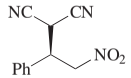


(84) er 87.3:12.7

538



*ent*-**164b** (10 mol %),
toluene, rt, 0.25 h

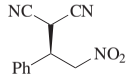


(85) er 62.5:37.5

87



**164b** (5 mol %),
$CO_2$ (l), 100 bar, rt, 4 h

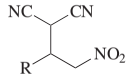


(81) er 90.0:10.0

415



**231** (10 mol %),
4 Å MS, toluene, –10°



539

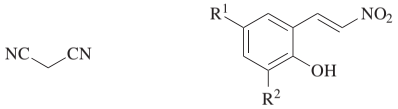
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 8 | (59) | 81.0:19.0 |
| *c*-$C_6H_{11}$ | 44 | (93) | 91.0:9.0 |
| Ph | 8 | (70) | 84.0:16.0 |
| 2-$ClC_6H_4$ | 8 | (94) | 82.0:18.0 |
| 4-$ClC_6H_4$ | 8 | (67) | 71.5:28.5 |
| 2-$MeOC_6H_4$ | 8 | (96) | 90.0:10.0 |
| 4-$MeOC_6H_4$ | 8 | (90) | 75.0:25.0 |
| 3-$O_2NC_6H_4$ | 8 | (57) | 73.5:26.5 |
| 4-$O_2NC_6H_4$ | 8 | (77) | 91.5:8.5 |
| 4-$Me_2NC_6H_4$ | 8 | (85) | 71.5:28.5 |
| 4-$MeC_6H_4$ | 8 | (87) | 83.0:17.0 |

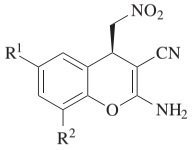
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$





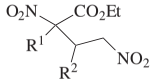
**69b** (10 mol %), $CHCl_3$, 60°, 24 h

| $R^1$ | $R^2$ | | er | |
|---|---|---|---|---|
| H | H | (66) | 95.5:4.5 | |
| H | MeO | (71) | 61.5:38.5 | 540 |
| H | EtO | (76) | 52.0:48.0 | |
| Br | H | (90) | 83.0:17.0 | |
| Br | Br | (73) | 85.5:14.5 | |
| Cl | H | (59) | 89.0:11.0 | |
| Cl | Cl | (43) | 56.5:43.5 | |
| $O_2N$ | H | (57) | 78.0:22.0 | |

$C_{3-4}$



Catalyst (*x* mol %), THF



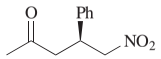
196

| $R^1$ | $R^2$ | Catalyst | *x* | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|---|
| Me | $n$-$C_5H_{11}$ | **226a** | 15 | –20 | 84 | (78) | 93:7 | 96.0:4.0 |
| Me | Ph | **226a** | 15 | –20 | 60 | (78) | 92:8 | 96.0:4.0 |
| Me | Ph | **228** | 15 | –20 | 60 | (74) | 89:11 | 94.5:5.5 |
| Me | Ph | **251** | 15 | –20 | 60 | (80) | 95:5 | 94.0:6.0 |
| Et | Ph | **226a** | 20 | –50 | 144 | (77) | 95:5 | 98.0:2.0 |

$C_4$



**250** (0.1 mol %), $CHCl_3$/THF (4:1), rt, 6 h

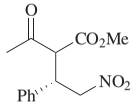


(87) er 95.5:4.5

541



**231** (10 mol %), toluene, rt, 16 h



(80) dr 1:1
er 90.0:10.0

517

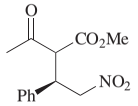
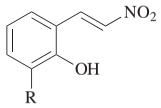
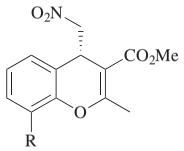
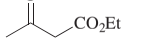
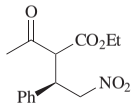
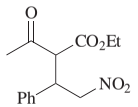
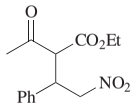
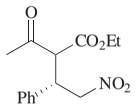
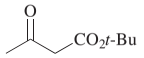
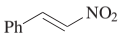
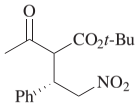
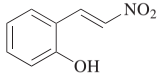
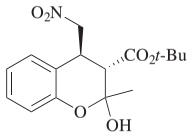
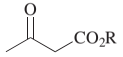
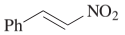
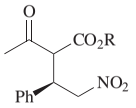
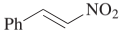
| | | | | |
|---|---|---|---|---|
|  | **249** (5 mol %), toluene, –10°, 65 h |  | (75) dr 1:1<br>er 82.5:17.5 | 542 |
|  | 1. **252a** (10 mol %), toluene, rt<br>2. PTSA (20 mol %), toluene, 100°, 2 h |  | R: MeO; Time (h): 2; (93); er: 99.5:0.5<br>R: Me; Time (h): 3; (92); er: 99.5:0.5 | 543 |
|  | *ent*-**164b** (10 mol %), toluene, rt, 0.5 h |  | (91) er 94.5:5.5 | 87 |
|  | **226a** (10 mol %), 1 M in THF, rt, 6 h |  | (93) dr 1:1<br>er 95.5:4.5 | 195 |
|  | **229a** (10 mol %), $CH_2Cl_2$, rt, 16 h |  | (98) dr 90:10<br>er 94.5:5.5 | 515 |
|  | **252b** (10 mol %), $Et_2O$, 0°, 16 h |  | (92) dr 55:45<br>er (major) 92.5:7.5<br>er (minor) 93.0:7.0 | 544 |

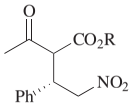
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **208** (10 mol %), toluene, –40°, 20 h |  (92) dr 2:1 er (major) 97.0:3.0 er (minor) 91.0:9.0 | 545 |
| |  | 1. **252a** (10 mol %), toluene, rt 2. PTSA (20 mol %), toluene, 100°, 2 h |  (79) | 543 |
|  |  | **126** (1 mol %), $CH_2Cl_2$, 12–36 h |  | 364 |

| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| Me | (92) | 1.1:1 | 93.0:7.0 | 90.0:10.0 |
| Et | (91) | 1.1:1 | 93.5:6.5 | 93.0:7.0 |
| *t*-Bu | (86) | 12:1 | 93.0:7.0 | 93.0:7.0 |

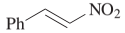


**232b** (0.5 mol %), solvent, rt

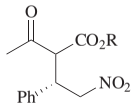


518

| R | Solvent | Time | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| Me | $CH_2Cl_2$ | 1.5 h | (94) | 1:1 | >99.5:0.5 | >99.5:0.5 |
| Me | brine | <10 min | (95) | 1:1 | >99.5:0.5 | >99.5:0.5 |
| Et | $CH_2Cl_2$ | 40 min | (95) | 1.4:1 | >99.5:0.5 | >99.5:0.5 |
| Et | brine | <10 min | (94) | 1.5:1 | >99.5:0.5 | >99.5:0.5 |
| *t*-Bu | $CH_2Cl_2$ | 9 h | (92) | 2.1:1 | 98.5:1.5 | 97.0:3.0 |
| *t*-Bu | brine | <10 min | (90) | 4.9:1 | 99.0:1.0 | 99.0:1.0 |

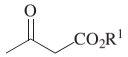


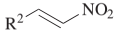
*ent*-**234** (5.5 mol %),
$Mg(OTf)_2$ (5 mol %),
NMM (6 mol %),
$CHCl_3$, MS, rt



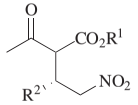
| R | | dr | er |
|---|---|---|---|
| Et | (95) | 1:1 | 95.0:5.0 |
| *i*-Bu | (92) | 1:1 | 94.0:6.0 |
| *t*-Bu | (94) | 1:1 | 64.5:35.5 |

102, 103





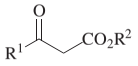
**235a** (2 mol %), solvent, rt

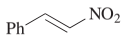


525, 33

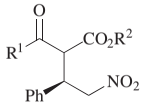
| $R^1$ | $R^2$ | Solvent | Time (h) | | dr | er | er |
|---|---|---|---|---|---|---|---|
| Me | Ph | THF | 6 | (94) | 1:1 | 97.0:3.0 | 97.0:3.0 |
| Et | Ph | toluene | 2 | (96) | 1:1 | 96.5:3.5 | 96.5:3.5 |
| *t*-Bu | Ph | THF | 5 | (97) | 1.5:1 | 96.5:3.5 | 96.5:3.5 |
| *t*-Bu | 4-Br$C_6H_4$ | THF | 5 | (97) | 1.7:1 | 97.0:3.0 | 95.5:4.5 |

$C_{4-9}$





**237** (2 mol %),
toluene, –20°, 48 h



| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | Me | (95) | 79.0:21.0 |
| Et | Me | (97) | 94.5:5.5 |
| *i*-Pr | Me | (97) | 97.0:3.0 |
| Ph | Et | (96) | 96.0:4.0 |

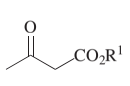
96

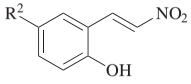
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

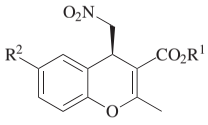
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_4$



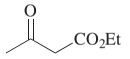


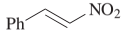
1. **252a** (10 mol %), toluene, rt
2. PTSA (20 mol %), toluene, 100°, 2 h



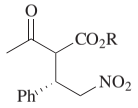
543

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | H | 3 | (90) | 99.0:1.0 |
| Me | Br | 3 | (95) | 99.0:1.0 |
| Me | $O_2N$ | 4 | (78) | 74.5:25.5 |
| Me | $MeO_2C$ | 2.5 | (90) | 94.0:6.0 |
| Et | H | 3 | (92) | 81.0:19.0 |
| $MeO(CH_2)_2$ | H | 3 | (89) | 89.5:10.5 |
| *i*-Pr | H | 4 | (82) | 65.0:35.0 |



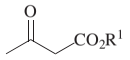


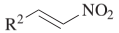
**253** (5 mol %), $C_6H_5OLi$ (5 mol %), $CHCl_3$, rt, 48 h



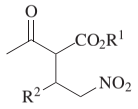
(99) dr 1:1
er 99.5:0.5
er 55.0:45.0

546



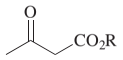


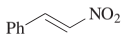
**254** (1 mol %), $CH_2Cl_2$, rt, 12–24 h



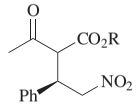
543

| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Et | (84) | 98:2 | 97.5:2.5 |
| Ph | Et | (93) | 1.2:1 | 94.0:6.0 |
| Ph | *t*-Bu | (91) | 1.3:1 | 98.5:1.5 |



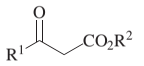


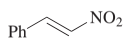
**255** (2 mol %),
$CH_2Cl_2$, rt



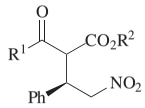
192

| R | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| Me | 18 | (75) | 1:1 | 98.0:2.0 | 99.0:1.0 |
| Et | 8 | (89) | 1.6:1 | 98.5:1.5 | 98.0:2.0 |
| *t*-Bu | 12 | (95) | 1.6:1 | 98.0:2.0 | 98.0:2.0 |

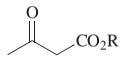


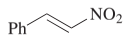


Catalyst (2 mol %), $CH_2Cl_2$, rt

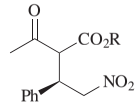


| $R^1$ | $R^2$ | Catalyst | Time (h) | | dr | er (major) | er (minor) | |
|---|---|---|---|---|---|---|---|---|
| Me | Me | **259** | 16 | (98) | 1:1 | 94.5:5.5 | 94.5:5.5 | 548 |
| Me | Et | **259** | 24 | (85) | 1:1 | 96.5:3.5 | 96.0:4.0 | 548 |
| Me | *t*-Bu | **259** | 60 | (60) | 2.2:1 | 94.5:5.5 | 95.5:4.5 | 548 |
| $MeOCH_2$ | Me | **255** | 8 | (83) | 1.3:1 | 97.0:3.0 | 93.0:7.0 | 192 |
| Et | Me | **255** | 9 | (90) | 5:1 | 98.0:2.0 | 95.0:5.0 | 192 |





**256** (1 mol %),
$CH_2Cl_2$, 15°, 48 h



549

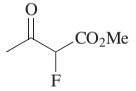
| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| Me | (90) | 1.2:1 | 95.5:4.5 | 95.5:4.5 |
| Et | (88) | 1.5:1 | 95.5:4.5 | 96.0:4.0 |

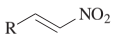
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

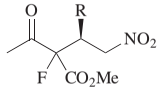
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_4$



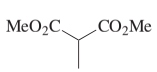


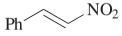
**240** (1 mol %), $ClCH_2CH_2Cl$, rt



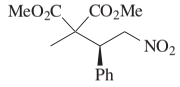
197

| R | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 48 | (94) | 4:1 | 99.5:0.5 | 99.5:0.5 |
| 2-$C_4H_3S$ | 48 | (97) | 3.5:1 | 99.5:0.5 | 99.0:1.0 |
| *n*-$C_5H_{11}$ | 36 | (75) | 4:1 | 99.0:1.0 | 98.0:2.0 |
| Ph | 24 | (97) | 3:1 | 98.5:1.5 | 98.0:2.0 |
| 3-$BrC_6H_4$ | 24 | (94) | 3.5:1 | 99.0:1.0 | 98.5:1.5 |
| 4-$BrC_6H_4$ | 24 | (97) | 3.5:1 | 98.5:1.5 | 97.0:3.0 |
| 4-$ClC_6H_4$ | 24 | (98) | 3:1 | 99.0:1.0 | 98.5:1.5 |
| 4-$FC_6H_4$ | 24 | (95) | 3:1 | 99.0:1.0 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 24 | (95) | 3:1 | 99.0:1.0 | 97.5:2.5 |
| 2-$BnOC_6H_4$ | 48 | (90) | 1.7:1 | 98.5:1.5 | 97.5:2.5 |
| 4-$BnOC_6H_4$ | 24 | (96) | 3:1 | 99.0:1.0 | 98.5:1.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 48 | (95) | 3:1 | 98.5:1.5 | 99.5:0.5 |
| 4-$MeC_6H_4$ | 24 | (92) | 9:1 | 99.5:0.5 | 99.0:1.0 |



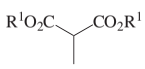


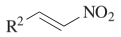
*ent*-**164b** (10 mol %), toluene, rt, 36 h



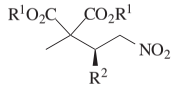
(82) er 96.5:3.5

86, 87



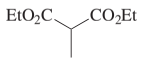


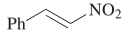
**234** (1.1 mol %), $Mg(OTf)_2$ (1 mol %), NMM (1.3 mol %), $CHCl_3$, $H_2O$, MS, rt



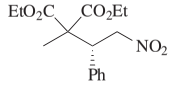
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | 3-BnO-4-$MeOC_6H_3$ | 18 | (87) | 93.5:6.5 |
| Et | 2-$C_4H_3O$ | 18 | (92) | 96.0:4.0 |
| Et | 2-$C_4H_3S$ | 21 | (99) | 96.0:4.0 |
| Et | Ph | 16 | (99) | 96.5:3.5 |
| Et | 4-$BrC_6H_4$ | 21 | (96) | 97.0:3.0 |
| Et | 2-$O_2NC_6H_4$ | 19 | (92) | 99.5:0.5 |
| Et | 4-$CF_3OC_6H_4$ | 20 | (66) | 96.5:3.5 |
| Et | 2-$CF_3C_6H_4$ | 67 | (77) | 99.0:1.0 |
| Et | 3-$CF_3C_6H_4$ | 45 | (86) | 95.0:5.0 |

532



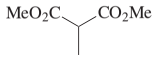


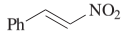
*ent*-**234** (5.5 mol %), $Mg(OTf)_2$ (5 mol %), morpholine (6 mol %), $CHCl_3$, MS, rt



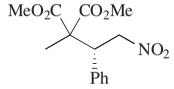
(46) er 85.5:14.5

103



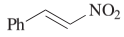


**235a** (10 mol %), toluene, rt, 48 h

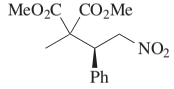


(95) er 97.5:2.5

525, 33



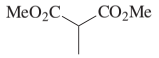
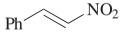
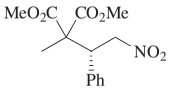
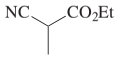
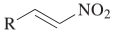
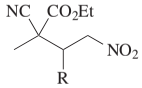
**237** (2 mol %), toluene, –20°, 48 h



(95) er 98.5:1.5

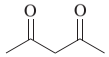
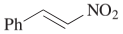
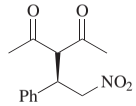
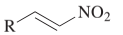
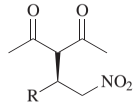
96

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **238a** (10 mol %), toluene, –18°, 72 h |  (57) er 98.0:2.0 | 523 |
|  |  | Catalyst (*x* mol %), THF |  | 196 |

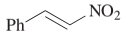
| R | Catalyst | *x* | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|
| *n*-$C_5H_{11}$ | **226a** | 15 | –20 | 84 | (75) | 93:7 | 99.0:1.0 |
| Ph | **226c** | 20 | –50 | 144 | (77) | >98:2 | >99.5:0.5 |
| Ph | **228** | 20 | –20 | 144 | (76) | 86:14 | 97.5:2.5 |
| Ph | **251** | 20 | –20 | 144 | (74) | 86:14 | 94.0:6.0 |

$C_5$

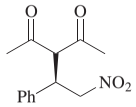
| | | | | |
|---|---|---|---|---|
|  |  | **1** (20 mol %), MeOH, rt, 4 d |  (64) er 53.5:46.5 | 137 |
| |  | **50** (10 mol %), toluene, –40° |  | 550 |

| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 50 | (>99) | 97.0:3.0 |
| 4-Me-2-$C_4H_2O$ | 48 | (>99) | 92.5:7.5 |
| Ph | 23 | (93) | 98.0:2.0 |
| 4-$ClC_6H_4$ | 50 | (91) | 94.0:6.0 |
| 2-$MeOC_6H_4$ | 60 | (89) | 96.0:4.0 |

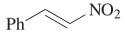
| | | | |
|---|---|---|---|
| 3-$MeOC_6H_4$ | 70 | (>99) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 70 | (>99) | 94.0:6.0 |
| 2,4-$(MeO)_2C_6H_3$ | 60 | (>99) | 92.0:8.0 |
| 2-$CF_3OC_6H_4$ | 16 | (81) | 97.5:2.5 |
| 3-$CF_3OC_6H_4$ | 12 | (82) | 94.5:5.5 |
| 4-$CF_3OC_6H_4$ | 16 | (76) | 95.5:4.5 |
| 4-$BnOC_6H_4$ | 60 | (96) | 92.5:7.5 |
| 4-$MeC_6H_4$ | 48 | (80) | 94.5:5.5 |
| PhCH=CH | 48 | (85) | 90.5:9.5 |
| 1-Np | 40 | (97) | 97.5:2.5 |



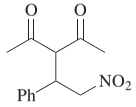
**68** (30 mol %), $PhCO_2H$ (20 mol %), toluene, rt, 4 d



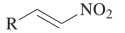
(25) er 81.5:18.5 279



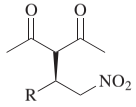
**69b** (10 mol %), toluene, rt, 1 h



(95) er 98.5:1.5 551

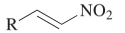


**126** (1 mol %), $CH_2Cl_2$, rt, 12–36 h

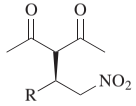


| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (90) | 86.5:13.5 |
| 2-$C_4H_3S$ | (89) | 91.5:8.5 |
| Ph | (96) | 96.5:3.5 |
| 2-$BrC_6H_4$ | (90) | 96.0:4.0 |
| 4-$BrC_6H_4$ | (92) | 90.5:9.5 |
| 4-$FC_6H_4$ | (88) | 94.0:6.0 |
| 4-$MeOC_6H_4$ | (92) | 98.0:2.0 |
| 4-$MeC_6H_4$ | (91) | 94.0:6.0 |

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**127** (1 mol %), $CH_2Cl_2$, rt, 12–36 h



| R | | er |
|---|---|---|
| Ph | (89) | 93.5:6.5 |
| 4-$MeOC_6H_4$ | (92) | 96.0:4.0 |

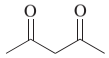
364

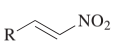
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

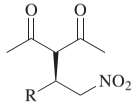
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_5$

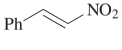




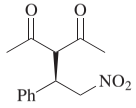
**132** (*x* mol %), $Et_2O$, rt, 1–2 h



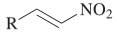
| R | *x* | | er | Refs. |
|---|---|---|---|---|
| *i*-Pr | 1 | (80) | 91.5:8.5 | 552 |
| *i*-Pr | 5 | (81) | 90.5:9.5 | |
| *i*-Bu | 5 | (83) | 91.0:9.0 | |
| *n*-$C_5H_{11}$ | 5 | (85) | 92.5:7.5 | |
| Ph | 1 | (97) | 98.5:1.5 | |
| 2-$BrC_6H_4$ | 1 | (97) | 98.0:2.0 | |
| 3-$BrC_6H_4$ | 1 | (96) | 98.0:2.0 | |
| 4-$BrC_6H_4$ | 1 | (97) | 97.5:2.5 | |
| 3-$ClC_6H_4$ | 1 | (87) | 99.0:1.0 | |
| 4-$FC_6H_4$ | 1 | (96) | 99.5:0.5 | |
| 2-$MeOC_6H_4$ | 1 | (97) | 97.5:2.5 | |
| 3-$MeOC_6H_4$ | 1 | (96) | 98.5:1.5 | |
| 4-$MeOC_6H_4$ | 1 | (93) | 99.0:1.0 | |
| 2-$MeC_6H_4$ | 1 | (95) | 99.0:1.0 | |
| 4-$MeC_6H_4$ | 1 | (96) | 97.5:2.5 | |



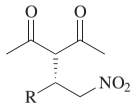
*ent*-**164b** (10 mol %), toluene, rt, 1 h



(80) er 94.5:5.5 — 87



**208** (10 mol %),
toluene, −40°



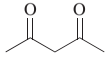
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 24 | (91) | 96.0:4.0 |
| 5-Cl-2-$C_4H_2S$ | 24 | (82) | 97.5:2.5 |
| Ph | 10 | (91) | 97.0:3.0 |
| 4-$BrC_6H_4$ | 12 | (84) | 95.0:5.0 |
| 4-$ClC_6H_4$ | 12 | (89) | 97.0:3.0 |
| 4-$FC_6H_4$ | 12 | (86) | 96.5:3.5 |
| 3-$MeOC_6H_4$ | 24 | (95) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 24 | (92) | 98.0:2.0 |
| 2-$O_2NC_6H_4$ | 12 | (81) | 98.5:1.5 |
| 4-$MeC_6H_4$ | 24 | (91) | 96.5:3.5 |
| PhCH=CH | 72 | (79) | 91.0:9.0 |
| 1-Np | 48 | (90) | 96.0:4.0 |
| 2-Np | 48 | (87) | 97.0:3.0 |

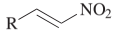
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

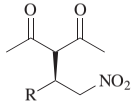
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_5$



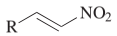


**209** (10 mol %), toluene, –40°

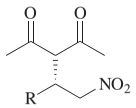


| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 24 | (90) | 92.5:7.5 |
| 5-Cl-2-$C_4H_2S$ | 24 | (84) | 95.0:5.0 |
| Ph | 10 | (90) | 93.0:7.0 |
| 4-$BrC_6H_4$ | 12 | (86) | 91.5:8.5 |
| 4-$ClC_6H_4$ | 12 | (87) | 92.5:7.5 |
| 4-$FC_6H_4$ | 12 | (86) | 91.0:9.0 |
| 3-$MeOC_6H_4$ | 24 | (91) | 93.5:6.5 |
| 4-$MeOC_6H_4$ | 24 | (93) | 92.5:7.5 |
| 2-$O_2NC_6H_4$ | 12 | (85) | 92.5:7.5 |
| 4-$MeC_6H_4$ | 24 | (94) | 95.5:4.5 |
| PhCH=CH | 72 | (76) | 89.5:10.5 |
| 1-Np | 48 | (90) | 88.5:11.5 |
| 2-Np | 48 | (88) | 91.0:9.0 |

545

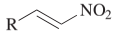


**231** (10 mol %), toluene, rt, 16 h

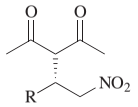


| R | | er |
|---|---|---|
| *i*-Bu | (80) | 88.0:12.0 |
| Ph | (82) | 96.5:3.5 |
| 4-$BrC_6H_4$ | (84) | 97.0:3.0 |
| 4-$ClC_6H_4$ | (86) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (85) | 96.0:4.0 |
| 2,3-$(MeO)_2C_6H_3$ | (83) | 98.0:2.0 |
| 2-$BnOC_6H_4$ | (78) | 98.0:2.0 |
| 4-$BnOC_6H_4$ | (83) | 95.0:5.0 |
| 4-$MeC_6H_4$ | (80) | 96.5:3.5 |
| 4-$CF_3C_6H_4$ | (81) | 95.5:4.5 |

517

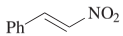


**232b** (*x* mol %), solvent, rt

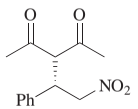


518

| R | *x* | Solvent | Time | | er |
|---|---|---|---|---|---|
| *i*-Bu | 0.5 | $CH_2Cl_2$ | 2 h | (94) | >99.5:0.5 |
| *i*-Bu | 0.5 | brine | <10 min | (91) | >99.5:0.5 |
| 2-$C_4H_3S$ | 2 | $CH_2Cl_2$ | 8 h | (88) | >99.5:0.5 |
| 2-$C_4H_3S$ | 2 | brine | <10 min | (90) | >99.5:0.5 |
| Ph | 0.5 | $CH_2Cl_2$ | 2 h | (97) | >99.5:0.5 |
| Ph | 0.5 | brine | <10 min | (98) | >99.5:0.5 |
| 4-Br$C_6H_4$ | 0.5 | $CH_2Cl_2$ | 1 h | (93) | >99.5:0.5 |
| 4-Br$C_6H_4$ | 0.5 | brine | <20 min | (96) | >99.5:0.5 |
| 4-Cl$C_6H_4$ | 0.5 | $CH_2Cl_2$ | 1 h | (98) | >99.5:0.5 |
| 4-Cl$C_6H_4$ | 0.5 | brine | <20 min | (99) | >99.5:0.5 |
| 4-F$C_6H_4$ | 0.5 | $CH_2Cl_2$ | 48 h | (89) | >99.5:0.5 |
| 4-F$C_6H_4$ | 0.5 | brine | <40 min | (89) | >99.5:0.5 |
| 4-MeO$C_6H_4$ | 0.5 | $CH_2Cl_2$ | 3 h | (91) | 99.5:0.5 |
| 4-MeO$C_6H_4$ | 0.5 | brine | <20 min | (91) | 99.0:1.0 |
| 4-Me$C_6H_4$ | 0.5 | $CH_2Cl_2$ | 4 h | (97) | 99.0:1.0 |
| 4-Me$C_6H_4$ | 0.5 | brine | <10 min | (92) | 99.0:1.0 |

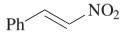


**235a** (2 mol %), toluene, rt, 110 h

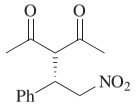


(84) er 93.0:7.0

33



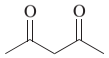
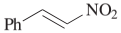
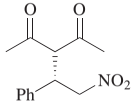
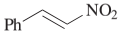
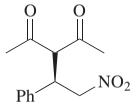
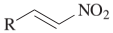
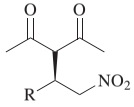
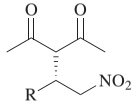
**235b** (2 mol %), solvent, rt



| Solvent | Time (h) | | er |
|---|---|---|---|
| THF | 72 | (88) | 95.0:5.0 |
| toluene | 18 | (94) | 94.0:6.0 |

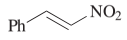
33

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

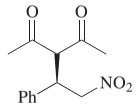
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **238a** (10 mol %), toluene, –18°, 4 h |  (99) er 96.5:3.5 | 523, 526 |
| |  | **238b** (2 mol %), toluene, –20°, 48 h |  (90) er 53.5:46.5 | 96 |
| |  | Catalyst (10 mol %), toluene, –30°, 12 h |  **I** +  **II** | 528 |

| R | Catalyst | | er **I/II** |
|---|---|---|---|
| *i*-Bu | **243** | (85) | 79.5:20.5 |
| *i*-Bu | **244** | (81) | 10.5:89.5 |
| 2-$C_4H_3O$ | **243** | (83) | 96.0:4.0 |
| 2-$C_4H_3O$ | **244** | (86) | 5.0:95.0 |
| 2-$C_4H_3S$ | **243** | (90) | 95.0:5.0 |
| 2-$C_4H_3S$ | **244** | (91) | 4.5:95.5 |
| Ph | **243** | (91) | 95.0:5.0 |
| Ph | **244** | (89) | 4.5:95.5 |
| 2-$ClC_6H_4$ | **243** | (90) | 97.0:3.0 |
| 2-$ClC_6H_4$ | **244** | (91) | 4.0:96.0 |
| 3-$ClC_6H_4$ | **243** | (96) | 95.0:5.0 |
| 3-$ClC_6H_4$ | **244** | (95) | 9.5:90.5 |
| 4-$ClC_6H_4$ | **243** | (88) | 98.0:2.0 |
| 4-$ClC_6H_4$ | **244** | (89) | 3.5:96.5 |
| 4-$FC_6H_4$ | **243** | (97) | 95.5:4.5 |

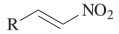
| | | | |
|---|---|---|---|
| 4-$FC_6H_4$ | **244** | (95) | 5.0:95.0 |
| 2-$MeOC_6H_4$ | **243** | (98) | 91.0:9.0 |
| 2-$MeOC_6H_4$ | **244** | (98) | 10.0:90.0 |
| 4-$MeC_6H_4$ | **243** | (95) | 98.0:2.0 |
| 4-$MeC_6H_4$ | **244** | (92) | 2.5:97.5 |



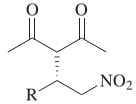
**246** (20 mol %), toluene, rt, 24 h



(98) er 91.5:8.5 529

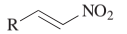


**252b** (10 mol %), $Et_2O$, 0°

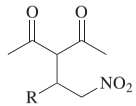


544

| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 42 | (83) | 96.0:4.0 |
| Ph | 16 | (99) | 96.0:4.0 |
| 4-$BrC_6H_4$ | 41 | (78) | 93.0:7.0 |
| 2-$ClC_6H_4$ | 18 | (95) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 28 | (81) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 64 | (81) | 94.0:6.0 |
| 4-$MeC_6H_4$ | 41 | (85) | 95.0:5.0 |



**254** (1 mol %), $CH_2Cl_2$, rt, 12–24 h



547

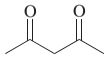
| R | | er |
|---|---|---|
| 2-$C_4H_3S$ | (96) | >99.5:0.5 |
| Ph | (93) | 98.5:1.5 |
| 2-$BrC_6H_4$ | (88) | 96.5:3.5 |
| 4-$BrC_6H_4$ | (94) | 95.0:5.0 |
| 2-$ClC_6H_4$ | (90) | 97.0:3.0 |
| 2,4-$Cl_2C_6H_3$ | (87) | 97.5:2.5 |
| 4-$FC_6H_4$ | (94) | 98.0:2.0 |
| 2-$MeOC_6H_4$ | (83) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | (89) | 95.0:5.0 |
| 4-$MeC_6H_4$ | (87) | 94.5:5.5 |

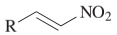
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

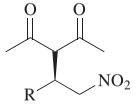
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_5$



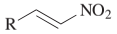


**255** (0.5 mol %), $CH_2Cl_2$, rt

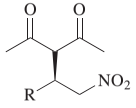


| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 10 | (98) | 98.5:1.5 |
| Ph | 8 | (94) | >99.5:0.5 |
| 2-$BrC_6H_4$ | 10 | (98) | 99.0:1.0 |
| 3-$BrC_6H_4$ | 12 | (89) | 98.5:1.5 |
| 4-$BrC_6H_4$ | 10 | (99) | 99.0:1.0 |
| 2,4-$Cl_2C_6H_3$ | 9 | (98) | 99.0:1.0 |
| 2-$FC_6H_4$ | 8 | (96) | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 24 | (99) | 99.0:1.0 |
| 2-$O_2NC_6H_4$ | 20 | (96) | 98.5:1.5 |
| 4-$MeC_6H_4$ | 9 | (98) | 98.5:1.5 |

192

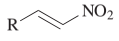


**256** (1 mol %), $CH_2Cl_2$, 15°, 48 h

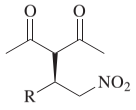


| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (90) | 88.5:11.5 |
| 2-$C_4H_3S$ | (89) | 89.0:11.0 |
| Ph | (92) | 96.5:3.5 |
| 2-$BrC_6H_4$ | (91) | 98.0:2.0 |
| 4-$BrC_6H_4$ | (90) | 96.5:3.5 |
| 2-$ClC_6H_4$ | (90) | 97.0:3.0 |
| 4-$ClC_6H_4$ | (89) | 94.0:6.0 |
| 4-$FC_6H_4$ | (90) | 95.0:5.0 |
| 2-$MeOC_6H_4$ | (92) | 93.0:7.0 |
| 4-$MeOC_6H_4$ | (90) | 95.0:5.0 |
| 4-$MeC_6H_4$ | (88) | 94.5:5.5 |
| 4-$CF_3C_6H_4$ | (92) | 87.0:13.0 |

549

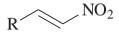


**257** (1 mol %), $Et_2O$, rt

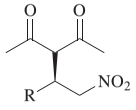


| R | Time (h) | | er |
|---|---|---|---|
| Ph | 26 | (87) | 97.5:2.5 |
| 4-$BrC_6H_4$ | 27 | (89) | 97.5:2.5 |
| 4-$ClC_6H_4$ | 24 | (91) | 98.5:1.5 |
| 2-$MeOC_6H_4$ | 30 | (92) | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 36 | (92) | 98.5:1.5 |
| 2,3-$(MeO)_2C_6H_3$ | 36 | (87) | 96.0:4.0 |
| 2,4-$(MeO)_2C_6H_3$ | 36 | (88) | 95.5:4.5 |
| 2-$BnOC_6H_4$ | 48 | (80) | 94.5:5.5 |
| 4-$BnOC_6H_4$ | 26 | (90) | 97.0:3.0 |
| 3-BnO-4-$MeOC_6H_3$ | 60 | (78) | 94.0:6.0 |
| 4-$MeC_6H_4$ | 36 | (84) | 96.5:3.5 |
| 4-$CF_3C_6H_4$ | 24 | (86) | 91.5:8.5 |

553



**258** (10 mol %),
$CH_2Cl_2$, rt, 18 h



| R | | er |
|---|---|---|
| Ph | (93) | 91.5:8.5 |
| 4-$ClC_6H_4$ | (84) | 92.0:8.0 |
| 4-$MeOC_6H_4$ | (67) | 77.5:22.5 |
| 4-$MeC_6H_4$ | (71) | 91.0:9.0 |
| 4-$CF_3C_6H_4$ | (78) | 92.5:7.5 |

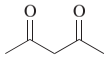
554

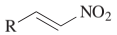
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

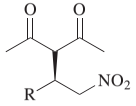
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_5$





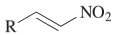
**259** (4 mol %), $CH_2Cl_2$, rt, 6 h



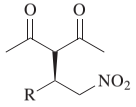
Catalyst Recycling (R = Ph)

| Run | | er |
|---|---|---|
| 1 | (92) | 96.0:4.0 |
| 2 | (93) | 96.0:4.0 |
| 3 | (83) | 96.0:4.0 |
| 4 | (72) | 94.5:5.5 |
| 5 | (75) | 96.0:4.0 |
| 6 | (76) | 95.5:4.5 |
| 7 | (76) | 97.0:3.0 |
| 8 | (76) | 93.0:7.0 |
| 9 | (64) | 94.0:6.0 |
| 10 | (71) | 96.0:4.0 |

548

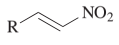


**259** (2 mol %), $CH_2Cl_2$, rt

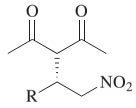


548

| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 15 | (91) | 97.0:3.0 |
| Ph | 8 | (88) | 97.5:2.5 |
| 3-$BrC_6H_4$ | 24 | (85) | 93.5:6.5 |
| 4-$BrC_6H_4$ | 13 | (87) | 96.0:4.0 |
| 2,4-$Cl_2C_6H_3$ | 13 | (91) | 96.5:3.5 |
| 2-$MeOC_6H_4$ | 13 | (91) | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 24 | (81) | 96.0:4.0 |
| 4-$MeC_6H_4$ | 13 | (87) | 97.0:3.0 |



**260** (*x* mol %),
MeCN, 4 Å MS, –40°



| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 5 | 36 | (79) | 95.0:5.0 |
| 2-$C_4H_3O$ | 10 | 36 | (87) | 93.5:6.5 |
| Ph | 5 | 24 | (91) | 95.0:5.0 |
| Ph | 10 | 24 | (93) | 99.0:1.0 |
| 4-$BrC_6H_4$ | 5 | 24 | (75) | 93.5:6.5 |
| 4-$BrC_6H_4$ | 10 | 24 | (80) | 94.5:5.5 |
| 2-$ClC_6H_4$ | 5 | 24 | (93) | 97.5:2.5 |
| 2-$ClC_6H_4$ | 10 | 24 | (95) | 99.5:0.5 |
| 3-$ClC_6H_4$ | 5 | 24 | (90) | 88.5:11.5 |
| 3-$ClC_6H_4$ | 10 | 24 | (93) | 91.5:8.5 |
| 4-$ClC_6H_4$ | 5 | 24 | (84) | 96.0:4.0 |
| 4-$ClC_6H_4$ | 10 | 24 | (91) | 97.0:3.0 |
| 4-$FC_6H_4$ | 5 | 24 | (80) | 97.0:3.0 |
| 4-$FC_6H_4$ | 10 | 24 | (85) | 97.5:2.5 |

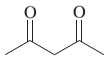
| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| 2-$MeOC_6H_4$ | 5 | 24 | (77) | 97.5:2.5 |
| 2-$MeOC_6H_4$ | 10 | 24 | (83) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 5 | 24 | (95) | 94.5:5.5 |
| 4-$MeOC_6H_4$ | 10 | 24 | (98) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | 5 | 24 | (66) | 93.5:6.5 |
| 4-$O_2NC_6H_4$ | 10 | 24 | (89) | 94.0:6.0 |
| 4-$MeC_6H_4$ | 10 | 24 | (75) | 95.0:5.0 |
| 4-$CF_3C_6H_4$ | 10 | 72 | (76) | 94.5:5.5 |
| $BnCH_2$ | 10 | 72 | (28) | 87.0:13.0 |
| PhCH=CH | 10 | 72 | (46) | 91.0:9.0 |
| 1-Np | 5 | 36 | (87) | 98.0:2.0 |
| 1-Np | 10 | 36 | (94) | 98.0:2.0 |

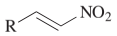
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

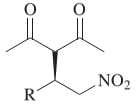
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_5$



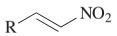


**262** (10 mol %),
**263** (10 mol %),
toluene, rt

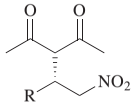


556

| R | Time (h) | | er |
|---|---|---|---|
| 4-Br-2-$C_4H_2S$ | 3 | (62) | 87.0:13.0 |
| Ph | 6 | (63) | 88.0:12.0 |
| 4-$ClC_6H_4$ | 24 | (65) | 85.0:15.0 |
| 2-$MeOC_6H_4$ | 24 | (78) | 92.0:8.0 |
| 4-$MeOC_6H_4$ | 24 | (79) | 83.0:17.0 |
| 2-$O_2NC_6H_4$ | 24 | (67) | 93.0:7.0 |
| 3-$O_2NC_6H_4$ | 24 | (79) | 83.0:17.0 |
| 1-Np | 24 | (74) | 90.0:10.0 |

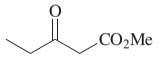


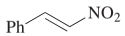
**264** (10 mol %),
0.1 M in MeCN,
4 Å MS, –40°, 24 h



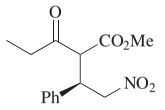
| R | | er |
|---|---|---|
| Ph | (87) | 95.0:5.0 |
| 4-$BrC_6H_4$ | (82) | 97.5:2.5 |
| 2-$ClC_6H_4$ | (95) | 95.0:5.0 |
| 3-$ClC_6H_4$ | (85) | 95.0:5.0 |
| 4-$ClC_6H_4$ | (90) | 94.0:6.0 |
| 4-$FC_6H_4$ | (89) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (81) | 95.5:4.5 |
| 4-$O_2NC_6H_4$ | (89) | 95.0:5.0 |
| 4-$MeC_6H_4$ | (89) | 95.0:5.0 |
| 4-$CF_3C_6H_4$ | (92) | 98.5:1.5 |
| 1-Np | (93) | 95.5:4.5 |

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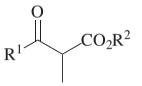
**126** (1 mol %), $CH_2Cl_2$, 12–36 h

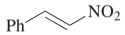


(90) dr 1:1
er 93.0:7.0
er 90.0:10.0

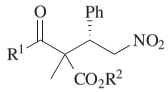
364

$C_{5-7}$





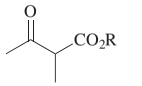
*ent*-**164b** (10 mol %), toluene, rt

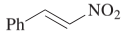


87

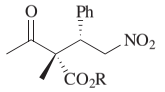
| $R^1$ | $R^2$ | Time (h) | | dr (2*R*/2*S*) | er |
|---|---|---|---|---|---|
| Me | Et | 6 | (93) | 22:78 | 97.0:3.0 |
| *i*-Pr | Me | 48 | (95) | 36:64 | 97.0:3.0 |

$C_5$



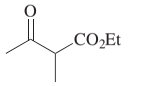


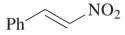
**231** (10 mol %), $CH_2Br_2$, rt



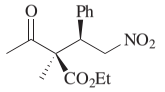
557

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Et | 168 | (90) | 97:3 | 97.5:2.5 |
| *t*-Bu | 192 | (85) | 56:44 | 98.5:1.5 |





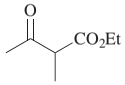
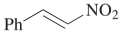
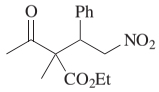
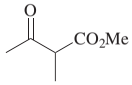
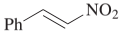
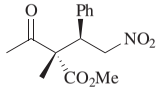
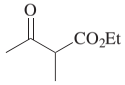
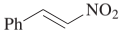
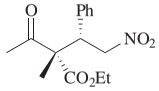
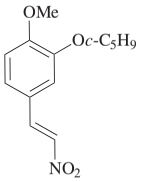
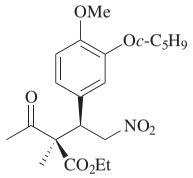
**238a** (10 mol %), toluene, –18°, 14 h

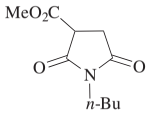


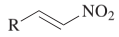
(98) dr 77:23
er 98.0:2.0

558

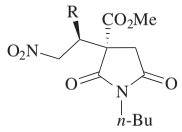
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | Catalyst (15 mol %), THF, –20°, 63 h |  | 196 |
| | | | Catalyst (73) dr er<br>**240** (73) 91:9 >99.5:0.5<br>**251** (75) 89:11 98.0:2.0 | |
|  |  | **261** (10 mol %), neat, rt, 36 h |  (73) dr 3.3:1 er 98.0:2.0 | 559 |
|  |  | **266** (10 mol %), $CH_2Cl_2$, –45°, 48 h |  (90) dr 85:15 er 96.0:4.0 | 560 |
| |  | **238a** (10 mol %), toluene, –18° |  (95) dr 80:20 er (major) 94.5:5.5 er (minor) 95.5:4.5 | 558 |



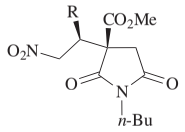


**230a** (10 mol %),
0.16 M in $CH_2Cl_2$,
–20°, 48 h



**I**

+

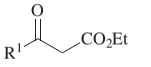


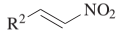
**II**

561

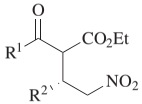
| R | | dr **I/II** | er **I** | er **II** |
|---|---|---|---|---|
| 2-$C_4H_3O$ | (90) | 1.5:1 | 97.0:3.0 | 95.5:4.5 |
| Ph | (81) | 1.9:1 | 97.0:3.0 | 94.5:5.5 |
| 2-$BrC_6H_4$ | (88) | 4.1:1 | 97.5:2.5 | 95.0:5.0 |
| 2-$ClC_6H_4$ | (85) | 4.5:1 | 98.0:2.0 | 93.5:6.5 |
| 4-$MeOC_6H_4$ | (78) | 3.5:1 | 98.0:2.0 | 95.5:4.5 |
| 3-$MeC_6H_4$ | (84) | 2.2:1 | 95.5:4.5 | 92.0:8.0 |
| 2-Np | (96) | 2.1:1 | 97.5:2.5 | 95.0:5.0 |

$C_{6–10}$





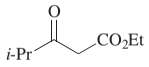
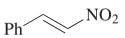
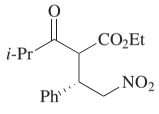
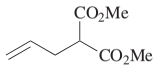
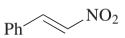
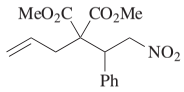
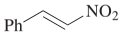
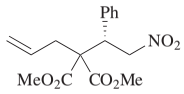
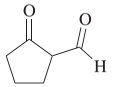
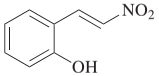
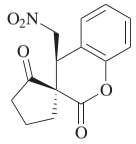
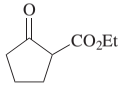
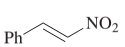
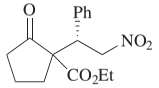
*ent*-**234** (5.5 mol %),
$Mg(OTf)_2$ (5 mol %),
NMM (6 mol %),
$CHCl_3$, MS

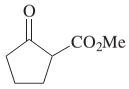


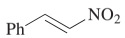
102, 103

| $R^1$ | $R^2$ | Temp | | dr | er |
|---|---|---|---|---|---|
| *i*-Pr | Ph | rt | (90) | 1:1 | 97.0:3.0 |
| *n*-$C_7H_{15}$ | Ph | rt | (95) | 1:1 | 96.0:4.0 |
| *n*-$C_7H_{15}$ | 3-MeO-4,5-$(OCH_2O)C_6H_2$ | 35° | (89) | 1:1 | 94.0:6.0 |

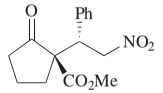
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_6$ | | | | |
|  |  | **235a** (10 mol %), toluene, rt, 4 h |  (96) dr 1:1<br>er 96.5:3.5<br>er 96.5:3.5 | 525, 33 |
|  |  | Catalyst (10 mol %), solvent, rt, 48 h |  | 566 |
| | | | Catalyst / Solvent / er: **69b** toluene (78) 95.0:5.0 (*R*); *ent*-**164b** toluene (95) 96.0:4.0 (*S*); **226a** THF (94) 95.0:5.0 (*R*) | |
| |  | **234** (1.1 mol %), $Mg(OTf)_2$ (1 mol %), NMM (1.3 mol %), $CHCl_3$, $H_2O$, MS, rt, 45 h |  (72) er 91.0:9.0 | 532 |
|  |  | 1. *ent*-**164b** (10 mol %), $CH_2Cl_2$, rt, 10 min<br>2. PCC, $CH_2Cl_2$ |  (51) er 91.5:8.5 | 563 |
|  |  | **126** (1 mol %), $CH_2Cl_2$, 12–36 h |  (85) dr 24:1<br>er (major) 91.5:8.5<br>er (minor) 93.5:6.5 | 364 |



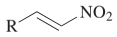


*ent*-**164b** (10 mol %), toluene, –50°, 24 h

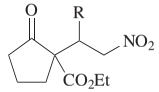


(96) dr 93:7 er 96.5:3.5

87

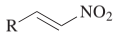


Catalyst (10 mol %), THF, –60°

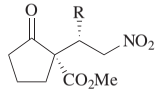


196

| R | Catalyst | Time (h) | | dr | er |
|---|---|---|---|---|---|
| *i*-Bu | **226c** | 96 | (87) | >98:2 | 99.5:0.5 |
| Ph | **226c** | 48 | (94) | 95:5 | 99.5:0.5 |
| Ph | **251** | 48 | (97) | 97:3 | 99.0:1.0 |
| Ph | **267** | 48 | (97) | 94:6 | >99.5:0.5 |

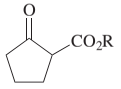


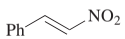
**231** (10 mol %), $CH_2Br_2$, rt



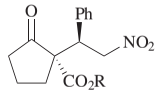
557

| R | Temp | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Ph | rt | 4 | (98) | 86:14 | >99.5:0.5 |
| 4-$ClC_6H_4$ | rt | 3 | (97) | 84:16 | 97.5:2.5 |
| 4-$FC_6H_4$ | rt | 3 | (96) | 86:14 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | rt | 18 | (90) | 82:18 | 94.0:6.0 |
| 4-$MeC_6H_4$ | –40° | 36 | (91) | 85:15 | 95.5:4.5 |





**232a** (0.5 mol %), solvent, rt



518

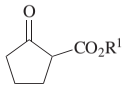
| R | Solvent | Time (min) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| Me | $CH_2Cl_2$ | 60 | (90) | 99:1 | >99.5:0.5 | 84.0:16.0 |
| Me | brine | <20 | (87) | 99:1 | >99.5:0.5 | 92.0:8.0 |
| Et | $CH_2Cl_2$ | 2 | (94) | >99:1 | 99.0:1.0 | 86.0:14.0 |
| Et | brine | <10 | (88) | >99:1 | 99.5:0.5 | 89.0:11.0 |

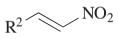
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

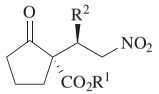
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$





**238a** (*x* mol %), toluene

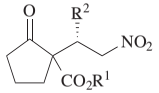


558

| $R^1$ | $R^2$ | *x* | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|
| Me | 2-$C_4H_3O$ | 2 | –50 | 10 | (99) | 97:3 | 98.0:2.0 |
| Me | Ph | 2 | –50 | 20 | (99) | >98:2 | 97.0:3.0 |
| Me | Ph | 10 | –18 | 0.5 | (99) | 98:2 | 95.0:5.0 |
| Me | 4-$ClC_6H_4$ | 2 | –50 | 24 | (98) | 96:4 | 96.0:4.0 |
| Me | 4-$FC_6H_4$ | 2 | –50 | 48 | (98) | >98:2 | 97.0:3.0 |
| Me | 4-$MeOC_6H_4$ | 2 | –50 | 60 | (96) | 96:4 | 96.0:4.0 |
| Me | 2-$O_2NC_6H_4$ | 2 | –50 | 16 | (97) | 97:3 | 97.0:3.0 |
| Me | $PhCH_2CH_2$ | 5 | –50 | 36 | (96) | >98:2 | 96.0:4.0 |
| Et | Ph | 10 | –18 | 0.5 | (99) | 95.5 | 96.0:4.0 |

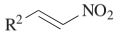


**243** (10 mol %),
toluene, –60°, 12 h

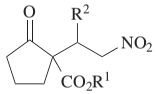


528

| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| Me | Ph | (98) | 97:3 | 96.0:4.0 |
| Et | 2-$C_4H_3O$ | (98) | 99:1 | 91.5:8.5 |
| Et | Ph | (99) | 99:1 | 95.0:5.0 |
| Et | 3-$BrC_6H_4$ | (99) | 98:2 | 90.5:9.5 |
| Et | 2-$ClC_6H_4$ | (99) | 94:6 | 92.5:7.5 |
| Et | 3-$ClC_6H_4$ | (99) | 97:3 | 92.0:8.0 |
| Et | 4-$FC_6H_4$ | (99) | 99:1 | 94.0:6.0 |
| Et | 2-$MeOC_6H_4$ | (99) | 97:3 | >99.5:0.5 |
| Et | 2-Np | (99) | 99:1 | >99.5:0.5 |

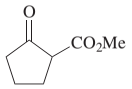


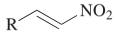
**247** (10 mol %), toluene



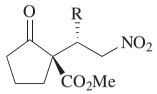
530

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| Et | Ph | 0 | 12 | (99) | 99:1 | 81.5:18.5 |
| *t*-Bu | Ph | 0 | 12 | (99) | 99:1 | 89.0:11.0 |
| *t*-Bu | Ph | –15 | 20 | (99) | 99:1 | 91.0:9.0 |
| *t*-Bu | 4-$MeOC_6H_4$ | –15 | 20 | (82) | 97:3 | 80.0:20.0 |
| *t*-Bu | 4-$O_2NC_6H_4$ | –15 | 20 | (95) | 96:4 | 86.0:14.0 |
| *t*-Bu | 4-$MeC_6H_4$ | –15 | 20 | (99) | 99:1 | 85.5:14.5 |





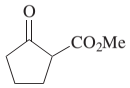
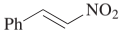
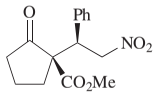
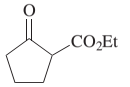
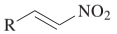
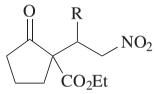
**249** (*x* mol %), toluene



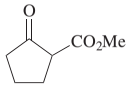
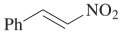
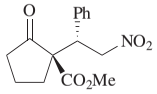
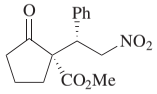
542

| R | *x* | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *i*-Bu | 5 | –10 | 48 | (95) | >20:1 | 95.0:5.0 |
| 2-$C_4H_3S$ | 10 | 0 | 139 | (73) | >20:1 | 90.0:10.0 |
| Ph | 5 | –10 | 48 | (95) | >20:1 | 97.5:2.5 |
| 2-$BrC_6H_4$ | 5 | –10 | 45 | (93) | >20:1 | 96.5:3.5 |
| 2-$ClC_6H_4$ | 5 | –10 | 75.5 | (96) | >20:1 | 96.5:3.5 |
| 4-$ClC_6H_4$ | 5 | –10 | 24 | (91) | >20:1 | 98.0:2.0 |
| 4-$FC_6H_4$ | 5 | 0 | 28.5 | (95) | >20:1 | 97.0:3.0 |
| 3-$MeOC_6H_4$ | 5 | –10 | 31 | (98) | 20:1 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 5 | 0 | 85.5 | (94) | >20:1 | 96.5:3.5 |
| 2-$MeC_6H_4$ | 5 | 0 | 70 | (79) | 16:1 | 97.0:3.0 |
| 4-$MeC_6H_4$ | 5 | –10 | 47 | (89) | >20:1 | 96.5:3.5 |

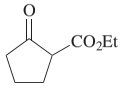
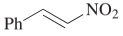
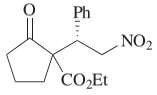
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

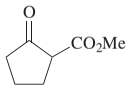
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_6$ | | | | |
|  |  | **252b** (10 mol %), $Et_2O$, 0°, 18 h |  (>99) dr 90:10<br>er (major) 86.0:14.0<br>er (minor) 89.5:10.5 | 544 |
|  |  | **254** (1 mol %), $CH_2Cl_2$, rt, 12–24 h |  | 547 |

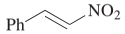
| R | | dr | er |
|---|---|---|---|
| 2-$C_4H_3S$ | (92) | >99:1 | 99.0:1.0 |
| Ph | (93) | >99:1 | 97.0:3.0 |
| 4-$BrC_6H_4$ | (95) | >99:1 | 98.5:1.5 |
| 2-$ClC_6H_4$ | (87) | >99:1 | 98.5:1.5 |
| 2-$MeOC_6H_4$ | (85) | >99:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (89) | >99:1 | 98.5:1.5 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
|  |  | **255** (2 mol %), $CH_2Cl_2$, rt, 24 h |  | **I** | + |  | **II** 192 |

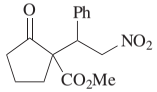
(75) dr **I/II** 50:1
er (major) 96.5:3.5; er (minor) 88.5:11.5

| | | | | |
|---|---|---|---|---|
|  |  | **256** (1 mol %), $CH_2Cl_2$, 15°, 48 h |  (84) dr 96:4<br>er (major) 98.0:2.0<br>er (minor) 83.5:16.5 | 549 |



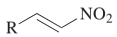


**259** (2 mol %),
$CH_2Cl_2$, rt, 24 h

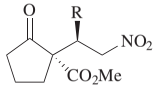


(89) dr 29:1
er (major) 98.0:2.0
er (minor) 93.5:6.5

548



**261** (*x* mol %), solvent, rt

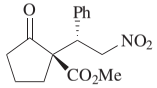


559

| R | *x* | Solvent | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 2.5 | — | 3 | (93) | >30:1 | 96.0:4.0 |
| Ph | 2.5 | — | 8 | (>99) | 25:1 | 98.5:1.5 |
| 2-$BrC_6H_4$ | 2.5 | — | 14 | (77) | 27:1 | 97.0:3.0 |
| 3-$BrC_6H_4$ | 2.5 | — | 4 | (88) | 30:1 | 98.5:1.5 |
| 4-$BrC_6H_4$ | 2.5 | — | 5 | (95) | >30:1 | 99.0:1.0 |
| 4-$ClC_6H_4$ | 0.1 | THF | 48 | (98) | 16:1 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 0.2 | THF | 24 | (87) | >30:1 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 2.5 | — | 4 | (94) | >30:1 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 2.5 | — | 17 | (93) | 9:1 | 97.0:3.0 |
| 4-$MeC_6H_4$ | 2.5 | — | 10 | (93) | 22:1 | 98.0:2.0 |
| $BnCH_2$ | 2.5 | — | 7 | (96) | >30:1 | 97.5:2.5 |



**265** (10 mol %),
$CH_2Cl_2$, –40°, 40 h



(90) dr >50:1
er 95.0:5.0

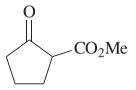
564

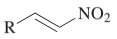
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

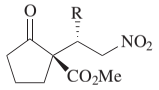
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



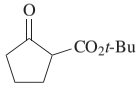



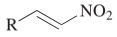

**266** (*x* mol %),
$CH_2Cl_2$, 12–20 h



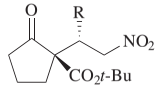

560

| R | *x* | Temp (°) | | dr | er |
|---|---|---|---|---|---|
| *i*-Pr | 10 | 0 | (93) | 97:3 | 95.0:5.0 |
| *i*-Bu | 10 | 0 | (92) | 97:3 | 97.0:3.0 |
| amyl | 10 | 0 | (89) | 96:4 | 97.0:3.0 |
| *c*-$C_6H_{11}$ | 10 | 0 | (89) | 97:3 | 95.0:5.0 |
| Ph | 5 | –45 | (98) | 98:2 | 98.5:1.5 |
| Ph | 10 | –45 | (98) | 98:2 | 99.5:0.5 |
| 2-$BrC_6H_4$ | 10 | –45 | (94) | 97:3 | 99.5:0.5 |
| 2-$ClC_6H_4$ | 10 | –45 | (95) | 97:3 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 10 | –45 | (90) | 98:2 | 99.5:0.5 |
| 4-$FC_6H_4$ | 10 | –45 | (89) | 97:3 | 99.5:0.5 |
| 3-$MeOC_6H_4$ | 10 | –45 | (90) | 96:4 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 10 | –45 | (91) | 94:6 | 98.5:1.5 |
| 2-$MeC_6H_4$ | 10 | –45 | (97) | 98:2 | 99.5:0.5 |
| 3-$MeC_6H_4$ | 10 | –45 | (95) | 97:3 | 99.5:0.5 |
| 4-$MeC_6H_4$ | 10 | –45 | (91) | 99:1 | 99.5:0.5 |




**269** (2 mol %),
EtOAc, –15°, 32 h



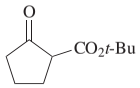

| R | | *syn*/*anti* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (99) | 99:1 | 95.0:5.0 |
| 2-$C_4H_3S$ | (99) | >99:1 | 96.5:3.5 |
| Ph | (98) | 99:1 | 97.5:2.5 |
| 4-$BrC_6H_4$ | (99) | 99:1 | 97.5:2.5 |
| 2-$ClC_6H_4$ | (99) | >99:1 | 97.5:2.5 |
| 3-$ClC_6H_4$ | (82) | >99:1 | 97.5:2.5 |
| 4-$ClC_6H_4$ | (95) | >99:1 | 97.5:2.5 |
| 4-$FC_6H_4$ | (93) | 99:1 | 98.5:1.5 |
| 3-$MeOC_6H_4$ | (82) | >99:1 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | (80) | 98:2 | 97.0:3.0 |
| 3-PhO-4-$FC_6H_3$ | (93) | >99:1 | 98.0:2.0 |
| 4-$MeC_6H_4$ | (99) | 96:4 | 96.0:4.0 |
| PhCH=CH | (99) | >99:1 | 96.5:3.5 |
| 4-$MeOC_6H_4CH$=CH | (83) | 99:1 | 96.5:3.5 |
| 1-Np | (80) | >99:1 | 95.5:4.5 |
| 2-Np | (99) | 85:15 | 98.0:2.0 |
| 4-$PhC_6H_4$ | (80) | 99:1 | 98.0:2.0 |

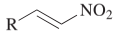
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

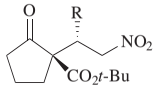
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



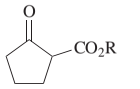


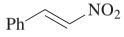
**269** (*x* mol %), solvent, –15°



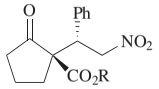
193

| R | *x* | Solvent | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|---|
| *c*-$C_6H_{11}$ | 5 | EtOAc | 48 | (70) | 99:1 | 96.0:4.0 |
| 2,4-$Cl_2C_6H_3$ | 5 | EtOAc | 48 | (99) | 99:1 | 98.0:2.0 |
| 2,6-$Cl_2C_6H_3$ | 5 | EtOAc | 48 | (54) | 88:12 | 91.5:8.5 |
| 3,4-$(MeO)_2C_6H_3$ | 5 | EtOAc/THF (1:1) | 48 | (75) | >99:1 | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | 4 | EtOAc | 32 | (94) | 99:1 | 96.0:4.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 5 | EtOAc/THF (1:1) | 48 | (76) | >99:1 | 97.5:2.5 |
| 2-$MeC_6H_4$ | 3 | EtOAc | 32 | (98) | 89:11 | 98.0:2.0 |
| 3-$MeC_6H_4$ | 3 | EtOAc | 32 | (90) | 99:1 | 97.5:2.5 |



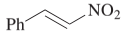


**269** (5 mol %), THF, 0°, 20 h

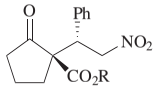


193

| R | | *syn*/*anti* | er |
|---|---|---|---|
| Et | (98) | 95:5 | 93.5:6.5 |
| *t*-Bu | (97) | 96:4 | 95.0:5.0 |
| *c*-$C_6H_{11}$ | (96) | 97:3 | 95.0:5.0 |
| 1-adamantyl | (94) | 98:2 | 96.5:3.5 |

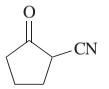


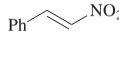
**270** (10 mol %),
$CH_2Cl_2$, –40°, 40 h



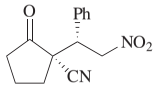
| R | | dr | er |
|---|---|---|---|
| Me | (95) | >50:1 | 95.5:4.5 |
| Et | (96) | >50:1 | 95.0:5.0 |

564



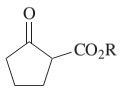


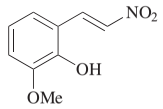
**272** (10 mol %),
$CH_2Cl_2$, –40°, 24 h



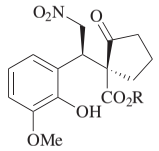
(98) dr >99:1
er 99.5:0.5

565



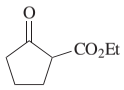


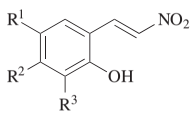
1. **69b** (10 mol%),
0.3 M in $CH_2Cl_2$, rt
2. PTSA (10 mol %),
0.075 M in DCE, 80°, 3–4 h



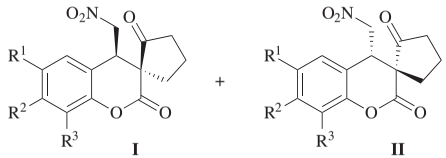
| R | | dr | er |
|---|---|---|---|
| Et | (90) | >99.5:0.5 | 99.0:1.0 |
| *i*-Pr | (90) | >99.5:0.5 | 99.5:0.5 |

566





1. Catalyst (10 mol %),
0.3 M in $CH_2Cl_2$, rt
2. PTSA (10 mol %),
0.075 M in DCE, 80°, 3–4 h



566

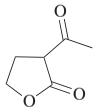
| $R^1$ | $R^1$ | $R^3$ | Catalyst | Time (h) | | dr | er **I/II** |
|---|---|---|---|---|---|---|---|
| H | H | OH | **268** | 12 | (70) | >99.5:0.5 | 12.0:88.0 |
| H | MeO | H | **69b** | 3–4 | (65) | >99.5:0.5 | 92.0:8.0 |
| Br | H | H | **69b** | 3–4 | (70) | >99.5:0.5 | 93.5:6.5 |
| Br | H | H | **268** | 3–4 | (80) | >99.5:0.5 | 0.1:>99.9 |
| Cl | H | H | **69b** | 3–4 | (70) | >99.5:0.5 | 93.5:6.5 |
| F | H | H | **69b** | 3–4 | (81) | >99.5:0.5 | 94.0:6.0 |
| MeO | H | H | **69b** | 3–4 | (70) | >99.5:0.5 | 95.0:5.0 |
| Me | H | H | **69b** | 8 | (75) | >99.5:0.5 | 98.0:2.0 |
| Me | H | H | **268** | 8 | (75) | >99.5:0.5 | 0.5:99.5 |

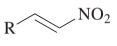
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

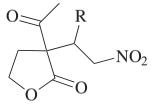
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$





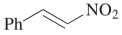
Catalyst (10 mol %),
THF, –60°



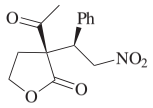
196

| R | Catalyst | Time (h) | | dr | er |
|---|---|---|---|---|---|
| *i*-Bu | **240** | 48 | (82) | 98:2 | 99.5:0.5 |
| 4-$ClC_6H_4$ | **226c** | 44 | (87) | 98:2 | 99.5:0.5 |
| 4-$ClC_6H_4$ | **251** | 44 | (92) | 97:3 | 99.0:1.0 |
| 4-$ClC_6H_4$ | **267** | 44 | (92) | 97:3 | 99.0:1.0 |



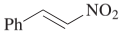


**238a** (10 mol %), toluene

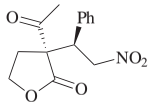


558

| Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|
| –60 | 6 | (94) | 83:17 | 99.0:1.0 |
| –40 | 1.5 | (89) | 81:19 | 97.0:3.0 |
| –18 | 0.75 | (95) | 70:30 | 96.0:4.0 |

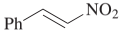


**252b** (10 mol %),
$Et_2O$, 0°, 17 h

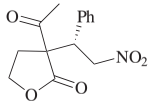


(>99) dr 72:28
er (major) 83.5:16.5
er (minor) 78.5:21.5

544

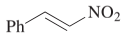


**255** (2 mol %),
$CH_2Cl_2$, rt, 12 h

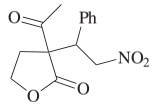


(65) dr 4:1
er (major) 97.0:3.0
er (minor) 95.5:4.5

192

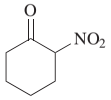


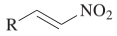
**259** (2 mol %),
$CH_2Cl_2$, rt, 24 h



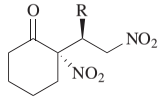
(62) dr 5:1
er (major) 91.5:8.5
er (minor) 94.0:6.0

548



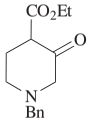


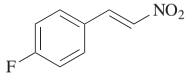
**273** (10 mol %),
$CH_2Cl_2$, 0°, 17 h



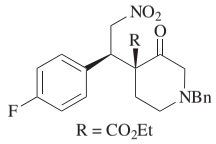
567

| R | | *anti*/*syn* | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (73) | 97:3 | 96.0:4.0 |
| Ph | (77) | 99:1 | 97.0:3.0 |
| 4-$BrC_6H_4$ | (82) | 88:12 | 97.0:3.0 |
| 2-$ClC_6H_4$ | (58) | 89:11 | 97.0:3.0 |
| 4-$ClC_6H_4$ | (73) | 91:9 | 97.0:3.0 |
| 2-$FC_6H_4$ | (90) | 91:9 | 98.0:2.0 |
| 4-$FC_6H_4$ | (75) | 93:7 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (88) | 97:3 | 98.0:2.0 |
| 4-$MeC_6H_4$ | (78) | 93:7 | 98.0:2.0 |





**238a** (10 mol %),
toluene, –18°, 20 h



R = $CO_2Et$

(85) dr >99:1
er 97.0:3.0

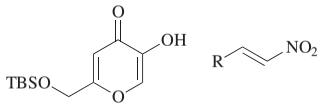
558

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

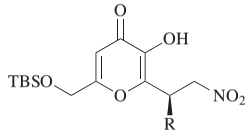
$C_6$







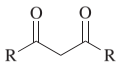
**274** (*x* mol %), MeOH, –10°, 4 d

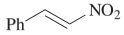



568

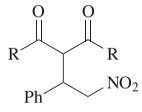
| R | *x* | | er |
|---|---|---|---|
| 2-$C_4H_3S$ | 20 | (58) | 98.5:1.5 |
| *c*-$C_6H_{11}$ | 10 | (68) | 94.5:5.5 |
| Ph | 10 | (95) | 95.0:5.0 |
| 2-$BrC_6H_4$ | 10 | (87) | 91.5:8.5 |
| 3-$BrC_6H_4$ | 10 | (89) | 93.5:6.5 |
| 4-$BrC_6H_4$ | 10 | (83) | 97.0:3.0 |
| 2-$ClC_6H_4$ | 10 | (99) | 90.5:9.5 |
| 2,4-$Cl_2C_6H_3$ | 10 | (92) | 91.5:8.5 |
| 4-$ClC_6H_4$ | 10 | (86) | 96.5:3.5 |
| 4-$FC_6H_4$ | 10 | (85) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 10 | (80) | 94.0:6.0 |
| 2-$O_2NC_6H_4$ | 10 | (80) | 93.0:7.0 |
| 4-$O_2NC_6H_4$ | 10 | (84) | 94.5:5.5 |
| 4-$MeC_6H_4$ | 10 | (77) | 93.5:6.5 |
| 1-Np | 10 | (86) | 95.5:4.5 |

$C_{7–15}$



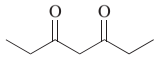

**69b** (10 mol %), toluene, rt

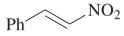



| R | Time (h) | | er |
|---|---|---|---|
| Et | 1 | (92) | 98.0:2.0 |
| *i*-Pr | 6 | (84) | 96.5:3.5 |
| *t*-Bu | 96 | (30) | 99.5:0.5 |
| Ph | 4 | (93) | 97.0:3.0 |

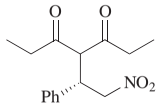
551

$C_7$

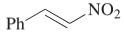




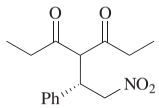
**232b** (0.5 mol %), solvent, rt



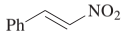
| Solvent | Time (h) | | er | |
|---|---|---|---|---|
| $CH_2Cl_2$ | 12 | (97) | >99.5:0.5 | 518 |
| brine | <0.33 | (96) | >99.5:0.5 | |



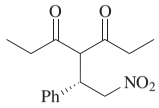
**235a** (2 mol %), toluene, rt, 148 h



(90) er 93.5:6.5 33

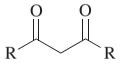


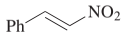
**235b** (2 mol %), toluene, rt, 30 h



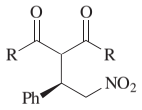
(91) er 96.0:4.0 33

$C_{7-9}$





**237** (2 mol %), toluene, –20°, 48 h



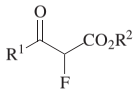
| R | | er | |
|---|---|---|---|
| Et | (98) | 98.5:1.5 | 96 |
| *i*-Pr | (99) | 98.5:1.5 | |

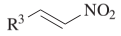
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

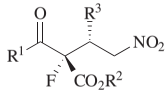
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{7-13}$





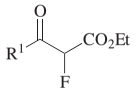
**231** (10 mol %), toluene, rt

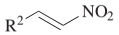


569

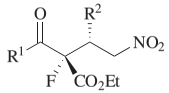
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| 2-$C_4H_3S$ | *i*-Pr | Ph | 42 | (95) | 1.5:1 | 95.5:4.5 |
| Ph | Me | Ph | 23 | (95) | 3:1 | 94.0:6.0 |
| Ph | Et | Ph | 20 | (97) | 2.9:1 | 98.0:2.0 |
| Ph | *i*-Pr | *i*-Bu | 72 | (91) | 3.3:1 | 95.5:4.5 |
| Ph | *i*-Pr | 2-$C_4H_3O$ | 44 | (84) | 1.6:1 | 99.0:1.0 |
| Ph | *i*-Pr | 2-$C_4H_3S$ | 44 | (98) | 2.8:1 | 94.0:6.0 |
| Ph | *i*-Pr | Ph | 40 | (98) | 4.3:1 | 99.0:1.0 |
| Ph | *i*-Pr | 2-$ClC_6H_4$ | 94 | (93) | 3:1 | >99.5:0.5 |
| Ph | *i*-Pr | 2-$FC_6H_4$ | 94 | (96) | 4:1 | 99.5:0.5 |
| Ph | *i*-Pr | 4-$MeOC_6H_4$ | 115 | (94) | 3.5:1 | 99.0:1.0 |
| Ph | *i*-Pr | 4-$MeC_6H_4$ | 115 | (98) | 3.6:1 | >99.5:0.5 |
| Ph | *i*-Pr | 2-Np | 48 | (84) | 3.8:1 | 96.5:3.5 |
| Ph | *t*-Bu | Ph | 57 | (56) | 2.3:1 | 99.0:1.0 |
| 4-$BrC_6H_4$ | *i*-Pr | Ph | 23 | (93) | 3.4:1 | 97.0:3.0 |
| 3-$ClC_6H_4$ | *i*-Pr | Ph | 44 | (96) | 5:1 | 95.5:4.5 |
| 4-$CF_3C_6H_4$ | *i*-Pr | Ph | 66 | (93) | 3.7:1 | 96.5:3.5 |
| 2-Np | *i*-Pr | Ph | 38 | (96) | 3.4:1 | 98.5:1.5 |

$C_{7-10}$





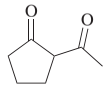
**268** (10 mol %), toluene

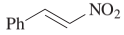


570

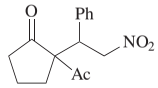
| $R^1$ | $R^2$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *t*-Bu | 4-$BrC_6H_4$ | rt | 24 | (90) | 19:1 | 98.5:1.5 |
| *t*-Bu | 4-$MeOC_6H_4$ | rt | 24 | (90) | 19:1 | 99.0:1.0 |
| 3-$ClC_6H_4$ | Ph | –20 | 12 | (98) | 4:1 | 98.0:2.0 |
| 3-$ClC_6H_4$ | 4-$FC_6H_4$ | –20 | 12 | (97) | 4:1 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Ph | –20 | 12 | (97) | 4:1 | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | Ph | –20 | 12 | (98) | 4:1 | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | 3-$BrC_6H_4$ | –20 | 12 | (98) | 4:1 | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | 4-$MeC_6H_4$ | –20 | 12 | (96) | 3:1 | 98.0:2.0 |
| 4-$CF_3C_6H_4$ | Ph | –20 | 12 | (97) | 3:1 | 97.5:2.5 |
| 4-$CF_3C_6H_4$ | 2-$ClC_6H_4$ | –20 | 12 | (96) | 3:1 | 97.5:2.5 |

$C_7$



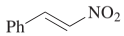


**69b** (10 mol %),
toluene, rt, 12 h

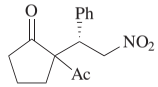


(89) dr 1.2:1
er 85.0:15.0

557



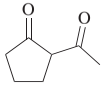
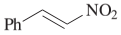
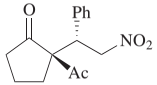
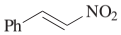
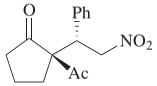
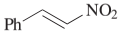
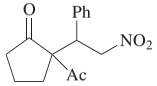
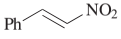
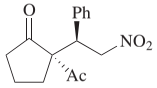
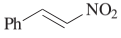
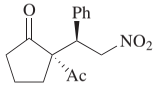
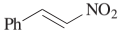
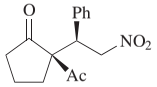
**126** (1 mol %),
$CH_2Cl_2$, 12–36 h



(81) dr 1:1
er 94.0:6.0
er 93.0:7.0

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TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_7$ | | | | |
|  |  | **132** (5 mol %), $Et_2O$, –50°, 10 h |  (92) dr 85:15<br>er (major) 98.0:2.0<br>er (minor) 95.0:5.0 | 552 |
| |  | *ent*-**164b** (10 mol %), toluene, –60°, 24 h |  (94) dr 93:7<br>er 90.5:9.5 | 87 |
| |  | Catalyst (10 mol %), THF, –60°, 48 h |  | 196 |
| |  | **232b** (2 mol %), solvent, rt |  | 518 |
| |  | **238a** (10 mol %), toluene, –18°, 2.5 h |  (93) dr 87:13<br>er 96.0:4.0 | 558 |
| |  | **252b** (10 mol %), $Et_2O$, 0°, 19 h |  (98) dr 94:16<br>er (major) 87.5:12.5<br>er (minor) 89.5:10.5 | 544 |

| Catalyst | | dr | er |
|---|---|---|---|
| **226c** | (76) | 86:14 | 99.5:0.5 |
| **251** | (80) | 90:10 | 98.0:2.0 |
| **267** | (70) | 88:12 | 99.0:1.0 |

| Solvent | Time (h) | | dr |
|---|---|---|---|
| $CH_2Cl_2$ | 120 | (78) | 3.2:1 |
| brine | 20 | (85) | 7.3:1 |

er >99.5:0.5

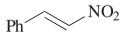
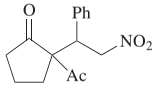
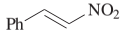
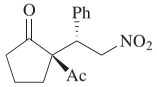
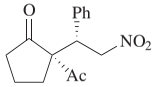
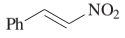
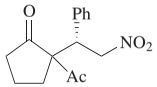
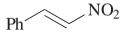
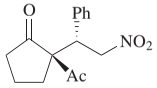
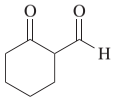
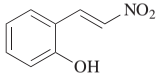
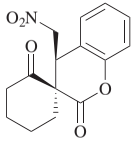
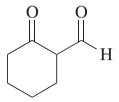
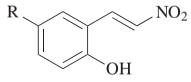
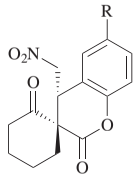
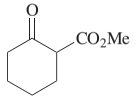
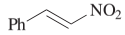
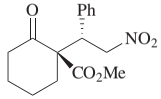
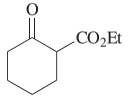
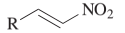
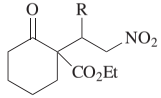
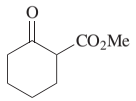
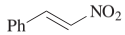
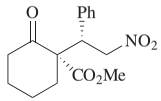
| | | | | |
|---|---|---|---|---|
|  | **254** (1 mol %), $CH_2Cl_2$, rt, 12–24 h |  | (87) dr 4:1<br>er 94.5:5.5 | 547 |
|  | **255** (2 mol %), $CH_2Cl_2$, rt, 24 h |  **I** +  **II** | (96) dr **I**/**II** 18:1<br>er **I** 99.0:1.0; er **II** 98.0:2.0 | 192 |
|  | **256** (1 mol %), $CH_2Cl_2$, 15°, 48 h |  | (80) dr 1.6:1<br>er (major) 94.5:5.5<br>er (minor) 86.5:13.5 | 549 |
|  | **266** (10 mol %), $CH_2Cl_2$, –45°, 11 h |  | (96) dr 96:4<br>er 98.0:2.0 | 560 |
|  |  <br>1. *ent*-**164b** (10 mol %), $CH_2Cl_2$, rt, 0.5 h<br>2. PCC, $CH_2Cl_2$ |  | (63) er 95.0:5.0 | 563 |

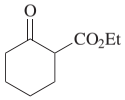
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

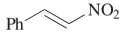
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_7$ | | | | |
|  |  | 1. **69b** (10 mol %), 0.3 M in $CH_2Cl_2$, rt, 3–4 h<br>2. PCC |  | 566 |
|  |  | *ent*-**164b** (10 mol %), toluene, –20°, 36 h |  | 87 |
|  |  | Catalyst (10 mol %), THF |  | 196 |

| R | Catalyst | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *i*-Bu | **240** | rt | 96 | (83) | >98:2 | 99.5:0.5 |
| 2-$C_4H_3S$ | **226a** | –20 | 74 | (91) | >98:2 | 99.5:0.5 |
| Ph | **226a** | –20 | 72 | (93) | >98:2 | 99.5:0.5 |
| 4-$BrC_6H_4$ | **226a** | –20 | 74 | (95) | >98:2 | >99.5:0.5 |
| 4-$BrC_6H_4$ | **228** | –20 | 74 | (96) | >98:2 | 99.5:0.5 |
| 4-$BrC_6H_4$ | **251** | –20 | 74 | (97) | >98:2 | 99.0:1.0 |

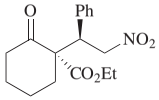
| R | | dr | er |
|---|---|---|---|
| H | (65) | >99.5:0.5 | 99.5:0.5 |
| Br | (70) | >99.5:0.5 | 89.5:10.5 |

| | | | | |
|---|---|---|---|---|
|  |  | **231** (10 mol %), $CH_2Br_2$, rt, 144 h |  | (75) *syn*/*anti* = 92:8<br>er 98.0:2.0 | 557 |



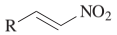


**238a** (10 mol %), toluene, –18°, 17 h

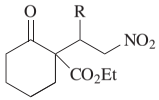


(99) dr 98:2 er 97.0:3.0

558

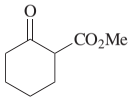


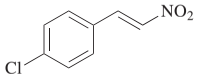
**254** (1 mol %), $CH_2Cl_2$, rt, 12–24 h



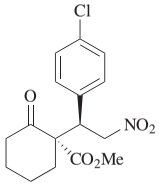
547

| R | | dr | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (84) | 98:2 | 97.5:2.5 |
| 2-$C_4H_3S$ | (90) | >99:1 | >99.5:0.5 |
| Ph | (92) | >99:1 | 96.5:3.5 |
| 4-$BrC_6H_4$ | (95) | >99:1 | 97.5:2.5 |
| 2-$ClC_6H_4$ | (91) | >99:1 | >99.5:0.5 |



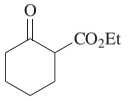


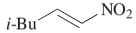
**261** (2.5 mol %), neat, rt, 24 h



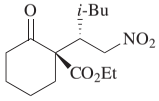
(75) dr >30:1 99.0:1.0

559





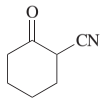
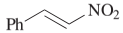
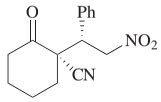
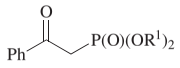
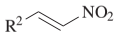
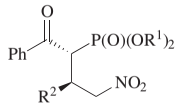
**266** (10 mol %), $CH_2Cl_2$, rt, 48 h



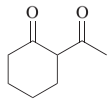
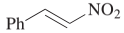
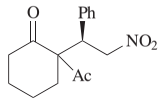
(89) dr >99:1 er 96.0:4.0

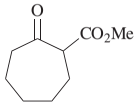
560

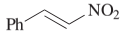
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_7$  |  | **272** (10 mol %), $CH_2Cl_2$, –40°, 40 h |  (97) dr 95:5 er 97.5:2.5 | 565 |
| $C_8$  |  | **271** (20 mol %), THF, rt |  | 571 |

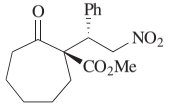
| $R^1$ | $R^2$ | Time (d) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| Me | Ph | 4.5 | (85) | 1.6:1 | 68.5:31.5 | 90.5:9.5 |
| Et | 2-$C_4H_3O$ | 4 | (84) | 1:1 | 75.0:25.0 | 97.0:3.0 |
| Et | Ph | 2.5 | (87) | 1.5:1 | 86.5:13.5 | 85.0:15.0 |
| Et | 2-$BrC_6H_4$ | 2.5 | (86) | 1.3:1 | 93.0:7.0 | 93.0:7.0 |
| Et | 4-$BrC_6H_4$ | 3 | (83) | 1.7:1 | 84.0:16.0 | 84.0:16.0 |
| Et | 2-$ClC_6H_4$ | 2.5 | (86) | 1.1:1 | 93.0:7.0 | 93.5:6.5 |
| Et | 4-$ClC_6H_4$ | 3 | (85) | 1.7:1 | 87.0:13.0 | 86.0:14.0 |
| Et | 2-$MeOC_6H_4$ | 3 | (84) | 1.6:1 | 96.0:4.0 | 96.0:4.0 |
| Et | 3-$CF_3C_6H_4$ | 2.5 | (85) | 1.3:1 | 80.5:19.5 | 80.5:19.5 |
| Et | 1-Np | 4 | (81) | 1.3:1 | 99.0:1.0 | 83.5:16.5 |

| | | | | |
|---|---|---|---|---|
|  |  | **231** (10 mol %), toluene, rt, 16 h |  (76) dr 94:6 er 91.5:8.5 | 517 |



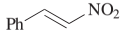


*ent*-**164b** (10 mol %), toluene, –40°, 24 h

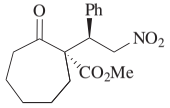


(76) dr 83:17 er 94.5:5.5

87

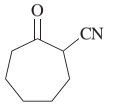


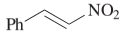
**238a** (10 mol %), toluene



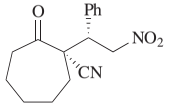
558

| Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|
| –8 | 4 | (97) | 90.0:10.0 | 97.0:3.0 |
| –50 | 9 | (95) | 92.0:8.0 | 99.0:1.0 |





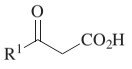
**272** (10 mol %), $CH_2Cl_2$, –40°, 24 h

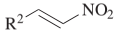


(98) dr >99:1 er 96.0:4.0

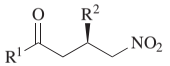
565

$C_9$





**235b** (2 mol %), THF, rt



33

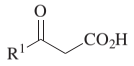
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | *n*-$C_5H_{11}$ | 160 | (51) | 88.5:11.5 |
| Ph | Ph | 24 | (95) | 95.0:5.0 |
| Ph | 4-$BrC_6H_4$ | 21 | (99) | 97.0:3.0 |
| Ph | 3,4-$(OCH_2O)C_6H_3$ | 80 | (77) | 95.0:5.0 |
| Ph | 4-$MeC_6H_4$ | 38 | (87) | 94.0:6.0 |
| Ph | PhCH=CH | 115 | (50) | 90.0:10.0 |
| 4-$FC_6H_4$ | Ph | 138 | (81) | 93.5:6.5 |
| 3-$MeOC_6H_4$ | Ph | 45 | (89) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | Ph | 36 | (80) | 95.0:5.0 |

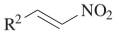
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

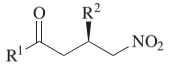
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_9$



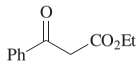


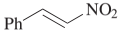
**250** (0.1 mol %), $CHCl_3$/THF (4:1), rt, 6 h



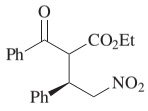
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 2-$C_4H_3S$ | Ph | (85) | 96.5:3.5 |
| Ph | 2-$C_4H_3O$ | (80) | 96.0:4.0 |
| Ph | 2-$C_4H_3S$ | (83) | 95.5:4.5 |
| Ph | Ph | (83) | 98.5:1.5 |
| Ph | 4-$BrC_6H_4$ | (87) | 93.5:6.5 |
| Ph | 4-$ClC_6H_4$ | (89) | 96.5:3.5 |
| Ph | 4-$FC_6H_4$ | (88) | 95.0:5.0 |
| Ph | 4-$MeOC_6H_4$ | (78) | 95.0:5.0 |
| Ph | 2-$O_2NC_6H_4$ | (82) | 96.5:3.5 |
| Ph | 4-$MeC_6H_4$ | (80) | 95.5:4.5 |
| Ph | $BnCH_2$ | (70) | 88.0:12.0 |
| Ph | 2-Np | (81) | 96.5:3.5 |
| 4-$BrC_6H_4$ | Ph | (80) | 97.5:2.5 |
| 2-$ClC_6H_4$ | Ph | (84) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | Ph | (80) | 93.5:6.5 |
| 4-$MeC_6H_4$ | Ph | (83) | 98.5:1.5 |
| 2-Np | Ph | (84) | 91.5:8.5 |

541



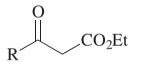


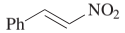
**126** (1 mol %), $CH_2Cl_2$, rt, 12–36 h



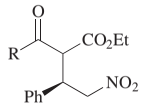
(90) dr 1:1
er 92.5:7.5
er 92.0:8.0

364



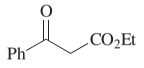


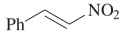
*ent*-**164b** (*x* mol %), toluene



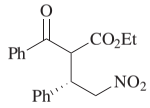
| R | *x* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | 2 | –40 | 24 | (96) | 97.0:3.0 |
| Ph | 5 | –40 | 24 | (95) | 97.0:3.0 |
| Ph | 10 | –40 | 24 | (93) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 10 | rt | 2 | (99) | 94.5:5.5 |

87



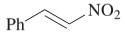


*ent*-**234** (5.5 mol %), $Mg(OTf)_2$ (5 mol %), NMM (6 mol %), $CHCl_3$, MS, 3 h

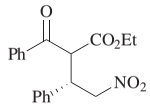


(83) er 93.5:6.5

103



**235a** (2 mol %), toluene, rt, 4 h



(99) dr 2.5:1
er 95.0:5.0
er 92.5:7.5

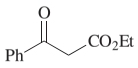
528, 33

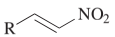
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

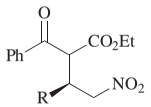
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

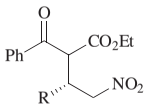
$C_9$





Catalyst (10 mol %), toluene, –30°, 12 h



**I** +  **II** 528

| R | Catalyst | | er **I/II** |
|---|---|---|---|
| *i*-Bu | **241** | (81) | 10.5:89.5 |
| *i*-Bu | **244** | (85) | 79.5:20.5 |
| 2-$C_4H_3O$ | **241** | (86) | 5.0:95.0 |
| 2-$C_4H_3O$ | **244** | (83) | 96.0:4.0 |
| 2-$C_4H_3S$ | **241** | (91) | 4.5:95.5 |
| 2-$C_4H_3S$ | **244** | (90) | 95.0:5.0 |
| Ph | **241** | (89) | 4.5:95.5 |
| Ph | **244** | (91) | 95.0:5.0 |
| 2-$ClC_6H_4$ | **241** | (91) | 4.0:96.0 |
| 2-$ClC_6H_4$ | **244** | (90) | 97.0:3.0 |
| 3-$ClC_6H_4$ | **241** | (95) | 9.5:90.5 |
| 3-$ClC_6H_4$ | **244** | (96) | 95.0:5.0 |
| 4-$ClC_6H_4$ | **241** | (89) | 3.5:96.5 |
| 4-$ClC_6H_4$ | **244** | (88) | 98.0:2.0 |
| 4-$FC_6H_4$ | **241** | (95) | 5.0:95.0 |
| 4-$FC_6H_4$ | **244** | (97) | 95.5:4.5 |
| 2-$MeOC_6H_4$ | **241** | (98) | 10.0:90.0 |
| 2-$MeOC_6H_4$ | **244** | (98) | 91.0:9.0 |
| 4-$MeC_6H_4$ | **241** | (92) | 2.5:97.5 |
| 4-$MeC_6H_4$ | **244** | (95) | 98.0:2.0 |

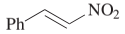
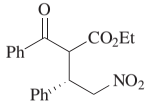
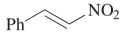
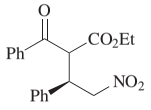
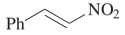
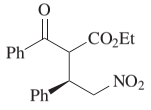
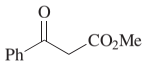
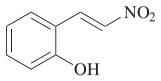
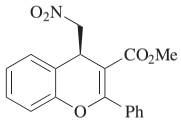
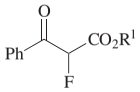
| | | | | | |
|---|---|---|---|---|---|
| |  | **252b** (10 mol %), $Et_2O$, 0°, 17 h |  | (96) dr 55:45<br>er (major) 92.0:8.0<br>er (minor) 91.5:8.5 | 544 |
| |  | **255** (2 mol %), $CH_2Cl_2$, rt, 24 h |  | (90) dr 2:1<br>er (major) 96.0:4.0<br>er (minor) 91.5:8.5 | 192 |
| |  | **256** (1 mol %), $CH_2Cl_2$, 15°, 48 h |  | (88) dr 1:1<br>er 94.5:5.5<br>er 95.0:5.0 | 549 |
|  |  | 1. **252a** (10 mol %), toluene, rt, 5 h<br>2. PTSA (20 mol %), toluene, 100°, 2 h |  | (76) er 90.0:10.0 | 543 |

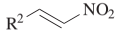
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

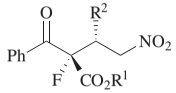
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_9$



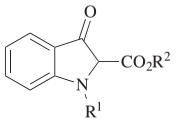


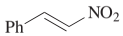
**268** (10 mol %), toluene



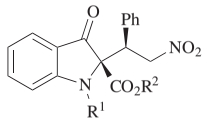
570

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| Et | *n*-Bu | –20 | 48 | (95) | 6:1 | 98.5:1.5 |
| Et | *i*-Bu | –20 | 48 | (96) | 6:1 | 98.0:2.0 |
| Et | 2-$C_4H_3S$ | –20 | 12 | (97) | 6:1 | 98.0:2.0 |
| Et | 3-$BrC_6H_4$ | –20 | 12 | (98) | 5:1 | 99.5:0.5 |
| Et | 4-$BrC_6H_4$ | –20 | 12 | (97) | 5:1 | 98.5:1.5 |
| Et | 2-$ClC_6H_4$ | –20 | 12 | (98) | 4:1 | 99.5:0.5 |
| Et | 4-$FC_6H_4$ | –20 | 12 | (99) | 5:1 | 99.0:1.0 |
| Et | 2-$MeOC_6H_4$ | –20 | 12 | (98) | 8:1 | 99.0:1.0 |
| Et | 4-$MeOC_6H_4$ | –20 | 12 | (96) | 5:1 | 98.5:1.5 |
| Et | 4-$MeC_6H_4$ | –20 | 12 | (96) | 5:1 | 97.0:3.0 |
| Et | 2-$CF_3C_6H_4$ | –20 | 12 | (97) | 3:1 | 99.5:0.5 |
| Et | 4-$NCC_6H_4$ | –20 | 12 | (99) | 5:1 | >99.5:0.5 |
| *t*-Bu | 2-$ClC_6H_4$ | rt | 48 | (65) | 2.5:1 | 99.0:1.0 |





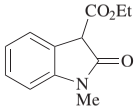
**69b** (10 mol %),
$CH_2Cl_2$, 0°, 42 h

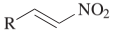


dr 20:1

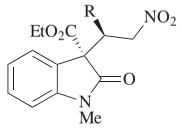
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ac | *i*-Pr | (91) | 95.5:4.5 |
| Boc | Me | (87) | 97.5:2.5 |

572



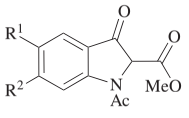


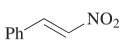
**69b** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$



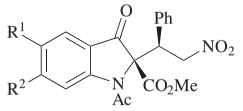
573

| R | Temp (°) | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| *n*-Pr | –60 | 36 | (90) | 60:40 | 91.0:9.0 | 97.0:3.0 |
| 2-$C_4H_3O$ | –70 | 24 | (95) | 67:33 | 93.0:7.0 | — |
| Ph | –70 | 24 | (99) | 88:12 | 98.5:1.5 | — |
| 2-$BrC_6H_4$ | –70 | 24 | (99) | 85:15 | 98.5:1.5 | — |
| 3-$BrC_6H_4$ | –70 | 24 | (99) | 87:13 | 98.0:2.0 | — |
| 4-$BrC_6H_4$ | –70 | 24 | (98) | 87:13 | 98.0:2.0 | — |
| 2-$ClC_6H_4$ | –70 | 24 | (99) | 86:14 | 98.5:1.5 | — |
| 4-$ClC_6H_4$ | –70 | 24 | (99) | 89:11 | 99.0:1.0 | — |
| 2,4-$Cl_2C_6H_3$ | –70 | 24 | (99) | 82:18 | 97.0:3.0 | — |
| 4-$FC_6H_4$ | –70 | 24 | (91) | 92:8 | 98.5:1.5 | — |
| 4-$MeOC_6H_4$ | –70 | 24 | (98) | 79:21 | 95.0:5.0 | — |
| 4-$O_2NC_6H_4$ | –70 | 36 | (93) | 89:11 | 96.0:4.0 | — |
| 4-$MeC_6H_4$ | –70 | 24 | (99) | 84:16 | 98.0:2.0 | — |
| 4-$CF_3C_6H_4$ | –70 | 24 | (98) | 90:10 | 97.0:3.0 | — |
| 2-Np | –70 | 24 | (97) | 86:14 | 96.5:3.5 | — |





**69b** (10 mol %),
$CH_2Cl_2$, 0°, 48 h



572

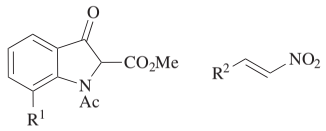
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| Br | H | (94) | >20:1 | 95.0:5.0 |
| H | Cl | (95) | 16:1 | 95.5:4.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

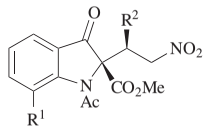
$C_{9-10}$







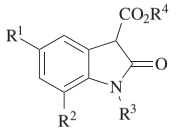
**69b** (10 mol %), $CH_2Cl_2$

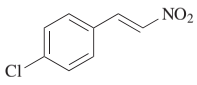



572

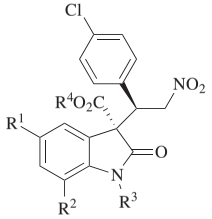
| $R^1$ | $R^2$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| H | *n*-Bu | rt | 48 | (87) | >20:1 | 87.5:12.5 |
| H | 2-$C_4H_3O$ | 0 | 24 | (83) | >20:1 | 95.0:5.0 |
| H | Ph | 0 | 24 | (90) | >20:1 | 97.5:2.5 |
| H | 3-$BrC_6H_4$ | 0 | 24 | (94) | >20:1 | 97.5:2.5 |
| H | 4-$BrC_6H_4$ | 0 | 24 | (92) | >20:1 | 97.0:3.0 |
| H | 3-$ClC_6H_4$ | 0 | 24 | (99) | >20:1 | 97.0:3.0 |
| H | 4-$ClC_6H_4$ | 0 | 24 | (98) | >20:1 | 97.0:3.0 |
| H | 4-$FC_6H_4$ | 0 | 24 | (95) | >20:1 | 97.5:2.5 |
| H | 2-$MeOC_6H_4$ | 0 | 72 | (90) | 8:1 | 98.0:2.0 |
| H | 3-$MeOC_6H_4$ | 0 | 72 | (98) | >20:1 | 93.5:6.5 |
| H | 3,4-$(OCH_2O)C_6H_3$ | 0 | 24 | (95) | >20:1 | 96.5:3.5 |
| H | 3-$O_2NC_6H_4$ | 0 | 24 | (95) | >20:1 | 97.0:3.0 |
| H | 4-$O_2NC_6H_4$ | 0 | 24 | (93) | >20:1 | 96.0:4.0 |
| H | 4-$MeC_6H_4$ | 0 | 24 | (97) | >20:1 | 98.0:2.0 |
| H | 3,4-$Me_2C_6H_3$ | 0 | 36 | (93) | >20:1 | 96.0:4.0 |
| H | 4-$CF_3C_6H_4$ | 0 | 24 | (90) | >20:1 | 97.0:3.0 |
| H | 2-Np | 0 | 24 | (95) | >20:1 | 96.5:3.5 |
| Me | Ph | 0 | 48 | (88) | 12:1 | 95.5:4.5 |

$C_9$





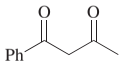
**69b** (10 mol %),
$PhCO_2H$ (10 mol %),
$CH_2Cl_2$, –70°, 24 h

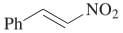


573

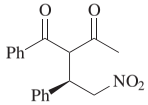
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | | dr | er |
|---|---|---|---|---|---|---|
| H | H | H | Et | (99) | 70:30 | 89.5:10.5 |
| H | H | Me | *i*-Bu | (98) | 86:14 | 97.5:2.5 |
| H | H | $EtO_2C$ | Et | (48) | — | — |
| H | H | MOM | Et | (96) | 78:22 | 97.5:2.5 |
| H | H | Bn | Et | (96) | 67.33 | 96.5:3.5 |
| H | Cl | Me | Et | (99) | 81:19 | 97.5:2.5 |
| Br | H | Me | Et | (98) | 80:20 | 97.0:3.0 |
| Cl | H | Me | Et | (99) | 82:18 | 97.0:3.0 |
| F | H | Me | Et | (99) | 84:16 | 97.5:2.5 |
| MeO | H | Me | Et | (99) | 95:5 | 98.5:1.5 |

$C_{10}$



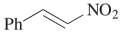


**255** (0.5 mol %),
$CH_2Cl_2$, rt, 9 h

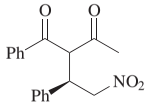


(91) dr 2:1
er (major) 97.5:2.5
er (minor) 97.0:3.0

192



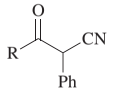
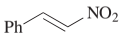
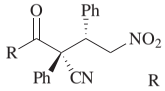
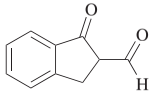
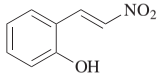
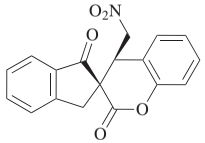
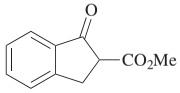
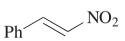
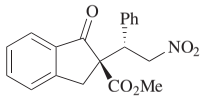
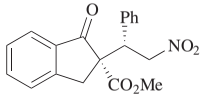
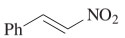
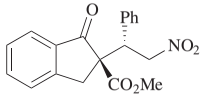
**259** (2 mol %),
$CH_2Cl_2$, rt, 9 h



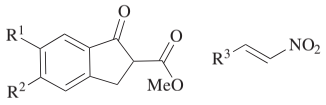
(88) dr 1.1:1
er (major) 95.0:5.0
er (minor) 96.0:4.0

548

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

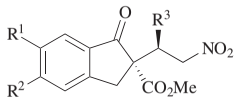
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_{10-15}$ | | | | |
|  |  | **272** (10 mol %), $CH_2Cl_2$, 24 h |  R = Me: –40 (89) dr 80:20 er 92.5:7.5; R = Ph: –70 (98) dr 79:21 er 97.5:2.5 | 565 |
| $C_{10}$ | | | | |
|  |  | 1. *ent*-**164b** (10 mol %), $CH_2Cl_2$, rt, 0.25 h<br>2. PCC, $CH_2Cl_2$ |  (59) er 90.0:10.0 | 563 |
|  |  | *ent*-**164b** (10 mol %), toluene, –50°, 3 h |  (96) dr 57:43 er 96.5:3.5 | 87 |
| |  | **231** (10 mol %), $CH_2Br_2$, rt, 1 h |  (95) *syn*/*anti* = 45:55 er >99.5:0.5 | 557 |
| |  | **249** (5 mol %), toluene, –10°, 42.5 h |  (99) dr 4:1 er 87.0:13.0 | 542 |

$C_{10-11}$





**57** (10 mol %),
toluene, –20°



574

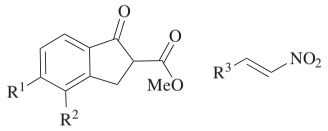
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| H | H | Ph | 24 | (86) | 4.6:1 | 85.0:15.0 |
| H | H | 2-$BrC_6H_4$ | 24 | (77) | 3.3:1 | 92.0:8.0 |
| H | H | 4-$BrC_6H_4$ | 24 | (72) | 4.6:1 | 86.5:13.5 |
| H | H | 2-$ClC_6H_4$ | 24 | (81) | 5.7:1 | 90.0:10.0 |
| H | H | 4-$ClC_6H_4$ | 24 | (81) | 4.9:1 | 85.5:14.5 |
| H | H | 2,4-$Cl_2C_6H_3$ | 24 | (79) | 4.6:1 | 84.5:15.5 |
| H | H | 4-$FC_6H_4$ | 24 | (85) | 4.9:1 | 88.5:11.5 |
| H | H | 4-$MeOC_6H_4$ | 24 | (78) | 3:1 | 85.5:14.5 |
| H | H | 4-$MeC_6H_4$ | 24 | (85) | 3.2:1 | 84.0:16.0 |
| H | H | 4-$NCC_6H_4$ | 24 | (76) | 5.7:1 | 83.5:16.5 |
| H | Br | 2-$BrC_6H_4$ | 24 | (78) | 3:1 | 84.0:16.0 |
| H | Br | 2-$ClC_6H_4$ | 48 | (87) | 2.8:1 | 82.0:18.0 |
| MeO | H | 2-$BrC_6H_4$ | 48 | (87) | 4.8:1 | 86.5:13.5 |
| MeO | H | 2-$ClC_6H_4$ | 48 | (85) | 5.3:1 | 85.0:15.0 |
| Me | H | 2-$BrC_6H_4$ | 48 | (72) | 2.7:1 | 85.5:14.5 |
| Me | H | 2-$ClC_6H_4$ | 48 | (83) | 3.2:1 | 80.0:20.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

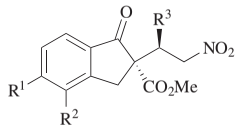
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{10-11}$



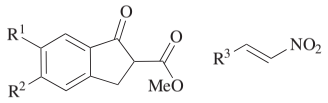


**57** (10 mol %),
toluene, –20°



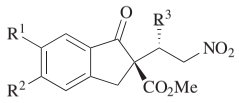
575

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|---|
| H | H | Ph | 24 | (87) | 80:20 | 87.0:13.0 | 66.0:34.0 |
| H | H | 2-$BrC_6H_4$ | 24 | (77) | 77:23 | 92.0:8.0 | 82.0:18.0 |
| H | H | 4-$BrC_6H_4$ | 24 | (72) | 82:18 | 87.0:13.0 | 61.0:39.0 |
| H | H | 2-$ClC_6H_4$ | 24 | (81) | 85:15 | 90.0:10.0 | 64.0:36.0 |
| H | H | 4-$ClC_6H_4$ | 24 | (81) | 83:17 | 86.0:14.0 | 63.0:37.0 |
| H | H | 2,4-$Cl_2C_6H_3$ | 24 | (79) | 82:18 | 85.0:15.0 | 52.0:48.0 |
| H | H | 4-$FC_6H_4$ | 24 | (85) | 83:17 | 89.0:11.0 | 65.0:35.0 |
| H | H | 4-$MeOC_6H_4$ | 24 | (78) | 75:25 | 86.0:14.0 | 57.0:43.0 |
| H | H | 4-$MeC_6H_4$ | 24 | (85) | 76:24 | 84.0:16.0 | 60.0:40.0 |
| H | H | 4-$NCC_6H_4$ | 24 | (76) | 85:15 | 84.0:16.0 | 65.0:35.0 |
| H | MeO | 2-$BrC_6H_4$ | 48 | (87) | 82:18 | 87.0:13.0 | 75.0:25.0 |
| H | MeO | 2-$ClC_6H_4$ | 48 | (85) | 84:16 | 85.0:15.0 | 62.0:38.0 |
| H | Me | 2-$BrC_6H_4$ | 48 | (71) | 73:27 | 86.0:14.0 | 71.0:29.0 |
| H | Me | 2-$ClC_6H_4$ | 48 | (83) | 76:24 | 80.0:20.0 | 78.0:22.0 |
| Br | H | 2-$BrC_6H_4$ | 48 | (78) | 75:25 | 84.0:16.0 | 50.0:50.0 |
| Br | H | 2-$ClC_6H_4$ | 48 | (87) | 74:26 | 82.0:18.0 | 50.0:50.0 |





**265** (10 mol %),
$CH_2Cl_2$, –40°, 42 h



564

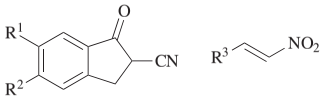
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| H | H | Ph | (98) | 5.1:1 | 96.0:4.0 |
| H | H | 3-$BrC_6H_4$ | (96) | 4.4:1 | 97.5:2.5 |
| H | H | 4-$BrC_6H_4$ | (98) | 3.5:1 | 96.5:3.5 |
| H | H | 2-$ClC_6H_4$ | (98) | 2.4:1 | 96.5:3.5 |
| H | H | 4-$FC_6H_4$ | (98) | 3.5:1 | 97.0:3.0 |
| H | H | 4-$MeOC_6H_4$ | (97) | 4.6:1 | 98.0:2.0 |
| H | H | 4-$MeC_6H_4$ | (98) | 3.3:1 | 95.0:5.0 |
| H | Br | Ph | (98) | 4.1:1 | 96.0:4.0 |
| H | Br | 4-$MeC_6H_4$ | (98) | 3.3:1 | 95.0:5.0 |
| H | MeO | 2-$C_3H_4S$ | (98) | 3:1 | 97.0:3.0 |
| H | MeO | Ph | (98) | 3.3:1 | 97.5:2.5 |
| MeO | H | Ph | (99) | 3.3:1 | 95.0:5.0 |
| Me | H | Ph | (97) | 5.9:1 | 96.5:3.5 |
| Me | H | 4-$FC_6H_4$ | (99) | 4.1:1 | 97.0:3.0 |
| Me | H | 4-$MeC_6H_4$ | (98) | 8.8:1 | 95.5:4.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

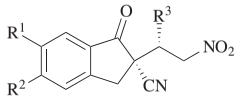
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{10}$

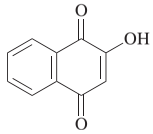


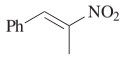

**272** (10 mol %), $CH_2Cl_2$, –40°



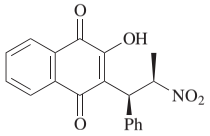

565

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| H | H | *n*-Bu | 94 | (95) | 99:1 | 96.5:3.5 |
| H | H | *i*-Bu | 12 | (97) | 97:3 | 95.5:4.5 |
| H | H | 2-$C_4H_3O$ | 54 | (90) | 86:14 | 96.0:4.0 |
| H | H | 2-$C_4H_3S$ | 10 | (97) | 90:10 | 97.5:2.5 |
| H | H | Ph | 11 | (98) | 97:3 | 98.5:1.5 |
| H | H | 2-$BrC_6H_4$ | 40 | (97) | 68:32 | 97.5:2.5 |
| H | H | 4-$BrC_6H_4$ | 24 | (98) | 94:6 | 98.5:1.5 |
| H | H | 2-$ClC_6H_4$ | 42 | (97) | 72:28 | 97.5:2.5 |
| H | H | 4-$ClC_6H_4$ | 24 | (98) | 93:7 | 98.5:1.5 |
| H | H | 4-$FC_6H_4$ | 24 | (95) | 98:2 | 98.5:1.5 |
| H | H | 4-$MeOC_6H_4$ | 24 | (98) | 96:4 | 98.5:1.5 |
| H | H | 2-$O_2NC_6H_4$ | 40 | (97) | 70:30 | 96.5:3.5 |
| H | H | 3-$O_2NC_6H_4$ | 12 | (90) | 96:4 | 98.5:1.5 |
| H | H | 4-$MeC_6H_4$ | 24 | (98) | 96:4 | 98.5:1.5 |
| H | H | $BnCH_2$ | 10 | (93) | 97:3 | 96.5:3.5 |
| H | H | 1-Np | 10 | (96) | 98:2 | 97.5:2.5 |
| H | MeO | Ph | 24 | (95) | 95:5 | 98.5:1.5 |
| MeO | MeO | Ph | 24 | (98) | 97:3 | 98.5:1.5 |





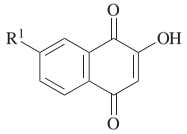
**275** (5 mol %), MeCN, –25°

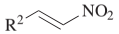


(65) dr >20:1
er 95.5:4.5

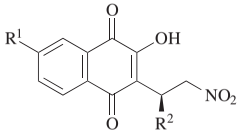
576

$C_{10-11}$





*ent*-**164b** (10 mol %), $CH_2Cl_2$, rt, 12 h



577

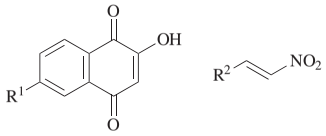
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| H | 2-$C_4H_3O$ | (85) | 94.5:5.5 |
| H | 2-$C_4H_3S$ | (77) | >99.5:0.5 |
| H | *c*-$C_6H_{11}$ | (63) | 97.5:2.5 |
| H | Ph | (82) | >99.5:0.5 |
| H | 4-$BrC_6H_4$ | (81) | >99.5:0.5 |
| H | 4-$ClC_6H_4$ | (75) | >99.5:0.5 |
| H | 4-$FC_6H_4$ | (71) | >99.5:0.5 |
| H | 2-$MeOC_6H_4$ | (75) | 94.5:5.5 |
| H | 4-$MeOC_6H_4$ | (75) | >99.5:0.5 |
| H | 4-$MeC_6H_4$ | (75) | >99.5:0.5 |
| H | $BnCH_2$ | (77) | 96.5:3.5 |
| MeO | Ph | (61) | 97.0:3.0 |
| Me | Ph | (77) | 97.0:3.0 |
| Me | 4-$MeC_6H_4$ | (73) | 97.5:2.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

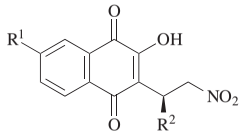
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{10}$





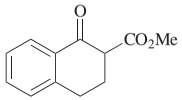
**275** (5 mol %), MeCN, –25°

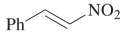


576

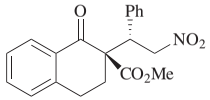
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| H | Et | 4 | (60) | >99.5:0.5 |
| H | *n*-Pr | 3 | (93) | 99.0:1.0 |
| H | *i*-Bu | 5.5 | (98) | >99.5:0.5 |
| H | 2-$C_4H_3O$ | 68 | (84) | >99.5:0.5 |
| H | 2-$C_4H_3S$ | 66 | (79) | >99.5:0.5 |
| H | *n*-$C_6H_{13}$ | 9 | (98) | 99.5:0.5 |
| H | *c*-$C_6H_{11}$ | 16 | (80) | 98.5:1.5 |
| H | Ph | 24 | (90) | 99.5:0.5 |
| H | 2-$BrC_6H_4$ | 40 | (90) | >99.5:0.5 |
| H | 4-$BrC_6H_4$ | 22 | (71) | >99.5:0.5 |
| H | 4-$ClC_6H_4$ | 12 | (85) | 98.5:1.5 |
| H | 4-$FC_6H_4$ | 66 | (71) | 99.0:1.0 |
| H | 2-$MeOC_6H_4$ | 31 | (96) | 99.5:0.5 |
| H | 4-$MeOC_6H_4$ | 20 | (78) | >99.5:0.5 |
| H | 4-$MeC_6H_4$ | 20 | (98) | >99.5:0.5 |
| H | 2-$CF_3C_6H_4$ | 56 | (89) | 99.0:1.0 |
| H | 4-$CF_3C_6H_4$ | 56 | (93) | >99.5:0.5 |
| H | $BnCH_2$ | 8 | (77) | >99.5:0.5 |
| H | PhCH=CH | 17 | (83) | 99.0:1.0 |
| H | 1-Np | 120 | (83) | >99.5:0.5 |
| MeO | Ph | — | (75) | 98.0:2.0 |

$C_{11}$

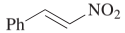




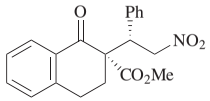
*ent*-**164b** (10 mol %), toluene, rt, 2 h



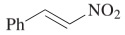
(97) dr 95:5 er 95.0:5.0 — 87



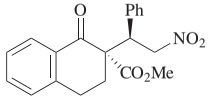
**231** (10 mol %), $CH_2Br_2$, rt, 96 h



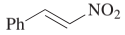
(89) *syn*/*anti* = 92:8 er 97.5:2.5 — 557



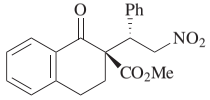
**238a** (10 mol %), toluene, –18°, 72 h



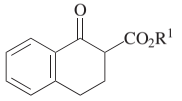
(89) dr 98:2 er 98.0:2.0 — 558

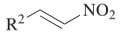


**249** (10 mol %), toluene, rt, 92 h

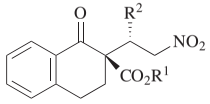


(71) dr >20:1 er 94.5:5.5 — 542





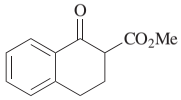
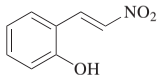
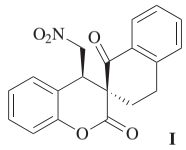
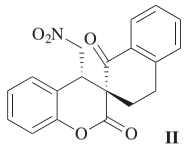
**275** (10 mol %), $CH_2Cl_2$



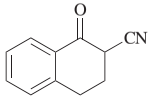
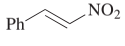
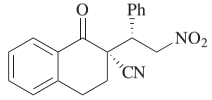
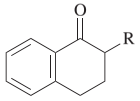
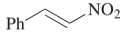
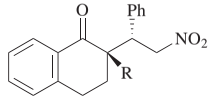
560

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| Me | *i*-Bu | 0 | 20 | (93) | 96:4 | 97.5:2.5 |
| Me | Ph | –25 | 15 | (90) | 99:1 | 99.0:1.0 |
| Et | Ph | –25 | 15 | (90) | 99:1 | 99.0:1.0 |

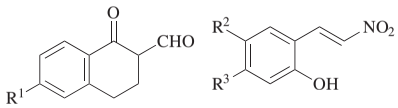
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{11}$ | | | | |
|  |  | 1. Catalyst (10 mol %), 0.3 M in $CH_2Cl_2$, rt, 3–4 h<br>2. PTSA (10 mol %), 0.075 M in DCE, 80°, 3–4 h |  +  **I** **II** | 566 |

| Catalyst | | dr | er **I/II** |
|---|---|---|---|
| **69b** | (60) | >99.5:0.5 | >99.9:0.1 |
| **268** | (60) | >99.5:0.5 | 1.5:98.5 |

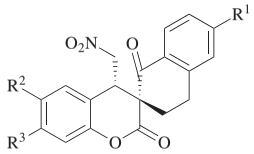
| | | | | |
|---|---|---|---|---|
|  |  | **272** (10 mol %), $CH_2Cl_2$, –40°, 42 h |  (97) dr 98:2 er 99.5:0.5 | 565 |
|  |  | **270** (10 mol %), $CH_2Cl_2$, –40°, 40 h |  | 564 |

| R | | dr | er |
|---|---|---|---|
| NC– | (83) | >50:1 | 81.5:18.5 |
| MeSOC | (72) | >50:1 | 78.5:21.5 |





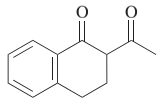
1. *ent*-**164b** (10 mol %), $CH_2Cl_2$, rt
2. PCC, $CH_2Cl_2$

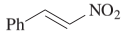


563

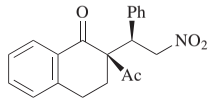
| $R^1$ | $R^2$ | $R^3$ | Time (min) | | er |
|---|---|---|---|---|---|
| H | H | H | 20 | (67) | 98.5:1.5 |
| H | H | MeO | 30 | (64) | 99.0:1.0 |
| H | Br | H | 20 | (51) | >99.5:0.5 |
| H | Cl | H | 20 | (56) | 99.0:1.0 |
| H | MeO | H | 30 | (59) | 99.0:1.0 |
| H | Me | H | 25 | (72) | 99.0:1.0 |
| MeO | H | H | 25 | (69) | 98.5:1.5 |
| MeO | Br | H | 20 | (61) | 99.0:1.0 |

$C_{12}$



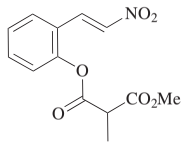


**252b** (10 mol %), $Et_2O$, 0°, 45 h

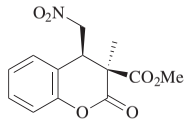


(53) dr 83:17
er (major) 97.0:3.0
er (minor) 93.5:6.5

544



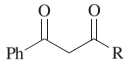
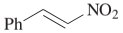
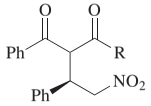
**238a** (10 mol %), toluene, –18°, 240 h



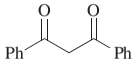
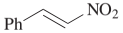
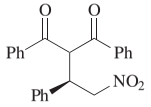
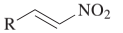
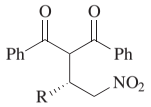
(65) dr 3:2
er 89:11

558

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{13–15}$  |  | **255** (0.5 mol %), $CH_2Cl_2$, rt |  | 192 |

| R | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 8 | (97) | 1.4:1 | 96.0:4.0 | 90.5:9.5 |
| Ph | 24 | (93) | — | 94.0:6.0 | — |

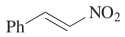
| | | | | | |
|---|---|---|---|---|---|
| $C_{15}$  |  | **132** (5 mol %), $Et_2O$, rt, 12 h |  | (95) er 92.5:7.5 | 552 |
| |  | **225c** (15 mol %), $Et_2O$, rt |  | | 578 |

Catalyst Recycling (R = Ph)

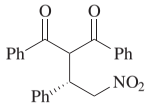
| Run | Time (h) | | er |
|---|---|---|---|
| 1 | 8 | (74) | 99.0:1.0 |
| 2 | 9 | (83) | 98.5:1.5 |
| 3 | 10 | (>99) | 98.5:1.5 |
| 4 | 12 | (95) | 98.0:2.0 |
| 5 | 15 | (>99) | 98.0:2.0 |
| 6 | 19 | (94) | 97.5:2.5 |
| 7 | 30 | (>99) | 97.0:3.0 |

Catalyst Recycling (R = 4-$ClC_6H_4$)

| Run | Time (h) | | er |
|---|---|---|---|
| 1 | 8 | (76) | >99.5:0.5 |
| 2 | 10 | (82) | 99.5:0.5 |
| 3 | 11 | (>99) | 99.0:1.0 |
| 4 | 13 | (96) | 98.5:1.5 |
| 5 | 16 | (>99) | 98.0:2.0 |
| 6 | 19 | (97) | 98.0:2.0 |
| 7 | 23 | (97) | 97.5:2.5 |

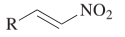


**252b** (10 mol %),
$Et_2O$, 0°, 42 h

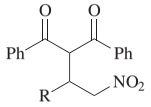


(67) er 93.5:6.5

544



**254** (1 mol %),
$CH_2Cl_2$, rt, 12–24 h

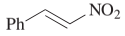


| R | | er |
|---|---|---|
| 2-$C_4H_3S$ | (92) | 95.5:4.5 |
| Ph | (91) | 97.5:2.5 |

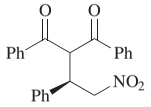
547

Catalyst Recycling (R = Ph)

| Run | Recovery Rate | | er |
|---|---|---|---|
| 1 | (92) | (94) | 95.5:4.5 |
| 2 | (91) | (93) | 95.0:5.0 |
| 3 | (89) | (96) | 95.0:5.0 |
| 4 | (87) | (91) | 95.5:4.5 |
| 5 | (85) | (93) | 96.0:4.0 |
| 6 | (83) | (90) | 95.0:5.0 |



**259** (2 mol %),
$CH_2Cl_2$, rt, 20 h



(56) er 93.0:7.0

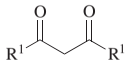
548

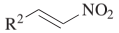
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

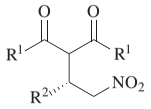
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{15–17}$





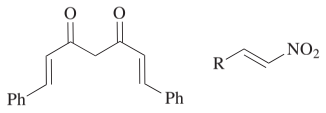
**225c** (*x* mol %), $Et_2O$, rt



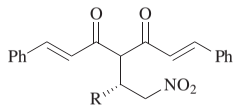
578

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | 2-$C_4H_3O$ | 15 | 16 | (91) | 99.0:1.0 |
| Ph | 3-$C_4H_3O$ | 15 | 12 | (91) | 98.5:1.5 |
| Ph | 2-$C_4H_3S$ | 15 | 12 | (92) | 98.5:1.5 |
| Ph | Ph | 15 | 8 | (96) | 99.0:1.0 |
| Ph | 4-$BrC_6H_4$ | 15 | 8 | (96) | >99.5:0.5 |
| Ph | 4-$ClC_6H_4$ | 15 | 8 | (97) | >99.5:0.5 |
| Ph | 2-$MeOC_6H_4$ | 15 | 16 | (94) | 99.5:0.5 |
| Ph | 3-$MeOC_6H_4$ | 15 | 16 | (91) | 96.5:3.5 |
| Ph | 4-$MeOC_6H_4$ | 15 | 12 | (92) | 98.0:2.0 |
| Ph | 2-$O_2NC_6H_4$ | 15 | 12 | (92) | 97.0:3.0 |
| Ph | 4-$O_2NC_6H_4$ | 15 | 24 | (86) | 97.0:3.0 |
| Ph | 4-$MeC_6H_4$ | 15 | 12 | (93) | 99.0:1.0 |
| Ph | PhCH=CH | 30 | 30 | (81) | 95.0:5.0 |
| Ph | 2-HC≡$CC_6H_4$ | 15 | 16 | (87) | 96.5:3.5 |
| Ph | 1-Np | 15 | 16 | (88) | 98.0:2.0 |
| 4-$MeC_6H_4$ | Ph | 15 | 24 | (85) | 98.5:1.5 |

$C_{19}$



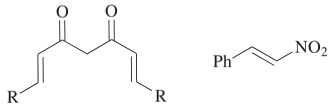
**276** (5 mol %), $CH_2Cl_2$, rt



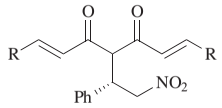
579

| R | Time (h) | | er |
|---|---|---|---|
| *n*-Pr | 48 | (82) | 96.0:4.0 |
| *i*-Pr | 96 | (72) (*E*)/(*Z*) 25:1 | 92.0:8.0 |
| 2-$C_4H_3O$ | 72 | (62) | 96.5:3.5 |
| Ph | 12 | (96) | 98.0:2.0 |
| 3-$BrC_6H_4$ | 18 | (81) | 95.0:5.0 |
| 2-$ClC_6H_4$ | 72 | (86) | 98.5:1.5 |
| 3-$ClC_6H_4$ | 72 | (81) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 72 | (74) | 95.0:5.0 |
| 2-$FC_6H_4$ | 18 | (85) | 97.5:2.5 |
| 3-$FC_6H_4$ | 72 | (76) | 96.0:4.0 |
| 4-$FC_6H_4$ | 72 | (93) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 24 | (82) | 94.5:5.5 |
| 2,3-$(MeO)_2C_6H_3$ | 24 | (92) | 98.0:2.0 |
| 2,4-$(MeO)_2C_6H_3$ | 24 | (73) | 97.5:2.5 |
| 4-$MeC_6H_4$ | 18 | (85) | 95.5:4.5 |
| 2-Np | 24 | (84) | 95.0:5.0 |

$C_{19–21}$



**276** (5 mol %), $CH_2Cl_2$, rt



579

| R | Time (h) | | er |
|---|---|---|---|
| 4-$ClC_6H_4$ | 72 | (72) | 96.0:4.0 |
| 2-$FC_6H_4$ | 72 | (76) | 98.0:2.0 |
| 3-MeO-4-$AcOC_6H_3$ | 72 | (82) | 96.0:4.0 |
| 4-$MeC_6H_4$ | 144 | (78) | 95.0:5.0 |

[a] The yield was determined by $^1$H-NMR.

[b] The imino analysis, ester was generated *in situ*.

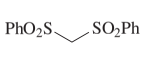
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)

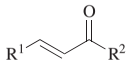
B. ENONES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

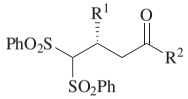
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_1$



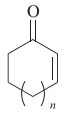


**225c** (20 mol %), $PhCO_2H$ (40 mol %), dioxane, 35°

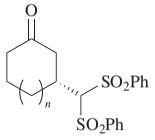


580

| $R^1$ | $R^2$ | Time (d) | | er |
|---|---|---|---|---|
| Me | Me | 2 | (88) | 97.5:2.5 |
| Me | Et | 5 | (93) | 98.5:1.5 |
| Et | Et | 4 | (87) | 98.5:1.5 |
| *n*-Pr | Me | 2 | (96) | 97.5:2.5 |
| *i*-Pr | Me | 4 | (54) | 97.5:2.5 |
| Me | *n*-Bu | 5 | (82) | 98.0:2.0 |
| Et | *n*-Pr | 4 | (90) | 98.5:1.5 |
| *i*-Bu | Me | 2 | (85) | 98.0:2.0 |
| *i*-Bu | Et | 4 | (85) | 99.0:1.0 |
| *n*-$C_5H_{11}$ | Me | 2 | (97) | 98.0:2.0 |
| *i*-Bu | *n*-Pr | 4 | (92) | 99.0:1.0 |
| *n*-$C_6H_{13}$ | Me | 2 | (94) | 98.0:2.0 |
| Ph | Me | 5 | (17) | — |
| PhCH=CH | Me | 4 | (88) | 95.0:5.0 |
| PhCH=CH | Et | 7 | (73) | 98.5:1.5 |
| PhCH=CH | *n*-Pr | 7 | (77) | 98.5:1.5 |

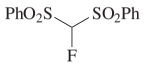


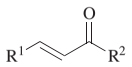
**225c** (20 mol %), $PhCO_2H$ (40 mol %), dioxane, 35°



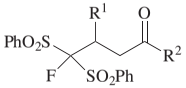
| *n* | Time (d) | | er |
|---|---|---|---|
| 1 | 2 | (81) | 97.5:2.5 |
| 2 | 2 | (92) | 96.0:4.0 |
| 10 | 4 | (74) | 99.0:1.0 |

580



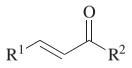


**225c** (10 mol %),
MTBE, rt, 5 d

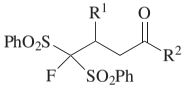


581

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | Et | (85) | 90.0:10.0 |
| Ph | Me | (87) | 95.5:4.5 |
| 4-$FC_6H_4$ | Me | (90) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Me | (92) | 96.5:3.5 |
| 4-$MeC_6H_4$ | Me | (90) | 95.0:5.0 |
| 1-Np | Me | (85) | 93.0:7.0 |



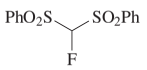
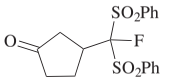
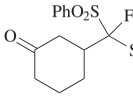
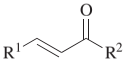
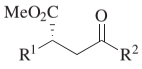
Catalyst (5 mol %),
$Cs_2CO_3$ (3 eq),
$CH_2Cl_2$, –40°, 1–2 d



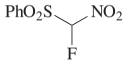
207

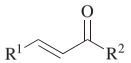
| $R^1$ | $R^2$ | Catalyst | | er | Abs. conf. |
|---|---|---|---|---|---|
| Me | Ph | **277** | (91) | 92.5:7.5 | (*R*) |
| Et | Ph | **277** | (69) | 95.0:5.0 | (*R*) |
| Et | Ph | **278** | (56) | 92.0:8.0 | (*S*) |
| Ph | Ph | **277** | (80) | 98.5:1.5 | (*S*) |
| Ph | Ph | **278** | (58) | 98.0:2.0 | (*R*) |
| Ph | 4-$BrC_6H_4$ | **277** | (82) | 97.5:2.5 | (*S*) |
| Ph | 4-$BrC_6H_4$ | **278** | (68) | 96.5:3.5 | (*R*) |
| Ph | 4-$ClC_6H_4$ | **277** | (52) | 95.5:4.5 | (*S*) |
| Ph | 4-$ClC_6H_4$ | **278** | (64) | 98.0:2.0 | (*R*) |
| 4-$BrC_6H_4$ | Ph | **277** | (82) | 97.5:2.5 | (*S*) |
| 4-$BrC_6H_4$ | Ph | **278** | (90) | 97.0:3.0 | (*R*) |
| 4-$BrC_6H_4$ | 4-$BocOC_6H_4$ | **277** | (32) | 97.5:2.5 | (*S*) |
| 3-$ClC_6H_4$ | Ph | **277** | (85) | 99.5:0.5 | (*S*) |
| 3-$ClC_6H_4$ | Ph | **278** | (77) | 91.5:8.5 | (*R*) |
| 4-$ClC_6H_4$ | Ph | **277** | (76) | 98.5:1.5 | (*S*) |
| 4-$ClC_6H_4$ | Ph | **278** | (64) | 98.0:2.0 | (*R*) |
| 4-$MeC_6H_4$ | Ph | **277** | (77) | 97.0:3.0 | (*S*) |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

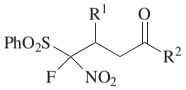
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_1$ | | | | |
|  |  | **225c** (10 mol %), MTBE, rt, 5 d |  (87) er 93.0:7.0 | 581 |
| |  | **225c** (10 mol %), MTBE, rt, 5 d |  (93) er 94.5:5.5 | 581 |
|  |  | 1. **80d** (10 mol %), $ClCH_2CO_2H$ (10 mol %), 0.5 M in THF, rt, 48 h<br>2. TBA-Oxone (5 eq), TMG (4.8 eq), $MeOH/CH_2Cl_2$, 0° to rt, 12 h |  | 582 |

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Me | (49) | 73.0:27.0 |
| Ph | Ph | (51) | 96.0:4.0 |
| Ph | 4-$ClC_6H_4$ | (66) | 94.0:6.0 |
| Ph | 4-$MeOC_6H_4$ | (55) | 97.0:3.0 |
| 4-$ClC_6H_4$ | Ph | (55) | 96.0:4.0 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | (48) | 93.0:7.0 |
| 4-$FC_6H_4$ | 4-$FC_6H_4$ | (60) | 94.0:6.0 |
| 4-$MeOC_6H_4$ | Ph | (53) | 94.0:6.0 |
| 2-$O_2NC_6H_4$ | Ph | (65) | 93.0:7.0 |
| 4-$O_2NC_6H_4$ | Ph | (57) | 94.0:6.0 |





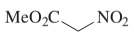
**69b** (10 mol %), toluene, –20°, 48 h



583

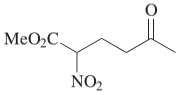
| $R^1$ | $R^2$ | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| Ph | Ph | (93) | 6:1 | 96.5:3.5 | 97.0:3.0 |
| Ph | 4-$ClC_6H_4$ | (82) | 7:1 | 96.0:4.0 | 95.0:5.0 |
| Ph | 4-$MeOC_6H_4$ | (89) | 7:1 | 97.5:2.5 | 96.5:3.5 |
| 4-$ClC_6H_4$ | Ph | (92) | 6:1 | 96.5:3.5 | 97.0:3.0 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | (91) | 9:1 | >99.5:0.5 | >99.5:0.5 |
| 4-$FC_6H_4$ | 4-$FC_6H_4$ | (95) | 6:1 | 97.0:3.0 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | Ph | (94) | 4.5:1 | 96.0:4.0 | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | Ph | (75) | 8:1 | 98.5:1.5 | — |

$C_2$



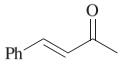


**1** (12 mol %), $Yb(OTf)_3$ (12 mol %), NaOH (20 mol %), $H_2O$, 60°, 4 h

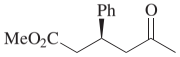


(87) er 79.5:20.5

584



1. **80b** (20 mol %), $PhCO_2H$ (40 mol %), $H_2O$, rt
2. *n*-$Bu_3SnH$, AIBN, benzene, reflux, 5 h



(81) er 94.5:5.5

585

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

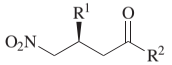
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_2$



1. **80b** (20 mol %), additive (40 mol %), $H_2O$, rt
2. $Et_3N$, $H_2O$, 50°, 5 h

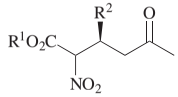


585

| $R^1$ | $R^2$ | Additive | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Et | $PhCO_2H$ | 2.3 | (94) | 91.5:8.5 |
| 2-$C_4H_3S$ | Me | $PhCO_2H$ | 2.5 | (96) | 86.5:13.5 |
| Ph | Me | $PhCO_2H$ | 2 | (98) | 96.5:3.5 |
| Ph | Et | $PhCO_2H$ | 2.2 | (97) | 94.5:5.5 |
| 4-$FC_6H_4$ | Me | 3-$NCC_6H_4CO_2H$ | 2.5 | (96) | 91.5:8.5 |
| 4-$MeOC_6H_4$ | Me | 3-$NCC_6H_4CO_2H$ | 2 | (95) | 90.5:9.5 |
| 4-$Et_2NC_6H_4$ | Me | $PhCO_2H$ | 2 | (97) | 82.5:17.5 |
| 1-Np | Me | 3-$NCC_6H_4CO_2H$ | 2 | (95) | 88.5:11.5 |

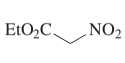


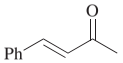
**80b** (10 mol %), (+)-CSA (10 mol %), xylene, rt, 24 h



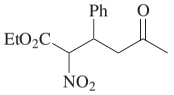
586

| $R^1$ | $R^2$ | | *anti*/*syn* | er (*anti*) | er (*syn*) |
|---|---|---|---|---|---|
| Et | Ph | (94) | 1:1 | 99.5:0.5 | 99.5:0.5 |
| Et | 4-$BrC_6H_4$ | (86) | 1.3:1 | 91.0:9.0 | 97.5:2.5 |
| Et | 2-$ClC_6H_4$ | (86) | 1.6:1 | 95.0:5.0 | 96.5:3.5 |
| Et | 4-$ClC_6H_4$ | (92) | 1.6:1 | 91.0:9.0 | 97.5:2.5 |
| Et | 4-$MeOC_6H_4$ | (89) | 1:1 | 96.0:4.0 | 98.5:1.5 |
| Et | 2-$O_2NC_6H_4$ | (93) | 1.5:1 | 98.0:2.0 | 98.5:1.5 |
| Et | 4-$O_2NC_6H_4$ | (77) | 1.4:1 | 99.0:1.0 | 97.0:3.0 |
| Et | 2-$CF_3C_6H_4$ | (88) | 1.2:1 | 98.0:2.0 | 98.5:1.5 |
| *t*-Bu | Ph | (50) | 2:1 | 96.0:4.0 | 97.0:3.0 |
| Bn | Ph | (89) | 1:1 | 50.0:50.0 | 52.0:48.0 |





Catalyst (20 mol %), neat, rt

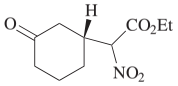


173

| Catalyst | Time (h) | | dr | er |
|---|---|---|---|---|
| **279** | 60 | (85) | 1:0.6 | 93.0:7.0 |
| **282** | 110 | (84) | 1:1 | 89.5:10.5 |



**80b** (10 mol %),
(+)-CSA (10 mol %),
xylene, rt, 24 h

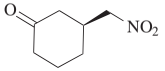


(91) dr 1:1
er 99.5:0.5
er 99.5:0.5

586



1. **80b** (20 mol %),
$PhCO_2H$ (40 mol %),
$H_2O$, rt, 2h
2. $Et_3N$, $H_2O$, 50°, 5 h

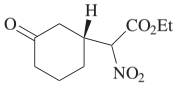


(93) er 92.5:7.5

585



*ent*-**221a** (5 mol %),
$PhCO_2H$ (5 mol %),
toluene, 50°, 20 h

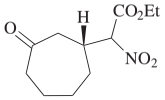


(96) dr 1:1
er 90.5:9.5

587



**80b** (10 mol %),
(+)-CSA (10 mol %),
xylene, rt, 24 h



(83) dr 1:1
er 98.0:2.0
er 99.5:0.5

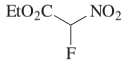
586

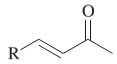
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

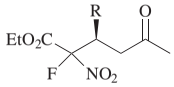
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_2$





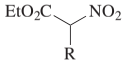
**80b** (10 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), toluene, rt

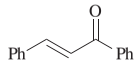


588

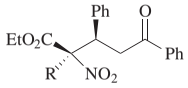
| R | Time (h) | | (2*S*,3*R*)/(2*R*,3*R*) | er (2*S*,3*R*) | er (2*R*,3*R*) |
|---|---|---|---|---|---|
| *n*-Bu | 36 | (80) | 1.2:1 | 96.5:3.5 | 99.0:1.0 |
| 2-$C_4H_3O$ | 36 | (75) | 1.5:1 | 99.0:1.0 | 99.5:0.5 |
| Ph | 24 | (90) | 1.8:1 | 99.5:0.5 | 99.5:0.5 |
| 4-$BrC_6H_4$ | 36 | (93) | 1.8:1 | 99.5:0.5 | 99.5:0.5 |
| 2-$ClC_6H_4$ | 36 | (85) | 2.4:1 | 99.5:0.5 | 99.5:0.5 |
| 3-$ClC_6H_4$ | 36 | (90) | 2.2:1 | 99.5:0.5 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 36 | (95) | 1.8:1 | 99.0:1.0 | 99.5:0.5 |
| 4-$FC_6H_4$ | 36 | (95) | 1.8:1 | 99.5:0.5 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 36 | (85) | 1.8:1 | 99.0:1.0 | 99.0:1.0 |
| 4-$MeC_6H_4$ | 36 | (86) | 1.8:1 | 99.0:1.0 | 99.5:0.5 |
| 4-$O_2NC_6H_4$ | 36 | (95) | 1.8:1 | 98.5:1.5 | 99.5:0.5 |
| 1-Np | 36 | (90) | 1.8:1 | 99.5:0.5 | 98.5:1.5 |

$C_{2-3}$





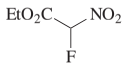
**238a** (10 mol %), neat, temps



589

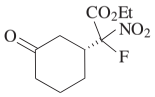
| R | Temp | Time (h) | | dr | er | er |
|---|---|---|---|---|---|---|
| H | rt | 24 | (90) | 47:53 | 85.0:15.0 | 85.0:15.0 |
| H | 50° | 6 | (100) | 59:41 | 77.0:23.0 | 81.0:19.0 |
| Me | rt | 36 | (85) | 71:29 | 77.0:23.0 | 90.0:10.0 |
| Me | 50° | 26 | (75) | 74:26 | 74.0:26.0 | 88.0:12.0 |

$C_2$



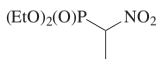


**80b** (10 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
toluene, rt, 36 h



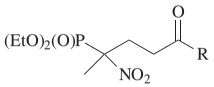
(84) dr 1.2:1
er (major) 99.5:0.5
er (minor) 99.5:0.5

588





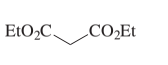
**280** (10 mol %),
mesitylene/xylene (85:15),
–65°, 32–40 h

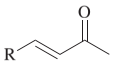


590

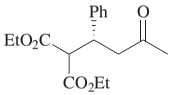
| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (78) | 71.0:29.0 |
| 2-$C_4H_3S$ | (82) | 71.5:28.5 |
| *c*-$C_6H_{11}$ | (70) | 72.0:28.0 |
| Ph | (81) | 72.5:27.5 |
| 3-$BrC_6H_4$ | (83) | 85.0:15.0 |
| 4-$MeOC_6H_4$ | (85) | 86.0:14.0 |
| 3,4-$(MeO)_2C_6H_3$ | (86) | 93.5:6.5 |
| 3,4,5-$(MeO)_3C_6H_2$ | (84) | 89.0:11.0 |
| 4-$O_2NC_6H_4$ | (75) | 67.5:32.5 |
| 4-$MeC_6H_4$ | (86) | 87.0:13.0 |
| 4-$CF_3C_6H_4$ | (80) | 84.5:15.5 |

$C_3$





**1** (15 mol %),
piperidine, MW,
neat, 55°



591

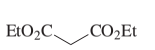
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 2 | (95) | 70.0:30.0 |
| 2-$C_4H_3S$ | 2 | (82) | 91.0:9.0 |
| Ph | 1.5 | (86) | 99.5:0.5 |

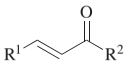
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

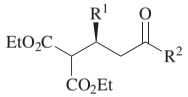
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





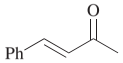
**4** (15 mol %), piperidine (*x* eq), $CHCl_3$, rt



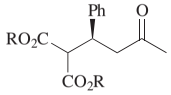
174

| $R^1$ | $R^2$ | *x* | Time (d) | | er |
|---|---|---|---|---|---|
| Me | Me | 1 | 3 | (82) | 82.0:18.0 |
| *i*-Pr | Me | 1 | 3 | (82) | 88.5:11.5 |
| 2-$C_4H_3O$ | Me | 1 | 3 | (85) | 92.5:7.5 |
| 2-$C_4H_3S$ | Me | 1 | 3 | (81) | 94.0:6.0 |
| *n*-$C_5H_{11}$ | Me | 1 | 3 | (86) | 93.5:6.5 |
| Ph | Me | 1 | 3 | (89) | 93.5:6.5 |
| 2-$BrC_6H_4$ | Me | 1 | 3 | (81) | 80.0:20.0 |
| 3-$BrC_6H_4$ | Me | 1 | 3 | (87) | 93.0:7.0 |
| 4-$BrC_6H_4$ | Me | 1 | 3 | (88) | 92.5:7.5 |
| 4-$ClC_6H_4$ | Me | 1 | 3 | (94) | 91.5:8.5 |
| 4-$HOC_6H_4$ | Me | 1 | 5 | (68) | 75.5:24.5 |
| 4-$MeOC_6H_4$ | Me | 1 | 3 | (88) | 92.0:8.0 |
| 3,4-$(MeO)_2C_6H_3$ | Me | 1 | 3 | (87) | 92.0:8.0 |
| 4-$BnOC_6H_4$ | Me | 1 | 3 | (82) | 92.5:7.5 |
| 4-$MeC_6H_4$ | Me | 1 | 3 | (93) | 94.0:6.0 |
| 4-$CF_3C_6H_4$ | Me | 1 | 3 | (82) | 89.5:10.5 |
| *N*-Me-2-indolyl | Me | 1 | 3 | (91) | 92.0:8.0 |
| 3-$C_8H_6N$ | Me | 1 | 3 | (83) | 89.5:10.5 |
| 2-Np | Me | 1 | 3 | (89) | 94.0:6.0 |
| Ph | Ph | 2 | 3 | (86) | 72.0:28.0 |
| 4-$PhC_6H_4$ | Me | 1 | 3 | (88) | 92.5:7.5 |



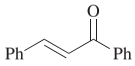


**4** (15 mol %), piperidine (1 eq), $CHCl_3$, rt, 3 d

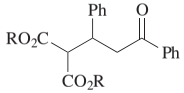


| R | | er |
|---|---|---|
| Me | (89) | 93.0:7.0 |
| Bn | (85) | 91.5:8.5 |

174

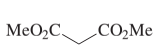


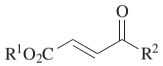
**70** (25 mol %), NAP/MgO (0.125 g), THF, –20°



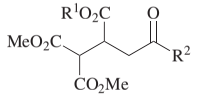
592

| R | Time (h) | | er |
|---|---|---|---|
| Me | 12 | (93) | 91.0:9.0 |
| Et | 15 | (95) | 88.0:12.0 |
| Bn | 18 | (92) | 92.5:7.5 |



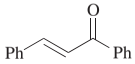


Catalyst (*x* mol %), toluene, rt

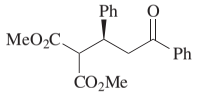


593

| $R^1$ | $R^2$ | Catalyst | *x* | Time (h) | | er |
|---|---|---|---|---|---|---|
| Me | Me | **160a** | 10 | 90 | (41) | 66.5:33.5 |
| Me | Me | **160b** | 10 | 93 | (46) | 67.5:32.5 |
| Me | Me | **160c** | 20 | 120 | (40) | 70.5:29.5 |
| Et | Ph | **160a** | 20 | 120 | (86) | 61.5:38.5 |



***202a*** (10 mol %), $La(Oi\text{-}Pr)_3$ (3.33 mol %), *t*-BuONa (10 mol %) toluene, –50°, 24 h



(93) er 88.5:11.5

50

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

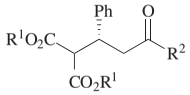
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





**202a** (15 mol %), *t*-BuOK (30 mol %), $CaCl_2$ (18 mol %), toluene, –15°, 24 h



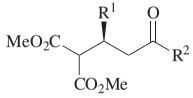
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | Ph | (90) | 71.0:29.0 |
| *i*-Pr | Me | (85) | 69.5:30.5 |

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**221a** (*x* mol %), $PhCO_2H$ (2.5 mol %), toluene, 50°



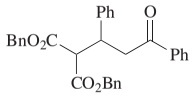
| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| $PMBO(CH_2)_2$ | Me | 5 | 96 | (62) | 98.0:2.0 |
| 2-$C_4H_3O$ | Me | 5 | 20 | (74) | 97.5:2.5 |
| 2-$C_4H_3S$ | Me | 5 | 20 | (69) | 98.5:1.5 |
| Ph | Me | 2 | 20 | (80–85) | 97.0:3.0 |
| Ph | Et | 5 | 72 | (96) | 98.5:1.5 |
| Ph | *i*-Pr | 5 | 120 | (65) | 96.0:4.0 |
| Ph | *i*-Bu | 5 | 96 | (74) | 95.5:4.5 |
| $BnCH_2$ | Me | 5 | 20 | (80) | 98.0:2.0 |
| 1-Np | Me | 5 | 20 | (65) | 96.0:4.0 |

584





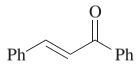
**227** (10 mol %), $Cs_2CO_3$, THF, 48 h



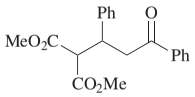
| Temp | | er |
|---|---|---|
| –20° | (19) | 86.0:14.0 |
| rt | (61) | 60.0:40.0 |

513



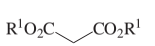


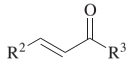
**281** (10 mol %),
$K_2CO_3$ (6 eq),
solvent, rt, 28 h



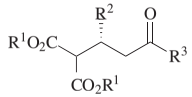
595

| Solvent | Time (h) | | er |
|---|---|---|---|
| DMSO | 6 | (96) | 80.5:19.5 |
| [bmim][$PF_6$] | 3 | (99) | 75.0:25.0 |
| [bmim][$BF_4$] | 4 | (97) | 72.0:28.0 |
| [bpy][$BF_4$] | 4 | (97) | 71.0:29.0 |





**283** (20 mol %),
TFA (20 mol %),
$H_2O$, temps



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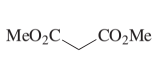
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| Et | Ph | Me | 40 | (68) | 94.5:5.5 |
| Et | Ph | Ph | 40 | (88) | 98.0:2.0 |
| Bn | *n*-$C_5H_{11}$ | Me | 60 | (51) | 96.0:4.0 |
| Bn | Ph | Me | 40 | (78) | 96.0:4.0 |
| Bn | Ph | Ph | 40 | (86) | 88.0:12.0 |
| Bn | 2-$ClC_6H_4$ | Me | 60 | (71) | 96.0:4.0 |
| Bn | 2-$FC_6H_4$ | Me | 60 | (92) | 96.5:3.5 |
| Bn | 3-$MeOC_6H_4$ | Me | 60 | (87) | 96.0:4.0 |

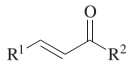
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

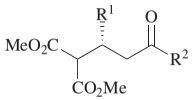
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



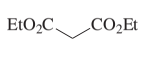


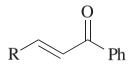
**283** (*x* mol %), TFA (20 mol %), $H_2O$, 50°



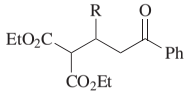
596

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | Me | 20 | 40 | (49) | 92.5:7.5 |
| *i*-Pr | Ph | 20 | 60 | (39) | 98.0:2.0 |
| 2-$C_4H_3O$ | Ph | 20 | 60 | (64) | 98.0:2.0 |
| Ph | Ph | 20 | 40 | (90) | 98.0:2.0 |
| 2-$BrC_6H_4$ | Ph | 20 | 40 | (86) | 98.0:2.0 |
| 4-$BrC_6H_4$ | Ph | 20 | 54 | (56) | 98.5:1.5 |
| 2-$ClC_6H_4$ | Ph | 10 | 54 | (85) | 99.0:1.0 |
| 2-$ClC_6H_4$ | Ph | 20 | 40 | (92) | 98.5:1.5 |
| 4-$ClC_6H_4$ | Ph | 20 | 54 | (80) | 97.5:2.5 |
| 2-$FC_6H_4$ | Ph | 10 | 54 | (78) | 99.0:1.0 |
| 2-$FC_6H_4$ | Ph | 20 | 42 | (98) | 98.5:1.5 |
| 4-$FC_6H_4$ | Ph | 20 | 42 | (86) | 98.0:2.0 |
| 2-$MeOC_6H_4$ | Ph | 20 | 42 | (88) | 98.0:2.0 |
| 3-$MeOC_6H_4$ | Ph | 10 | 64 | (88) | 98.5:1.5 |
| 3-$MeOC_6H_4$ | Ph | 20 | 64 | (95) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | Ph | 20 | 64 | (91) | 98.5:1.5 |
| 2-$MeC_6H_4$ | Ph | 20 | 40 | (78) | 98.5:1.5 |
| 3-$MeC_6H_4$ | Ph | 10 | 54 | (96) | 98.5:1.5 |
| 3-$MeC_6H_4$ | Ph | 20 | 40 | (91) | 99.0:1.0 |
| 4-$MeC_6H_4$ | Ph | 20 | 64 | (72) | 98.0:2.0 |
| 1-Np | Ph | 20 | 42 | (85) | 98.5:1.5 |



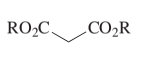


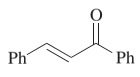
**292** (66 mol %),
LAH (33 mol %),
THF, rt, 4 h



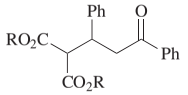
| R | | er |
|---|---|---|
| $O_2N$ | (93) | — |
| Me | (95) | 81.0:19.0 |

597



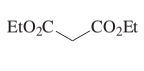


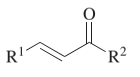
1. *ent*-**292** (40 mol %),
TBATB (40 mol %),
THF, 0°, 7 h
2. $H_2O_2$, NaOH (10%)



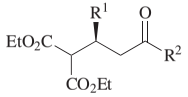
| R | | er |
|---|---|---|
| Et | (62) | 58.0:42.0 |
| *t*-Bu | (64) | 57.0:43.0 |
| Bn | (61) | 58.0:42.0 |

598



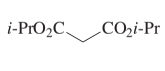


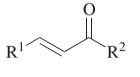
**293a**/**293b** (1:3, 10 mol %),
DMSO/$ClCH_2CH_2Cl$ (1:2), rt



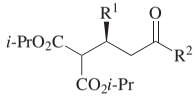
599

| $R^1$ | $R^2$ | Time (d) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Me | 3.5 | (88) | 95.0:5.0 |
| 2-$C_4H_3S$ | Me | 3.5 | (86) | 92.5:7.5 |
| *n*-$C_6H_{13}$ | Me | 6 | (69) | 92.5:7.5 |
| Ph | Me | 3 | (92) | 93.0:7.0 |
| Ph | Ph | 7 | (36) | 55.0:45.0 |





**296a** (*x* mol %),
$CHCl_3$, rt



600

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Me | 5 | 21 | (71) | 88.0:12.0 |
| Me | *n*-Pr | 20 | 46 | (73) | 87.0:13.0 |
| *n*-$C_5H_{11}$ | Me | 5 | 168 | (62) | 88.5:11.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

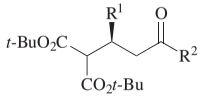
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





**296a** (20 mol %), CsF (20 mol %), $CHCl_3$, rt



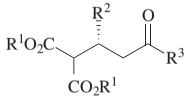
600

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Me | 48 | (65) | 94.0:6.0 |
| Me | Et | 96 | (84) | 88.0:12.0 |
| $n$-$C_5H_{11}$ | Me | 96 | (92) | 93.0:7.0 |
| Ph | Me | 96 | (52) | 88.0:12.0 |
| $BnCH_2$ | Me | 96 | (73) | 80.0:20.0 |





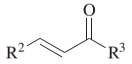
**297** (10 mol %), THF, 72 h



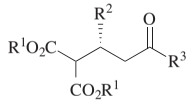
601

| $R^1$ | $R^2$ | $R^3$ | Temp | | er |
|---|---|---|---|---|---|
| Me | Ph | Me | rt | (92) | 97.0:3.0 |
| Me | 2-$O_2NC_6H_4$ | Me | rt | (93) | 96.5:3.5 |
| Et | $n$-Pr | Me | rt | (91) | 98.0:2.0 |
| Et | $n$-Bu | Me | rt | (90) | 98.5:1.5 |
| Et | 2-$C_4H_3S$ | Me | rt | (83) | 95.0:5.0 |
| Et | Ph | Me | rt | (92) | 98.0:2.0 |
| Et | Ph | Et | 40° | (80) | 91.5:8.5 |
| Et | 2-$BrC_6H_4$ | Me | rt | (94) | 97.0:3.0 |
| Et | 4-$BrC_6H_4$ | Me | rt | (94) | 97.0:3.0 |
| Et | 4-$ClC_6H_4$ | Me | rt | (95) | 96.5:3.5 |
| Et | 2-$MeOC_6H_4$ | Me | rt | (71) | 98.5:1.5 |
| Et | 2-$O_2NC_6H_4$ | Me | rt | (97) | 97.0:3.0 |
| Et | 4-$O_2NC_6H_4$ | Me | rt | (90) | 96.5:3.5 |

| | | | | | |
|---|---|---|---|---|---|
| Et | 2-$MeC_6H_4$ | Me | rt | (92) | 96.5:3.5 |
| Et | 3-$MeC_6H_4$ | Me | rt | (86) | 97.0:3.0 |
| Et | 4-$MeC_6H_4$ | Me | rt | (91) | 97.0:3.0 |
| *i*-Pr | Ph | Me | rt | (90) | 98.0:2.0 |

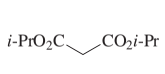
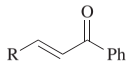
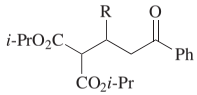


**299** (6 mol %),
$Sc(OTf)_3$ (5 mol %),
EtOH, 4 Å MS, 35°



| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Ph | Ph | 70 | (50) | 98.5:1.5 |
| Et | Ph | Ph | 45 | (93) | 99.5:0.5 |
| *i*-Pr | 2-$C_4H_3O$ | 2-$C_4H_3O$ | 45 | (81) | 98.0:2.0 |
| *i*-Pr | Ph | 2-$C_4H_3O$ | 40 | (92) | 99.5:0.5 |
| *i*-Pr | Ph | 2-$C_4H_3S$ | 40 | (94) | 99.5:0.5 |
| *i*-Pr | Ph | 4-$ClC_6H_4$ | 35 | (99) | 99.0:1.0 |
| *i*-Pr | Ph | 2-$MeOC_6H_4$ | 20 | (81) | 99.0:1.0 |
| *i*-Pr | Ph | 3-$MeOC_6H_4$ | 35 | (72) | 99.5:0.5 |
| *i*-Pr | Ph | 4-$MeOC_6H_4$ | 20 | (94) | 99.5:0.5 |
| *i*-Pr | Ph | 4-$O_2NC_6H_4$ | 45 | (70) | 98.0:2.0 |
| *i*-Pr | Ph | 2-Np | 40 | (94) | 99.0:1.0 |
| *t*-Bu | Ph | Ph | 65 | (90) | 99.0:1.0 |
| Bn | Ph | Ph | 70 | (40) | 98.5:1.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **299** (6 mol %), $Sc(OTf)_3$ (5 mol %), EtOH, 4 Å MS, 35° |  | 106 |

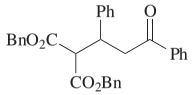
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 35 | (73) | 99.0:1.0 |
| 2-$C_4H_3S$ | 40 | (74) | 98.0:2.0 |
| 2-$C_5H_4N$ | 40 | (92) | 99.5:0.5 |
| *c*-$C_6H_{11}$ | 90 | (96) | 98.0:2.0 |
| Ph | 15 | (98) | 99.5:0.5 |
| 2-$ClC_6H_4$ | 40 | (96) | 99.5:0.5 |
| 3-$ClC_6H_4$ | 30 | (93) | 99.5:0.5 |
| 4-$ClC_6H_4$ | 90 | (80) | 99.5:0.5 |
| 2,4-$Cl_2C_6H_3$ | 35 | (92) | 99.5:0.5 |
| 4-$FC_6H_4$ | 35 | (95) | 99.5:0.5 |
| 2-$MeOC_6H_4$ | 40 | (92) | 98.5:1.5 |
| 3-$MeOC_6H_4$ | 45 | (93) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 90 | (87) | 99.0:1.0 |
| 3-$O_2NC_6H_4$ | 36 | (92) | 99.5:0.5 |
| 4-$O_2NC_6H_4$ | 36 | (97) | 99.0:1.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 40 | (60) | 99.0:1.0 |
| 3-$MeC_6H_4$ | 36 | (82) | 99.0:1.0 |
| 4-$MeC_6H_4$ | 36 | (90) | 98.5:1.5 |
| 4-$NCC_6H_4$ | 40 | (96) | 99.5:0.5 |
| PhCH=CH | 45 | (66) | 98.5:1.5 |
| 2-Np | 35 | (62) | 99.5:0.5 |





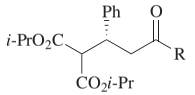


**300** (10 mol %),
$K_2CO_3$ (6 eq), toluene, rt



(99) er 53.0:47.0 602

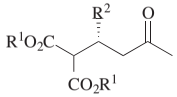
**302** (30 mol %),
DMSO/$CH_2Cl_2$ (1:1), rt, 7 d



| R | | er |
|---|---|---|
| Me | (63) | 85.0:15.0 |
| Ph | (47) | 55.0:45.0 |

603

**308** (20 mol %),
toluene, rt, 72 h



604

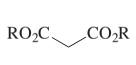
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | Ph | (98) | 97.0:3.0 |
| Et | Ph | (94) | 96.0:4.0 |
| *i*-Pr | Ph | (99) | 99.5:0.5 |
| Bn | *i*-Pr | (70) | 97.5:2.5 |
| Bn | Ph | (99) | 97.0:3.0 |
| Bn | 2-$BrC_6H_4$ | (99) | 91.5:8.5 |
| Bn | 4-$BrC_6H_4$ | (99) | 98.5:1.5 |
| Bn | 4-$ClC_6H_4$ | (99) | 99.0:1.0 |
| Bn | 2-$MeOC_6H_4$ | (84) | 90.0:10.0 |
| Bn | 4-$MeOC_6H_4$ | (94) | 97.0:3.0 |
| Bn | 3,4-$(MeO)_2C_6H_3$ | (75) | 97.0:3.0 |
| Bn | 4-$Me_2NC_6H_4$ | (62) | 93.5:6.5 |
| Bn | 3-$O_2NC_6H_4$ | (99) | 97.0:3.0 |
| Bn | 4-$O_2NC_6H_4$ | (99) | 97.0:3.0 |
| Bn | 4-$MeC_6H_4$ | (98) | 97.0:3.0 |
| Bn | 1-Np | (90) | 95.5:4.5 |

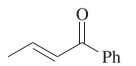
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

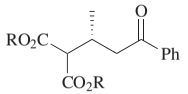
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



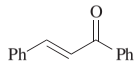


**313** (10 mol %),
DME, –40°, 56 h

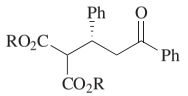


| R | | er |
|---|---|---|
| Me | (95) | 87.0:13.0 |
| Bn | (97) | 89.0:11.0 |

104

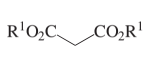


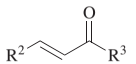
**313** (6 mol %),
$Co(OAc)_2 \cdot 4H_2O$ (4 mol %),
*i*-$Pr_2NEt$ (1.2 eq),
EtOH, rt, 15 h



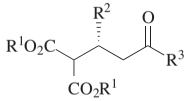
| R | | er |
|---|---|---|
| Et | (17) | 87.5:12.5 |
| *i*-Pr | (12) | 91.0:9.0 |
| *t*-Bu | (13) | 94.5:5.5 |

605



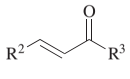


**314** (10 mol %),
$K_2CO_3$ (6 eq),
toluene, rt

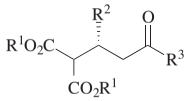


606

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Ph | Ph | 14–20 | (92) | 63.5:36.5 |
| Et | Ph | Ph | 14–20 | (70) | 73.0:27.0 |
| *i*-Pr | Ph | Ph | 14–20 | (77) | 77.5:22.5 |
| Bn | Ph | 2-$C_4H_3S$ | 18 | (94) | 75.5:24.5 |
| Bn | Ph | Ph | 18 | (91) | 85.0:15.0 |
| Bn | Ph | 4-$MeOC_6H_4$ | 18 | (91) | 73.5:26.5 |
| Bn | 4-$MeOC_6H_4$ | Ph | 18 | (88) | 72.5:27.5 |
| Bn | 2-Np | 3-$BrC_6H_4$ | 24 | (60) | 83.5:16.5 |
| Bn | 2-Np | 4-$BrC_6H_4$ | 24 | (58) | 79.5:20.5 |



**316** (3 mol %),
$K_2CO_3$ (10 mol %),
toluene





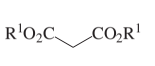
| $R^1$ | $R^2$ | $R^3$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|
| Me | Ph | Ph | 0 | 24 | (99) | 92.0:8.0 |
| Et | 2-$C_4H_3O$ | Ph | –20 | 24 | (99) | 93.0:7.0 |
| Et | 2-$C_4H_3S$ | Ph | –20 | 24 | (99) | 97.0:3.0 |
| Et | 2-$C_5H_4N$ | Ph | –30 | 48 | (99) | 95.0:5.0 |
| Et | Ph | 2-$C_4H_3S$ | –20 | 24 | (99) | 97.0:3.0 |
| Et | Ph | Ph | –20 | 24 | (99) | 95.0:5.0 |
| Et | Ph | Ph | 0 | 24 | (99) | 93.0:7.0 |
| Et | Ph | 4-$ClC_6H_4$ | –20 | 48 | (97) | 93.0:7.0 |
| Et | 4-$ClC_6H_4$ | Ph | –20 | 24 | (99) | 92.5:7.5 |
| Et | 4-$MeOC_6H_4$ | Ph | –20 | 24 | (99) | 93.5:6.5 |
| Et | 3,4-$(OCH_2O)C_6H_3$ | Ph | –20 | 24 | (99) | 94.5:5.5 |
| Et | 2-Np | Ph | –20 | 48 | (94) | 95.5:4.5 |
| *i*-Pr | Ph | Ph | –20 | 24 | (99) | 87.0:13.0 |
| Bn | Ph | Ph | –20 | 24 | (99) | 80.5:19.5 |

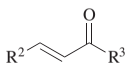
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

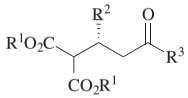
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



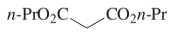


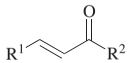
**315a** (20 mol %), TFA (20 mol %), $CHCl_3$, rt, 24 h



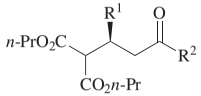
607

| $R^1$ | $R^2$ | $R^3$ | | er |
|---|---|---|---|---|
| Me | Ph | Me | (99) | 98.5:1.5 |
| Et | Ph | Me | (97) | 99.0:1.0 |
| *i*-Pr | Ph | Me | (72) | >99.5:0.5 |
| allyl | Ph | Me | (99) | 99.0:1.0 |
| Bn | *n*-Bu | Me | (66) | 99.0:1.0 |
| Bn | 2-$C_4H_3O$ | Me | (92) | 99.5:0.5 |
| Bn | Ph | Me | (99) | 99.5:0.5 |
| Bn | 4-$BrC_6H_4$ | Me | (96) | 99.5:0.5 |
| Bn | 2-$ClC_6H_4$ | Me | (99) | 99.5:0.5 |
| Bn | 3-$ClC_6H_4$ | Me | (90) | 99.5:0.5 |
| Bn | 4-$ClC_6H_4$ | Me | (91) | >99.5:0.5 |
| Bn | 4-$FC_6H_4$ | Me | (92) | 99.5:0.5 |
| Bn | 4-$MeOC_6H_4$ | Me | (93) | >99.5:0.5 |
| Bn | 4-$O_2NC_6H_4$ | Me | (96) | 99.5:0.5 |
| Bn | Ph | Et | (91) | 99.5:0.5 |
| Bn | 4-$MeC_6H_4$ | Me | (90) | >99.5:0.5 |
| Bn | 2-Np | Me | (91) | 99.5:0.5 |
| Bn | Ph | Ph | (82) | >99.5:0.5 |





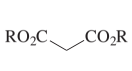
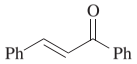
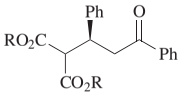
**317** (6 mol %),
$Sr(Oi\text{-}Pr)_2$ (5 mol %),
0.1 M in toluene,
4 Å MS, (100 mg), rt



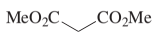
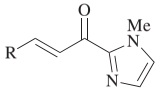
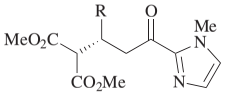


| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 2-$C_4H_3S$ | 7 | (73) | 98.5:1.5 |
| Ph | 1-$C_4H_4N$ | 24 | (93) | 99.5:0.5 |
| 5-Me-2-$C_4H_2O$ | Ph | 48 | (71) | 98.0:2.0 |
| Ph | Ph | 7 | (92) | 99.5:0.5 |
| Ph | 4-$ClC_6H_4$ | 7 | (98) | 99.5:0.5 |
| Ph | 4-$FC_6H_4$ | 7 | (92) | 99.5:0.5 |
| Ph | 4-$MeOC_6H_4$ | 7 | (85) | 99.5:0.5 |
| 2-$ClC_6H_4$ | Ph | 7 | (76) | 96.0:4.0 |
| 2-$ClC_6H_4$ | 4-$FC_6H_4$ | 7 | (80) | 96.5:3.5 |
| 4-$ClC_6H_4$ | Ph | 7 | (93) | 98.5:1.5 |
| 4-$ClC_6H_4$ | 4-$FC_6H_4$ | 7 | (97) | 98.5:1.5 |
| 4-$FC_6H_4$ | Ph | 7 | (92) | 99.0:1.0 |
| 4-$FC_6H_4$ | 4-$FC_6H_4$ | 7 | (91) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Ph | 7 | (80) | >99.5:0.5 |
| 4-$MeOC_6H_4$ | 4-$FC_6H_4$ | 7 | (81) | >99.5:0.5 |
| 3,4-$(MeO)_2C_6H_3$ | 4-$FC_6H_4$ | 7 | (61) | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | Ph | 7 | (94) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | Ph | 7 | (98) | 98.0:2.0 |
| 4-$FC_6H_4$ | 4-$MeC_6H_4$ | 7 | (90) | 99.0:1.0 |
| Ph | PhCH=CH | 7 | (97) | 93.0:7.0 |
| PhCH=CH | Ph | 7 | (62) | 98.5:1.5 |

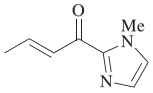
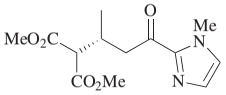
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

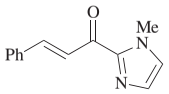
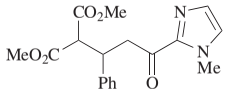
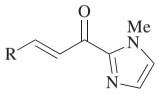
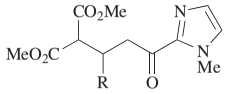
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **317** (6 mol %), $Sr(O\textit{i}\text{-}Pr)_2$ (5 mol %), 0.1 M toluene, 4 Å MS (100 mg), rt |  | 108 |

| R | Time (h) | | er |
|---|---|---|---|
| Me | 24 | (65) | 97.0:3.0 |
| Et | 18 | (91) | 98.5:1.5 |
| *i*-Pr | 21 | (83) | 94.5:5.5 |
| *n*-Bu | 3 | (85) | 98.0:2.0 |
| Bn | 18 | (85) | 92.0:8.0 |

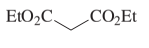
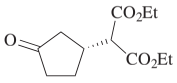
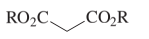
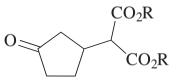
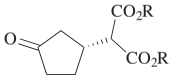
| | | | | |
|---|---|---|---|---|
|  |  | 1.3 mg/mL **285**, 0.3 mM [Cu(**284**)$(NO_3)_2$], pH 6.5 MOPS buffer solution, 5°, 3 d |  | 608 |

| R | Conv. (%) | er |
|---|---|---|
| Me | 92 | 79.0:21.0 |
| 2-$C_4H_3O$ | 96 | 93.0:7.0 |
| Ph | 92 | 96.0:4.0 |
| 2-$BrC_6H_4$ | 100 | 99.5:0.5 |
| 4-$ClC_6H_4$ | 75 | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 94 | 93.0:7.0 |

| | | | | | |
|---|---|---|---|---|---|
| |  | **286** (30 mol %), $Cu(H_2O)_6(NO_3)_2$ (15 mol %), pH 6.5 MOPS buffer solution, 0°, 3 d |  | 85% conv. er 92.5:7.5 | 609 |

| | | | | | |
|---|---|---|---|---|---|
| |  | 1 mM **287**, 0.15 mM Cu(**284**) |  | (—) er 96.5:3.5 | 610 |
| |  | 1 mM **287**, 0.15 mM Cu(**284**), pH 6.5 MOPS buffer solution, 2 d |  | | 611 |

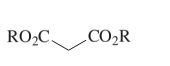
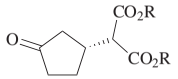
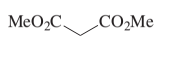
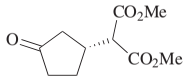
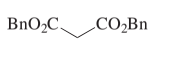
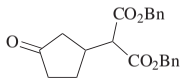
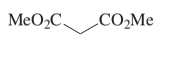
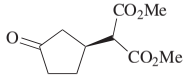
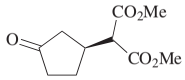
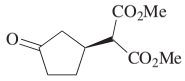
| R | er |
|---|---|
| Me | 78.0:22.0 |
| *i*-Pr | 55.0:45.0 |
| *n*-$C_5H_{11}$ | 57.5:42.5 |
| 4-$MeOC_6H_4$ | 97.0:3.0 |

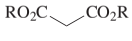
| | | | | | |
|---|---|---|---|---|---|
|  |  | **4** (15 mol %), piperidine (1 eq), $CHCl_3$, rt, 3 d |  | (88) er 65.0:35.0 | 174 |
|  |  | **70** (25 mol %), NAP/MgO (0.125 g), THF, –20°, 12 h |  | | 592 |
| |  | **160b** (20 mol %), $Et_3N$, –20° |  | | 612 |

| R | | | |
|---|---|---|---|
| Me | (94) | 92.0:8.0 | |
| Et | (93) | 93.0:7.0 | |

| R | Time (h) | | er |
|---|---|---|---|
| Me | 120 | (94) | 95.5:4.5 |
| Et | 120 | (93) | 96.0:4.0 |
| *i*-Pr | 192 | (84) | 98.0:2.0 |
| Bn | 120 | (99) | 96.0:4.0 |

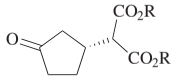
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | | Refs. |
|---|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | | |
| $C_3$ | | | | | |
|  |  | **202a** (15 mol %), *t*-BuOK (30 mol %), $CaCl_2$ (18 mol %), toluene, –15°, 24 h |  | R (Me) (75) er 94.0:6.0; (Et) (76) 93.5:6.5; (*i*-Pr) (68) 62.0:38.0 | 594 |
|  |  | **221a** (5 mol %), $PhCO_2H$ (5 mol %), THF, 50°, 72 h |  | (62) er 94.0:6.0 | 587 |
|  |  | **227** (10 mol %), $Cs_2CO_3$, THF, 48 h |  | Temp (–20°) (54) er 75.0:25.0; (rt) (79) 69.0:31.0 | 513 |
|  |  | **288a** (2 mol %), *t*-BuOH, 30–40° |  | (98) er 99.0:1.0 | 613 |
| |  | **288a** (*x* mol %) toluene, rt, 24 h |  | *x* (0.001) (97) >99.5:0.5; (0.002) (100) >99.5:0.5; (0.01) (100) >99.5:0.5; (0.02) (100) >99.5:0.5 | 614 |
| |  | **289** (9 mol %), $Et_3N$, $CH_2Cl_2$, –40°, 8 h |  | (78) er 66.5:33.5 | 615 |





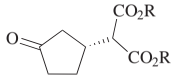
Catalyst (10 mol %), DME, 4°



| R | Catalyst | Time (h) | | er | |
|---|---|---|---|---|---|
| Me | **291a** | 85 | (96) | >99.5:0.5 | 104 |
| Bn | **291a** | 85 | (85) | >99.5:0.5 | 104 |
| Bn | **291b** | 87 | (92) | 90.0:10.0 | 616 |



**292** (66 mol %),
LAH (33 mol %),
THF, rt

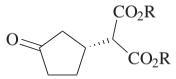


597

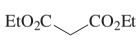
| R | Time (h) | | er |
|---|---|---|---|
| Et | 5 | (86) | 93.5:6.5 |
| *t*-Bu | 6 | (83) | 95.0:5.0 |
| Bn | 8 | (78) | 91.5:8.5 |



1. *ent*-**292** (40 mol %),
TBATB (40 mol %),
THF, 0°, 7 h
2. $H_2O_2$, NaOH (10 %)

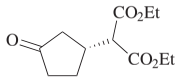


| R | | er | |
|---|---|---|---|
| Et | (62) | 67.5:32.5 | 598 |
| *t*-Bu | (64) | 70.0:30.0 | |
| Bn | (61) | 65.5:34.5 | |





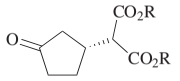
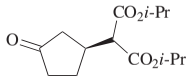
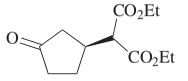
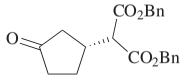
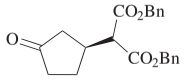
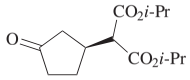
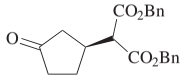
**293a/293b** (1:3) (10 mol %),
DMSO/$ClCH_2CH_2Cl$ (1:2),
rt, 7 d

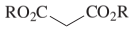


(61) er 86.5:13.5

599

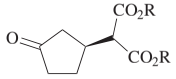
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | | Refs. |
|---|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | | |
| $C_3$ | | | | | |
| $RO_2C$ $CO_2R$ |  | **294** (10 mol %), $LaCl_3$ (3.33 mol %), *t*-BuONa (5 mol %), THF, rt, 20 h |  | R (Et) (82) er 89.0:11.0; (*t*-Bu) (86) 88.5:11.5; (Bn) (84) 96.5:3.5 | 617 |
| *i*-$PrO_2C$ $CO_2i$-Pr |  | **296a** (5 mol %), $CHCl_3$, rt, 59 h |  | (91) er 79.5:20.5 | 600 |
| $EtO_2C$ $CO_2Et$ |  | **297** (10 mol %), THF, 40°, 72 h |  | (64) er 81.5:18.5 | 470 |
| $BnO_2C$ $CO_2Bn$ |  | **301** (10 mol %), THF, 0° to rt, 60 h |  | (93) er 95.5:4.5 | 112 |
| |  | **301** (5 mol %), 0.4 M in DME/HFIP (20:1), rt, 25 h |  | (83) er >99.5:0.5 | 618 |
| *i*-$PrO_2C$ $CO_2i$-Pr |  | **302** (30 mol %), $DMSO/CH_2Cl_2$ (1:1), rt, 96 h |  | (47) er 77.5:22.5 | 603 |
| $BnO_2C$ $CO_2Bn$ |  | **304c** (11 mol %), $Bu_2Mg$, toluene, 4 Å MS, 50°, 40 h |  | (51) er 75.0:25.0 | 619 |





**318** (10 mol %), THF, 0°



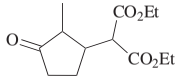
620

| R | Time (min) | | er |
|---|---|---|---|
| Me | 10 | (86) | 79.0:21.0 |
| Et | 15 | (92) | 66.5:33.5 |
| *i*-Pr | 15 | (89) | 68.0:32.0 |
| *t*-Bu | 45 | (83) | 70.0:30.0 |
| Bn | 240 | (75) | 70.5:29.5 |





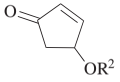
**294** (10 mol %),
$LaCl_3$ (3.33 mol %),
*t*-BuONa (5 mol %),
THF, rt, 20 h



(86) dr 80:20
er 62.5:37.5

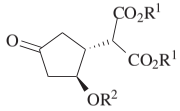
617





racemic

**301** (5 mol %),
base (4.5 mol %)
*x* M in THF, 4 Å MS, rt, 20 h



621

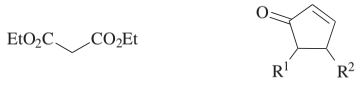
| $R^1$ | $R^2$ | Base | *x* | Conv. (%) | er |
|---|---|---|---|---|---|
| Me | MOM | *t*-BuONa | 0.5 | 40 | 97.0:3.0 |
| Me | TBDMS | *t*-BuOK | 0.5 | 49 | 96.5:3.5 |
| Me | TBDMS | *t*-BuONa | 0.5 | 48 | 97.5:2.5 |
| Me | TBDMS | *t*-BuONa | 1.2 | 48 | 98.0:2.0 |
| Me | TBDMS | — | 0.5 | 14 | 98.0:2.0 |
| Et | TBDMS | *t*-BuOK | 0.5 | 48 | 89.0:11.0 |
| Bn | TBDMS | *t*-BuOK | 0.5 | 24 | 97.5:2.5 |

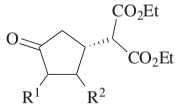
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



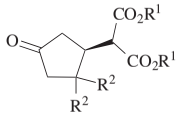


**1** (15 mol %), piperidine, MW, neat

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| H | H | 40 | 1.5 | (99) | 55.0:45.0 |
| H | H | 55 | 3 | (78) | 50.5:49.5 |
| H | Me | 55 | 2 | (32) | 50.5:49.5 |
| Me | H | 55 | 2 | (38) | 50.5:49.5 |

591



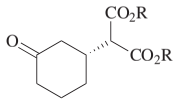


Catalyst (*x* mol %), *t*-BuOH

| $R^1$ | $R^2$ | Catalyst | *x* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|---|
| Me | H | **288a** | 1 | 60 | 24 | (99) | 98.5:1.5 |
| Me | H | **288a** | 2 | 40 | 24 | (99) | 99.0:1.0 |
| Me | Me | **288a** | 2 | 30 | 72 | (83) | >99.5:0.5 |
| Et | H | **288b** | 2 | 40 | 24 | (96) | 98.0:2.0 |

34



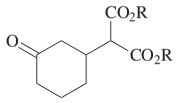


**4** (15 mol %), piperidine (1 eq), $CHCl_3$, rt, 3 d

| R | | er |
|---|---|---|
| Me | (87) | 91.5:8.5 |
| Et | (94) | 96.5:3.5 |
| Bn | (86) | 90.5:9.5 |

174





**70** (25 mol %), NAP/MgO (0.125 g), THF, –20°, 16 h

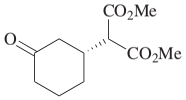
| R | | er |
|---|---|---|
| Me | (95) | 95.0:5.0 |
| Et | (90) | 95.0:5.0 |

592





**202a** (3 mol %),
LAH (1 mol %),
*t*-BuOK (27 mol %),
THF, 4 Å MS, rt, 72 h

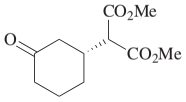


(96) er 99.5:0.5

622



**202a** (2 mol %),
LAH (1 mol %),
*t*-BuOK (0.9 mol %),
0.25 M in THF, 4 Å MS, rt, 72 h

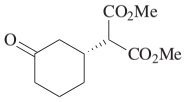


(99) er >99.5:0.5

623



**202a** (0.3 mol %),
LAH (0.1 mol %),
*t*-BuOK (0.09 mol %),
49 M THF, 4 Å MS

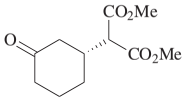


(91) er >99.5:0.5

624, 226



**202a** (*x* mol %),
LAH (0.05–0.25 mol %),
*t*-BuOK (0.45–2.25 mol %),
*y* M in THF, 4 Å MS



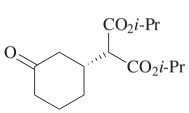
625

| *x* | *y* | Time (h) | | er |
|---|---|---|---|---|
| 0.05 | 98 | 48 | (94) | 99.0:1.0 |
| 0.10 | 49 | 24 | (92) | 99.0:1.0 |
| 0.10 | 49 | 10 | (74) | 99.0:1.0 |
| 0.20 | 24 | 24 | (95) | >99.5:0.5 |
| 0.25 | 20 | 15 | (95) | >99.5:0.5 |





**202a** (15 mol %),
$CaCl_2$ (18 mol %),
*t*-BuOK (30 mol %),
toluene, –15°, 24 h



(55) er 60.6:39.4

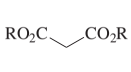
594

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

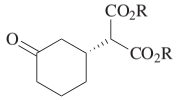
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$





**202a** (10 mol %), La(O*i*-Pr)$_3$ (3.33 mol %), *t*-BuONa (10 mol %), THF

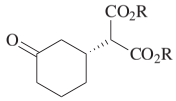


| R | Temp | Time (h) | | er |
|---|---|---|---|---|
| Me | rt | 12 | (98) | 91.5:8.5 |
| Et | rt | 12 | (97) | 90.5:9.5 |
| Bn | 0° | 24 | (97) | 94.0:6.0 |
| Bn | rt | 12 | (98) | 92.5:7.5 |

50



**227** (10 mol %), $Cs_2CO_3$, THF, 48 h

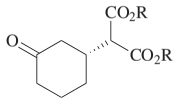


| R | Temp | | er |
|---|---|---|---|
| Me | rt | (48) | 58.5:41.5 |
| Bn | –40° | (45) | 95.0:5.0 |
| Bn | –20° | (47) | 93.5:6.5 |
| Bn | 0° | (75) | 91.0:9.0 |
| Bn | rt | (79) | 85.0:15.0 |

513
513
513
513
513, 626



**253** (5 mol %), $C_6H_5OLi$ (5 mol %), $CHCl_3$ (*x* mL), rt, 48 h

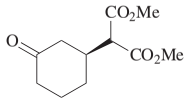


| R | *x* | | er |
|---|---|---|---|
| Me | 0.5 | (33) | 90.0:10.0 |
| Et | 0.5 | (99) | 92.5:7.5 |
| Et | 1 | (60) | 97.5:2.5 |

546



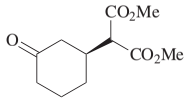
**288a** (*x* mol %)
toluene, rt, 48 h



| *x* | | er | |
|---|---|---|---|
| 0.001 | (26) | 99.5:0.5 | 614 |
| 0.002 | (42) | 99.0:1.0 | |



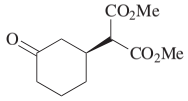
Catalyst (1–2 mol %),
*t*-BuOH, 30°, 48 h



| Catalyst | | er | |
|---|---|---|---|
| **288a** | (99) | 99.0:1.0 | 34 |
| **288b** | (93) | 98.0:2.0 | |



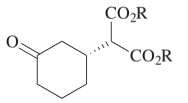
**290** (2 mol %),
benzene, 20°



| Time (h) | | er | |
|---|---|---|---|
| 72 | (91) | 95.0:5.0 | 627 |
| — | (>99) | 98.5:1.5 | 628 |



Catalyst (10 mol %), solvent



| R | Catalyst | Solvent | Temp | Time (h) | | er | |
|---|---|---|---|---|---|---|---|
| Me | **291b** | THF | 4° | 72 | (99) | 98.0:2.0 | 616 |
| Me | **291a** | DME | rt | 72 | (95) | >99.5:0.5 | 104 |
| Bn | **291b** | THF | 4° | 72 | (86) | 92.5:8.5 | 616 |
| Bn | **291a** | DME | 4° | 85 | (98) | >99.5:0.5 | 104 |
| Bn | **291a** | DME | rt | 72 | (94) | >99.5:0.5 | 104 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

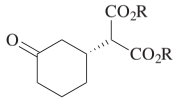
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





**292** (66 mol %),
LAH (33 mol %), THF, rt



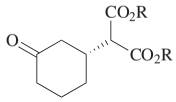
| R | Time (h) | | er |
|---|---|---|---|
| Et | 5 | (87) | 90.0:10.0 |
| *t*-Bu | 6 | (80) | 97.0:3.0 |
| Bn | 7 | (83) | 96.0:4.0 |

597





1. *ent*-**292** (40 mol %),
TBATB (40 mol %),
THF, 0°, 7 h
2. $H_2O_2$, 10% NaOH

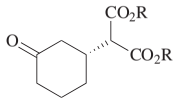


| R | | er |
|---|---|---|
| Et | (67) | 71.0:29.0 |
| *t*-Bu | (65) | 72.5:27.5 |
| Bn | (63) | 69.5:30.5 |

598



**293a**/**293b** (1:3) (5 mol %),
DMSO/$ClCH_2CH_2Cl$ (1:2), rt

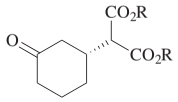


| R | Time (d) | | er |
|---|---|---|---|
| Me | 4 | (91) | 96.5:3.5 |
| Et | 5 | (91) | 97.5:2.5 |
| *i*-Pr | 3 | (85) | 97.5:2.5 |
| *t*-Bu | 7 | (47) | 93.0:7.0 |
| Bn | 3 | (92) | 96.0:4.0 |

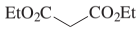
599



**294** (10 mol %),
$LaCl_3$ (3.33 mol %),
*t*-BuONa (5 mol %),
THF, rt, 20 h

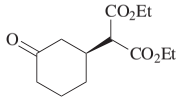


| R | | er | |
|---|---|---|---|
| Et | (85) | 88.5:11.5 | 617 |
| *t*-Bu | (80) | 90.0:10.0 | |
| Bn | (86) | 97.5:2.5 | |

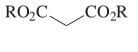




**295** (20 mol %),
LAH (20 mol %)
THF, 30°, 4 h

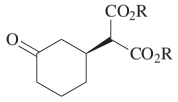


(90) er 97.5:2.5 629



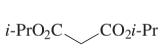


**296a** (*x* mol %), $CHCl_3$, rt



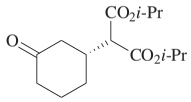
600

| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| Me | 10 | 15 | (88) | 70.0:30.0 |
| Et | 10 | 24 | (87) | 71.5:28.5 |
| *i*-Pr | 5 | 46 | (87) | 74.5:25.5 |
| *i*-Pr | 10 | 59 | (88) | 76.5:23.5 |
| *t*-Bu | 10 | 63 | (39) | 82.5:17.5 |
| Bn | 10 | 17 | (99) | 69.5:30.5 |



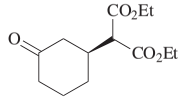
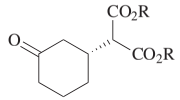
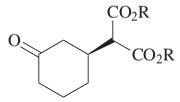
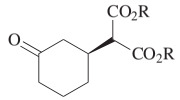


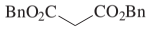
**296a** (20 mol %),
CsF (20 mol %),
$CHCl_3$, rt, 48 h



(84) er 82.5:17.5 600

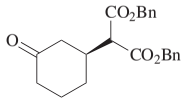
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
| $EtO_2C$ $CO_2Et$ |  | **298** (5 mol %), $C_6H_5OLi$ (5 mol %), dioxane, rt, 48 h |  (96) er 84.5:14.5 | 630 |
| $RO_2C$ $CO_2R$ |  | **301** (10 mol %), THF, 0° to rt, 72 h |  R: Me (90) er 96.5:3.5; Et (87) 97.5:2.5; Bn (88) 99.5:0.5 | 112 |
| |  | **301** (5 mol %), 0.4 M in solvent, rt, 25 h |  R: Me, Solvent: DME/HFIP (20:1), Time (h): 18 (86), er >99.5:0.5; Bn, DME, 24 (79), >99.5:0.5; Bn, DME/HFIP (20:1), 24 (95), >99.5:0.5 | 618 |
| |  | **302** (30 mol %), $DMSO/CH_2Cl_2$ (1:1), rt |  R: Me, Time (h): 72 (77), er 84.5:15.5; Et, 72 (61), 88.0:12.0; *i*-Pr, 96 (92), 89.5:10.5; Bn, 72 (77), 83.0:17.0 | 603 |





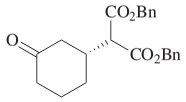
**304b** (11 mol %),
$Bu_2Mg$, toluene,
4 Å MS, 50°, 66 h



(52) er 79.0:21.0 619



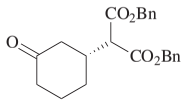
Catalyst (*x* mol %), THF, rt



| Catalyst | *x* | Time (h) | | er | |
|---|---|---|---|---|---|
| **305** | 10 | 68 | (42) | 99.5:0.5 | 631 |
| **307a** | 10 | 72 | (36) | 98.0:2.0 | 632 |
| **307b** | 10 | 72 | (91) | 96.5:3.5 | 632 |
| **310** | 20 | 45 | (72) | 83.0:17.0 | 616 |



**306** (10 mol %),
LAH (5 mol %),
*n*-BuLi (9 mol %), THF, rt

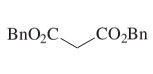
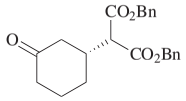
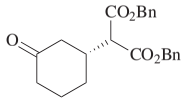
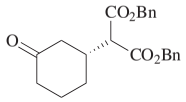
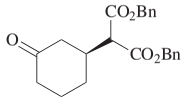


633

Catalyst Recycling

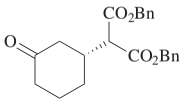
| Run | Cat. Recov. | | er |
|---|---|---|---|
| 1 | (100) | (78) | 96.5:3.5 |
| 2 | (98) | (66) | 94.5:5.5 |
| 3 | (97) | (68) | 94.0:6.0 |
| 4 | (95) | (56) | 88.0:12.0 |
| 5 | (95) | (51) | 86.5:13.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

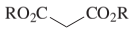
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **308** (20 mol %), toluene, rt, 72 h |  (61) er 59.0:41.0 | 604 |
| |  | **309** (10 mol %), LAH (3.33 mol %), *t*-BuONa (1.11 mol %), THF, 0°, 48 h |  Catalyst Recycling: Run 1 (63) er 95.5:4.5; Run 2 (63) er 96.5:3.5; Run 3 (57) er 97.0:3.0 | 634 |
| |  | **311** (20 mol %), LAH (20 mol %), *n*-BuLi (10 mol %), THF, 4 Å MS, rt, 48 h |  (86) er 98.0:2.0 | 635 |
| | | | Catalyst Recycling: Run 1, Time (h) 72, (88), er 98.0:2.0; Run 2, 98, (86), 93.5:6.5; Run 3, 98, (74), 92.5:7.5; Run 4, 98, (60), 88.5:11.5; Run 5, 98, (59), 88.5:11.5 | |
| |  | **312** (10 mol %), THF, rt, 72 h |  (73) er 95.5:4.5 | 636 |



**315a** (20 mol %), TFA (20 mol %), $CHCl_3$, 0°, 120 h

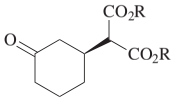


(71) er 95.0:5.0 607



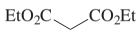


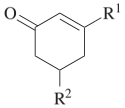
**318** (10 mol %), THF, 0°



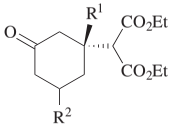
620

| R | Time (min) | | er |
|---|---|---|---|
| Me | 15 | (85) | 68.5:31.5 |
| Et | 20 | (88) | 67.0:33.0 |





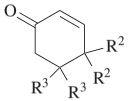
**1** (15 mol %), piperidine, MW, neat, 55°, 2 h



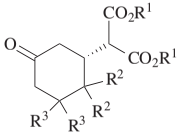
294

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| H | H | (96) | 74.0:26.0 |
| Me | Me | (50) | 52.0:48.0 |





**221a** (5 mol %), $PhCO_2H$ (5 mol %), toluene, 50°



587

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| Me | H | Me | 48 | (74) | 98.0:2.0 |
| Me | Me | H | 20 | (53) | 95.5:4.5 |
| Et | H | H | 20 | (72) | 99.0:1.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

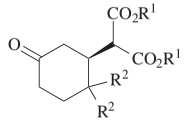
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



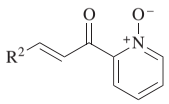


**297** (10 mol %), THF

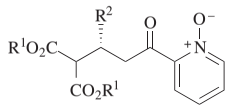


601

| $R^1$ | $R^2$ | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| Me | H | rt | 60 | (83) | 98.0:2.0 |
| Me | H | 40° | 18 | (91) | 96.5:3.5 |
| Et | H | rt | 12 | (95) | 98.0:2.0 |
| Et | Me | 40° | 72 | (77) | 95.5:4.5 |
| *i*-Pr | H | 40° | 18 | (95) | 98.0:2.0 |



**234**–$(ZnOTf)_2$ (5 mol %), $Et_3N$ (10 mol %), $CH_2Cl_2$, –25°

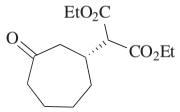


637

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | 2-$C_4H_3O$ | 36 | (96) | 97.0:3.0 |
| Me | *c*-$C_6H_{11}$ | 96 | (70) | 96.0:4.0 |
| Me | Ph | 30 | (96) | 96.0:4.0 |
| Me | 2-$ClC_6H_4$ | 30 | (95) | 98.0:2.0 |
| Me | 3-$ClC_6H_4$ | 48 | (96) | 93.5:6.5 |
| Me | 4-$ClC_6H_4$ | 30 | (97) | 95.5:4.5 |
| Me | 4-$FC_6H_4$ | 30 | (95) | 95.0:5.0 |
| Me | 4-$MeOC_6H_4$ | 48 | (87) | 94.0:6.0 |
| Me | 3-$O_2NC_6H_4$ | 36 | (92) | 94.0:6.0 |
| Me | PhCH=CH | 72 | (75) | 93.0:7.0 |
| Me | 1-Np | 48 | (83) | 98.0:2.0 |
| Et | Ph | 36 | (90) | 92.5:7.5 |
| *i*-Pr | Ph | 12 | (86) | 89.5:10.5 |
| *t*-Bu | Ph | 24 | (60) | 58.0:42.0 |
| Bn | Ph | 24 | (84) | 87.0:13.0 |



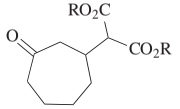
**4** (15 mol %), piperidine (1 eq), $CHCl_3$, rt, 3 d



(91) er 94.5:5.5 174



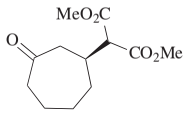
**70** (25 mol %), NAP/MgO (0.125 g), THF, –20°, 24 h



| R | | er | 592 |
|---|---|---|---|
| Me | (96) | 97.0:3.0 | |
| Et | (90) | 96.5:3.5 | |



Catalyst (1–2 mol %), *t*-BuOH, 30°

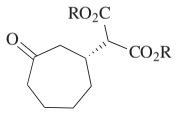


34

| Catalyst | Time (h) | | er |
|---|---|---|---|
| **288a** | 72 | (75) | >99.5:0.5 |
| **288b** | 48 | (53) | >99.5:0.5 |

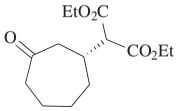
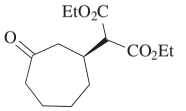
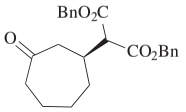
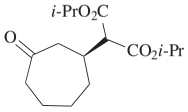
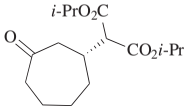
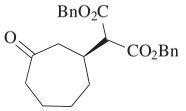


Catalyst (10 mol %), solvent, 4°



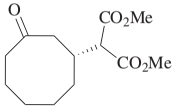
| R | Catalyst | Solvent | Time (h) | | er | |
|---|---|---|---|---|---|---|
| Me | **291a** | DME | 85 | (97) | >99.5:0.5 | 104 |
| Me | **291b** | THF | 72 | (70) | 96.5:3.5 | 616 |
| Bn | **291a** | DME | 85 | (96) | >99.5:0.5 | 104 |
| Bn | **291b** | THF | 72 | (83) | 94.5:5.5 | 616 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
| $EtO_2C$ $CO_2Et$ |  | **293a/293b** (1:3) (10 mol %), DMSO/$ClCH_2CH_2Cl$ (1:2), rt, 2 d |  | (89) er 98.5:1.5 | 599 |
| |  | **297** (10 mol %), THF, 40°, 72 h |  | (83) er 96.5:3.5 | 601 |
| $BnO_2C$ $CO_2Bn$ |  | **301** (5 mol %), 0.4 M in DME/HFIP (20:1), rt, 30 h |  | (85) er >99.5:0.5 | 618 |
| *i*-$PrO_2C$ $CO_2i$-Pr |  | **302** (30 mol %), DMSO/$CH_2Cl_2$ (1:1), rt, 96 h |  | (96) er 93.5:6.5 | 603 |
| |  | **303** (20 mol %), $CHCl_3$, rt, 9 h |  | (23) er 79.5:20.5 | 600 |
| $BnO_2C$ $CO_2Bn$ |  | **304a** (11 mol %), $Bu_2Mg$, toluene, 4 Å MS, 50°, 40 h |  | (39) er 69.5:30.5 | 619 |



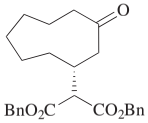
**291a** (10 mol %), DME/THF (9:1), rt, 96 h



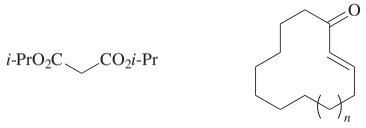
(82) er 99.5:0.5 104



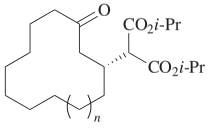
**291a** (10 mol %), DME, 4°, 120 h



(61) er 91.0:9.0 104



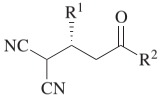
**296a** (20 mol %), CsF (20 mol %), $CHCl_3$, rt, 96 h



| *n* | | er | |
|---|---|---|---|
| 1 | (45) | 90.5:9.5 | 600 |
| 4 | (54) | 91.0:9.0 | |



**80d** (20 mol %), TFA (40 mol %), $CH_2Cl_2$



638

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| *n*-Pr | Me | 22 | 72 | (35) | 96.5:3.5 |
| *n*-Pr | Me | 40 | 72 | (39) | 96.0:4.0 |
| 2-$C_4H_3O$ | Me | 22 | 12 | (99) | 97.5:2.5 |
| Ph | Me | 22 | 12 | (93) | 97.5:2.5 |
| 4-$BrC_6H_4$ | Me | 22 | 48 | (84) | 96.5:3.5 |
| 4-$ClC_6H_4$ | Me | 22 | 18 | (85) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Me | 22 | 12 | (94) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | Me | 22 | 48 | (70) | 93.5:6.5 |
| Ph | Et | 22 | 12 | (85) | 98.5:1.5 |
| 4-$MeC_6H_4$ | Me | 22 | 22 | (87) | 96.5:3.5 |
| 2-Np | Me | 22 | 22 | (87) | 94.0:6.0 |
| Ph | Ph | 22 | 72 | (60) | 94.0:6.0 |
| Ph | 4-$MeOC_6H_4$ | 22 | 72 | (79) | 93.5:6.5 |
| 4-$FC_6H_4$ | Ph | 22 | 72 | (40) | 91.5:8.5 |
| 4-$FC_6H_4$ | Ph | 40 | 72 | (78) | 90.0:10.0 |
| 4-$MeOC_6H_4$ | Ph | 22 | 72 | (20) | 93.5:6.5 |
| 4-$MeOC_6H_4$ | Ph | 40 | 72 | (80) | 92.5:7.5 |

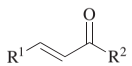
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

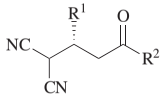
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



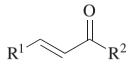


*ent*-**186** (30 mol %), toluene, 5–7 d

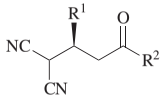


639

| $R^1$ | $R^2$ | Temp (°) | | er |
|---|---|---|---|---|
| Me | Ph | –18 | (30) | 74.5:25.5 |
| Me | Ph | 4 | (70) | 69.5:30.5 |
| *c*-$C_6H_{11}$ | Ph | 4 | (66) | 75.5:24.5 |
| Ph | Ph | –18 | (80) | 83.5:16.5 |
| Ph | 4-$MeOC_6H_4$ | –18 | (75) | 75.0:25.0 |
| Ph | 3,4-$Cl_2C_6H_3$ | –18 | (87) | 78.5:21.5 |
| 4-$BrC_6H_4$ | Ph | –18 | (63) | 81.0:19.0 |
| 4-$ClC_6H_4$ | Ph | –18 | (50) | 87.5:12.5 |
| Ph | 3-$MeC_6H_4$ | –18 | (60) | 76.5:23.5 |
| 4-$MeC_6H_4$ | Ph | –18 | (50) | 75.5:24.5 |
| 4-$CF_3C_6H_4$ | Ph | –18 | (71) | 83.0:17.0 |
| 4-$NCC_6H_4$ | Ph | –18 | (40) | 79.5:20.5 |
| 4-$NCC_6H_4$ | Ph | 4 | (98) | 82.5:17.5 |



**326** (*x* mol %),
toluene, –18°



640

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Ph | 20 | 120 | (28) | 50.0:50.0 |
| Ph | Me | 10 | 90 | (71) | 87.0:13.0 |
| Ph | 3-$C_4H_3O$ | 10 | 139 | (89) | 95.0:5.0 |
| Ph | *c*-$C_6H_{11}$ | 20 | 115 | (98) | 97.5:2.5 |
| Ph | Ph | 10 | 60 | (99) | 96.0:4.0 |
| Ph | 2-$ClC_6H_4$ | 10 | 68 | (99) | 97.0:3.0 |
| Ph | 4-$ClC_6H_4$ | 10 | 86 | (98) | 96.0:4.0 |
| Ph | 4-$MeOC_6H_4$ | 10 | 136 | (95) | 95.5:4.5 |
| 4-$BrC_6H_4$ | Ph | 10 | 90 | (90) | 97.0:3.0 |
| 4-$BrC_6H_4$ | 4-$MeOC_6H_4$ | 20 | 140 | (96) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | Ph | 10 | 111 | (98) | 95.0:5.0 |
| Ph | 4-$MeC_6H_4$ | 10 | 90 | (95) | 95.5:4.5 |
| Ph | 4-$CF_3C_6H_4$ | 10 | 70 | (88) | 95.5:4.5 |
| Ph | 4-$NCC_6H_4$ | 10 | 64 | (98) | 95.5:4.5 |
| 3-$MeC_6H_4$ | Ph | 10 | 68 | (99) | 95.5:4.5 |
| Ph | $BnCH_2$ | 10 | 130 | (96) | 94.0:6.0 |
| Ph | PhCH=CH | 20 | 186 | (74) | 94.5:5.5 |
| Ph | 2-Np | 20 | 134 | (88) | 95.0:5.0 |
| 2-Np | Ph | 10 | 92 | (93) | 95.0:5.0 |

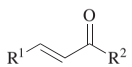
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

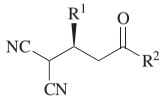
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



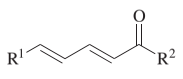


**327** (10 mol %),
Al(O*i*-Pr)$_3$ (10 mol %)
toluene, 0°, 80 h

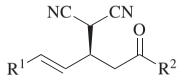


641

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| *t*-Bu | Ph | (72) | 96.5:3.5 |
| 2-$C_4H_3S$ | Ph | (83) | 93.0:7.0 |
| Ph | 2-$C_4H_3S$ | (92) | 88.5:11.5 |
| *c*-$C_6H_{11}$ | Ph | (80) | 96.0:4.0 |
| Ph | Ph | (92) | 95.0:5.0 |
| Ph | 4-$ClC_6H_4$ | (88) | 90.0:10.0 |
| Ph | 3-$MeOC_6H_4$ | (84) | 92.0:8.0 |
| 3-$ClC_6H_4$ | Ph | (92) | 93.5:6.5 |
| 4-$ClC_6H_4$ | Ph | (89) | 94.5:5.5 |
| 2,4-$Cl_2C_6H_3$ | Ph | (90) | 94.5:5.5 |
| 4-$FC_6H_4$ | Ph | (94) | 94.5:5.5 |
| 2-$MeOC_6H_4$ | Ph | (89) | 93.5:6.5 |
| 3-$MeOC_6H_4$ | Ph | (84) | 92.0:8.0 |
| 4-$MeOC_6H_4$ | Ph | (89) | 94.0:6.0 |
| 3,4-$(OCH_2O)C_6H_3$ | Ph | (85) | 93.5:6.5 |
| 4-$O_2NC_6H_4$ | Ph | (95) | 94.5:5.5 |
| 3-$MeC_6H_4$ | Ph | (84) | 95.0:5.0 |
| 4-$MeC_6H_4$ | Ph | (84) | 93.5:6.5 |
| 4-$NCC_6H_4$ | Ph | (93) | 94.5:5.5 |
| PhCH=CH | Ph | (94) | 94.0:6.0 |
| Ph | 2-Np | (97) | 92.5:7.5 |
| 2-Np | Ph | (86) | 94.0:6.0 |

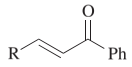


**328** (30 mol %),
TFA (60 mol %)
0.2 M in THF, $N_2$, rt, 7 d

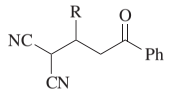


642

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Ph | (96) | 95.0:5.0 |
| Ph | 4-$BrC_6H_4$ | (93) | 97.0:3.0 |
| Ph | 4-$ClC_6H_4$ | (87) | 95.0:5.0 |
| Ph | 4-$FC_6H_4$ | (65) | 96.0:4.0 |
| Ph | 4-$MeOC_6H_4$ | (95) | 92.0:8.0 |
| 4-$MeOC_6H_4$ | Ph | (91) | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | Ph | (56) | 90.0:10.0 |
| Ph | 4-$MeC_6H_4$ | (97) | 92.0:8.0 |
| Ph | 4-$NCC_6H_4$ | (77) | 91.0:9.0 |



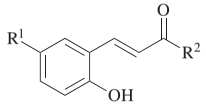
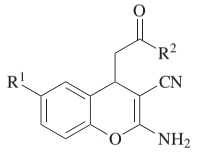
**332** (10 mol %),
toluene, rt, 5 d



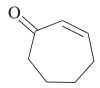
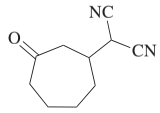
643

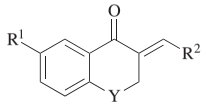
| R | | er |
|---|---|---|
| Ph | (72) | 81.0:19.0 |
| 4-$FC_6H_4$ | (57) | 75.0:25.0 |
| 4-$MeOC_6H_4$ | (44) | 74.5:25.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

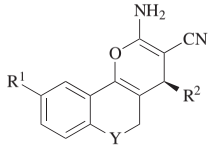
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$  |  | **225c** (20 mol %), **153** (20 mol %), $CH_2Cl_2$, rt, 96 h |  | 644 |

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| H | Me | (21) | 97.0:3.0 |
| H | Et | (66) | 93.0:7.0 |
| H | Ph | (63) | 95.5:4.5 |
| H | 4-$BrC_6H_4$ | (53) | 95.0:5.0 |
| Cl | Ph | (69) | 95.5:4.5 |
| Cl | 4-$BrC_6H_4$ | (54) | 93.0:7.0 |
| Cl | 2-$MeOC_6H_4$ | (58) | 87.5:12.5 |
| Cl | 3-$MeOC_6H_4$ | (70) | 92.5:7.5 |
| Cl | 4-$MeOC_6H_4$ | (67) | 97.5:2.5 |
| Cl | 4-$MeC_6H_4$ | (72) | 95.5:4.5 |

| | | | | |
|---|---|---|---|---|
|  | **80d** (20 mol %), TFA (40 mol %), $CH_2Cl_2$, 22°, 12 h |  | (60) er 97.5:2.5 | 638 |




**331** (10 mol %), toluene, rt





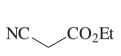

| Y | $R^1$ | $R^2$ | Time (d) | | er |
|---|---|---|---|---|---|
| O | H | *i*-Pr | 5 | (75) | 93.5:6.5 |
| O | H | 2-$C_4H_3S$ | 5 | (86) | 90.5:9.5 |
| O | H | *c*-$C_6H_{11}$ | 5 | (86) | 93.5:6.5 |
| O | H | Ph | 4 | (95) | 96.0:4.0 |
| O | H | 2-$BrC_6H_4$ | 3 | (99) | 93.0:7.0 |
| O | H | 3-$ClC_6H_4$ | 3 | (93) | 94.0:6.0 |
| O | H | 4-$ClC_6H_4$ | 3 | (92) | 95.0:5.0 |
| O | H | 3,4-$Cl_2C_6H_3$ | 3 | (88) | 96.0:4.0 |
| O | H | 2-F-4-$ClC_6H_3$ | 3 | (83) | 93.5:6.5 |
| O | H | 4-$MeOC_6H_4$ | 5 | (90) | 99.5:0.5 |
| O | H | 4-$O_2NC_6H_4$ | 2 | (72) | 96.5:3.5 |
| O | H | 3-$PhOC_6H_4$ | 3 | (90) | 93.5:6.5 |
| O | H | 2-$CH_2$=$CHCH_2OC_6H_4$ | 3 | (91) | 96.0:4.0 |
| O | H | 4-$CH_2$=$CHCH_2OC_6H_4$ | 5 | (85) | 95.0:5.0 |
| O | Cl | Ph | 3 | (88) | 96.0:4.0 |
| O | Me | Ph | 3 | (91) | 97.0:3.0 |
| O | H | 4-(*i*-Pr)$C_6H_4$ | 4 | (88) | 94.0:6.0 |
| S | H | Ph | 5 | (85) | 90.5:9.5 |
| $CH_2$ | H | Ph | 5 | (60) | 94.0:6.0 |

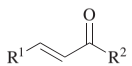
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

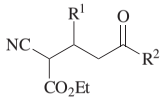
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



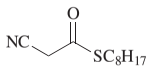


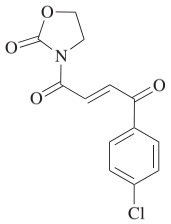
**323** (10 mol %), toluene, rt



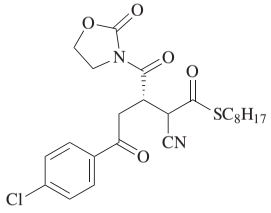
646

| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|
| Ph | 2-$C_4H_3O$ | 24 | (94) | 61:39 | 96.5:3.5 | 96.5:3.5 |
| Ph | 2-$C_4H_3S$ | 30 | (92) | 61:39 | 93.5:6.5 | 93.5:6.5 |
| 4-$BrC_6H_4$ | 2-$C_4H_3O$ | 24 | (90) | 63:37 | 97.0:3.0 | 96.5:3.5 |
| 4-$ClC_6H_4$ | 2-$C_4H_3O$ | 36 | (91) | 62:38 | 96.5:3.5 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 2-$C_4H_3O$ | 24 | (94) | 61:39 | 96.5:3.5 | 96.5:3.5 |
| 4-$ClC_6H_4$ | 2-$C_5H_4N$ | 20 | (80) | 60:40 | 97.0:3.0 | 97.5:2.5 |
| 4-$MeC_6H_4$ | 2-$C_4H_3O$ | 48 | (89) | 60:40 | 96.5:3.5 | 96.5:3.5 |
| Ph | Ph | 144 | (84) | 63:37 | 94.0:6.0 | 94.5:5.5 |
| Ph | 4-$ClC_6H_4$ | 72 | (88) | 62:38 | 96.0:4.0 | 97.0:3.0 |
| 4-$ClC_6H_4$ | Ph | 72 | (88) | 64:36 | 94.0:6.0 | 94.0:6.0 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | 24 | (89) | 63:37 | 94.0:6.0 | 94.0:6.0 |
| 4-$MeOC_6H_4$ | Ph | 144 | (82) | 59:41 | 91.5:8.5 | 91.5:8.5 |
| 4-$MeOC_6H_4$ | 4-$ClC_6H_4$ | 96 | (84) | 59:41 | 94.0:6.0 | 94.0:6.0 |
| 4-$O_2NC_6H_4$ | 4-$ClC_6H_4$ | 24 | (92) | 60:40 | 94.5:5.5 | 93.0:7.0 |
| 4-$MeC_6H_4$ | Ph | 144 | (82) | 60:40 | 94.0:6.0 | 94.5:5.5 |
| 4-$MeC_6H_4$ | 4-$ClC_6H_4$ | 120 | (93) | 60:40 | 95.5:4.5 | 95.5:4.5 |



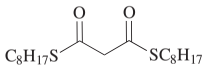


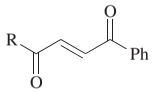
**160b** (10 mol %),
toluene, –60°, 24 h



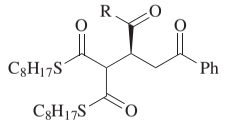
(80) dr 1:1
er 95.0:5.0
er 95.0:5.0

647





**160b** (20 mol %),
toluene, –20°, 48 h



647

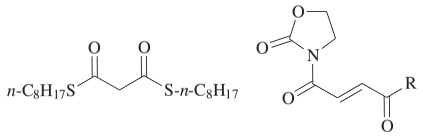
| R | | er |
|---|---|---|
| $Et_2N$ | (24) | 87.0:13.0 |
|  | (25) | 79.5:20.5 |
|  | (57) | 89.5:10.5 |
|  | (40) | 85.0:15.0 |
|  | (91) | 91.0:9.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

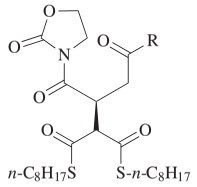
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



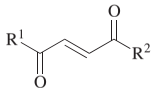


**160b** (*x* mol %), toluene

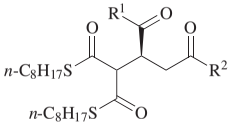


647

| R | *x* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 20 | –20 | 18 | (90) | 96.5:3.5 |
| Ph | 20 | –50 | 48 | (80) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 10 | –50 | 8 | (89) | 98.5:1.5 |
| 4-$BrC_6H_4$ | 10 | –20 | 1 | (99) | 94.5:5.5 |
| 4-$ClC_6H_4$ | 10 | –50 | 40 | (85) | 98.5:1.5 |
| 4-$ClC_6H_4$ | 10 | –20 | 4 | (83) | 96.0:4.0 |
| 4-$FC_6H_4$ | 10 | –50 | 48 | (80) | 98.5:1.5 |
| 3-$MeOC_6H_4$ | 20 | –60 | 36 | (90) | 95.0:5.0 |
| 2-$O_2NC_6H_4$ | 10 | –50 | 48 | (75) | 85.0:15.0 |
| 3-$NCC_6H_4$ | 10 | –20 | 24 | (81) | 97.5:2.5 |
| 4-$NCC_6H_4$ | 10 | –60 | 24 | (95) | 98.0:2.0 |
| 2-Np | 10 | –20 | 24 | (99) | 95.0:5.0 |
| 4-$PhC_6H_4$ | 10 | –20 | 24 | (87) | 96.0:4.0 |

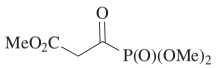


**326** (*x* mol %),
$K_2CO_3$ (1 eq), $H_2O$ (10 eq),
toluene, –50°



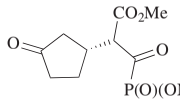
647

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Me | 2-$C_4H_3O$ | 10 | 24 | (80) | 94.5:5.5 |
| Me | 2-$C_4H_3S$ | 20 | — | (87) | 96.5:3.5 |
| Et | 2-$C_4H_3S$ | 20 | — | (82) | 96.5:3.5 |
| Me | Ph | 10 | 24 | (99) | 94.0:6.0 |
| Me | 4-$BrC_6H_4$ | 10 | 24 | (99) | 95.0:5.0 |
| Me | 4-$BrC_6H_4$ | 10 | 48 | (99) | 95.0:5.0 |
| Me | 4-$ClC_6H_4$ | 10 | 24 | (80) | 94.0:6.0 |
| Me | 3-$NCC_6H_4$ | 10 | 24 | (90) | 91.5:8.5 |
| *n*-Bu | 2-$C_4H_3S$ | 20 | — | (80) | 95.0:5.0 |
| 2-$C_4H_3S$ | 2-$C_4H_3S$ | 10 | — | (90) | 96.5:3.5 |
| Me | 3,5-$Me_2C_6H_3$ | 10 | 24 | (95) | 95.0:5.0 |
| Me | 2-Np | 10 | 24 | (88) | 92.0:8.0 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | 10 | — | (86) | 95.0:5.0 |





**202a** (1 mol %),
LAH (0.05 mol %),
*t*-BuONa (9 mol %), THF

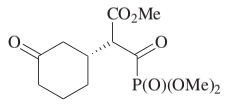


(64) er 99.5:0.5

113



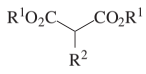
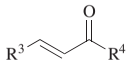
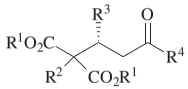
**202a** (1 mol %),
LAH (0.05 mol %),
*t*-BuONa (9 mol %), THF



(95) er 97.5:2.5

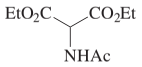
113

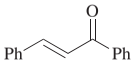
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{3-6}$  |  | **299**/$Sc(OTf)_2$ (1:1.1) (0.5–2.0 mol %), EtOH, 4 Å MS, 30–40° |  | 648 |

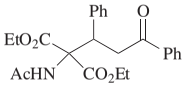
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Time (h) | | er |
|---|---|---|---|---|---|---|
| Me | H | $EtO_2C$ | Ph | 36 | (72) | 97.5:2.5 |
| Me | Cl | $EtO_2C$ | 2-$C_4H_3O$ | 30 | (84) | 96.5:3.5 |
| Me | Cl | $EtO_2C$ | 2-$C_4H_3S$ | 26 | (92) | 99.5:0.5 |
| Me | Cl | $EtO_2C$ | Ph | 20 | (95) | 99.5:0.5 |
| Me | Cl | $EtO_2C$ | 4-$BrC_6H_4$ | 24 | (96) | 99.5:0.5 |
| Me | Cl | $EtO_2C$ | 2-$ClC_6H_4$ | 24 | (96) | 97.5:2.5 |
| Me | Cl | $EtO_2C$ | 3-$ClC_6H_4$ | 28 | (95) | 99.5:0.5 |
| Me | Cl | $EtO_2C$ | 4-$ClC_6H_4$ | 24 | (95) | 99.5:0.5 |
| Me | Cl | $EtO_2C$ | 3,4-$Cl_2C_6H_3$ | 24 | (97) | 99.0:1.0 |
| Me | Cl | $EtO_2C$ | 4-$FC_6H_4$ | 28 | (95) | 99.0:1.0 |
| Me | Cl | $EtO_2C$ | 3-$MeOC_6H_4$ | 32 | (86) | 95.0:5.0 |
| Me | Cl | $EtO_2C$ | 4-$MeOC_6H_4$ | 32 | (90) | 99.0:1.0 |
| Me | Cl | $EtO_2C$ | 4-$MeC_6H_4$ | 24 | (96) | 99.5:0.5 |
| Me | Cl | $EtO_2C$ | 2-Np | 24 | (93) | 99.0:1.0 |
| Me | Cl | Ph | Ph | 48 | (78) | 99.0:1.0 |
| Et | H | $EtO_2C$ | Ph | 36 | (82) | 99.0:1.0 |
| Et | Me | $EtO_2C$ | Ph | 26 | (94) | 99.0:1.0 |
| Et | $CH_2$=$CHCH_2$ | $EtO_2C$ | Ph | 48 | (89) | >99.5:0.5 |
| *i*-Pr | H | $EtO_2C$ | Ph | 15 | (93) | 99.0:1.0 |
| *t*-Bu | H | $EtO_2C$ | Ph | 36 | (90) | 98.5:1.5 |

$C_3$

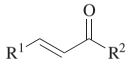




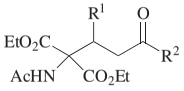
Catalyst (6 mol %),
KOH (6 mol %), 60°, 1 h



| Catalyst | | er | |
|---|---|---|---|
| **319a** | (51) | 88.0:12.0 | 649 |
| **319b** | (56) | 60.0:40.0 | |
| **321** | (52) | 83.0:17.0 | |
| **322** | (51) | 91.0:9.0 | |



**320** (10 mol %),
KOH (6 mol %),
solvent, 60°

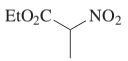


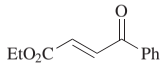
650

Catalyst Recycling ($R^1 = R^2 = Ph$)

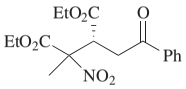
| Run | | er |
|---|---|---|
| 1 | (55) | 85.0:15.0 |
| 2 | (56) | 85.0:15.0 |
| 3 | (55) | 86.0:14.0 |
| 4 | (56) | 85.0:15.0 |

| $R^1$ | $R^2$ | Solvent | | er |
|---|---|---|---|---|
| Ph | Ph | — | (55) | 85.0:15.0 |
| Ph | 4-$ClC_6H_4$ | toluene | (80) | 52.0:48.0 |
| Ph | 4-$MeOC_6H_4$ | toluene | (80) | 71.0:29.0 |
| 2-$ClC_6H_4$ | Ph | — | (61) | 78.0:22.0 |
| 4-$ClC_6H_4$ | Ph | toluene | (73) | 52.0:48.0 |
| 4-$MeOC_6H_4$ | Ph | toluene | (67) | 55.0:45.0 |
| 4-$O_2NC_6H_4$ | Ph | — | (67) | 62.5:37.5 |





**268** (5 mol %),
0.5 M in xylene, rt



(99) dr 81:19
er 84.0:16.0
er 96.0:4.0

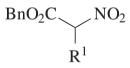
651

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

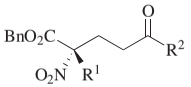
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{3-4}$





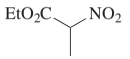
**301** (*x* mol %), THF



652

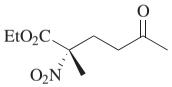
| $R^1$ | $R^2$ | *x* | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|
| Me | Me | 5 | –30 | 95 | (81) | 90.0:10.0 |
| Me | Me | 10 | –30 | 72 | (83) | 87.0:13.0 |
| Me | Et | 5 | –24 | 72 | (—) | 77.5:22.5 |
| Me | Et | 10 | –23 | 72 | (84) | 74.5:25.5 |
| Me | Ph | 10 | –24 | 72 | (86) | 52.5:47.5 |
| Me | Ph | 10 | rt | 18 | (87) | 54.0:46.0 |
| Et | Me | 10 | –21 | 72 | (86) | 73.5:26.5 |
| Et | Et | 10 | –23 | 72 | (84) | 66.5:33.5 |

$C_3$



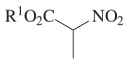


Catalyst (10 mol %),
$CH_2Cl_2$, –20°, 3 d



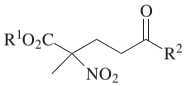
| Catalyst | | er |
|---|---|---|
| **324** | (100) | 90.0:10.0 |
| **325** | (100) | 95.0:5.0 |

230



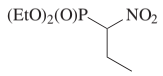


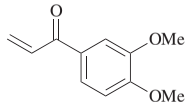
**330** (2 mol %),
100 mM in toluene, 4°



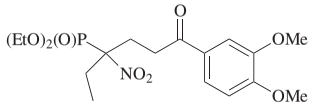
653

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Et | Me | (96) | 50.0:50.0 |
| *t*-Bu | Ph | (85) | 75.0:25.0 |





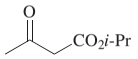
**280** (10 mol %),
mesitylene/xylene (85:15),
–65°, 32–40 h

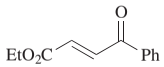


(89) er 97.0:3.0

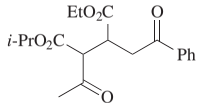
590

$C_4$



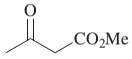


**299**/$Sc(OTf)_2$ (1:1.1)
(0.75 mol %),
EtOH, 4 Å MS, 40°, 30 h



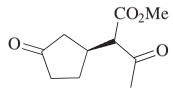
(85) dr 56:44
er (major) 95.0:5.0
er (minor) 95.0:5.0

648



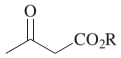


**288a** (*x* mol %)
toluene, rt, 24 h



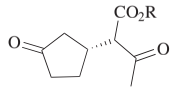
614

| *x* | | dr | er |
|---|---|---|---|
| 0.1 | (27) | 1:1 | 95.5:4.5 |
| 0.2 | (85) | 1:1 | 98.0:2.0 |





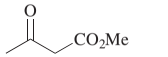
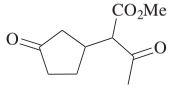
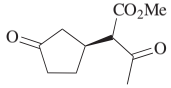
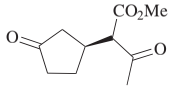
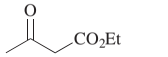
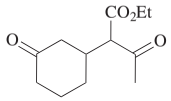
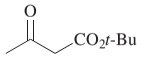
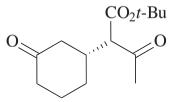
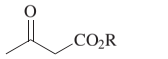
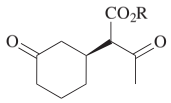
Catalyst (2 mol %),
toluene, rt



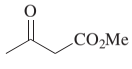
654

| R | Catalyst | | dr | er |
|---|---|---|---|---|
| Me | **288a** | (100) | 1:1 | 92.5:7.5 |
| Me | **288b** | (99) | 1:1 | 95.5:4.5 |
| *t*-Bu | **288a** | (93) | 1:1 | 86.0:14.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

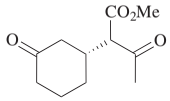
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **288b** (2 mol %), *t*-BuOH, 30–40° |  | (100) dr 1:1<br>er 95.5:4.5 | 613 |
| |  | **288b** (1–2 mol %), toluene, 40°, 24 h |  | (99) dr 1:1<br>er 95.5:4.5 | 34 |
| |  | **333b** (10 mol %), La(O*i*-Pr)$_3$ (10 mol %), THF/DME (9:1), rt, 24 h |  | (94) dr 1:1<br>er 86.5:13.5 | 655 |
|  |  | **1** (12 mol %), Yb(OTf)$_3$ (12 mol %), NaOH (20 mol %), $H_2O$, 90°, 12 h |  | (77) er 85.0:15.0 | 584 |
|  |  | **296a** (10 mol %), $CHCl_3$, rt |  | (77) dr 1:1<br>er 63.0:37.0 | 600 |
|  |  | **333b** (10 mol %), La(O*i*-Pr)$_3$ (10 mol %), THF/DME (9:1), rt |  | dr 1:1 | 655 |

| R | Time (h) | | er |
|---|---|---|---|
| Me | 24 | (82) | 96.0:4.0 |
| Et | 42 | (71) | 94.0:6.0 |

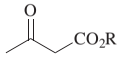




**333c** (10 mol %),
La(O*i*-Pr)$_3$ (5 mol %),
*i*-Pr$_2$NEt (30 mol %),
1 M in THF, rt, 24 h

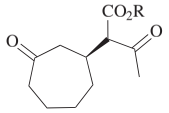


(77) er 96.0:4.0.0 656



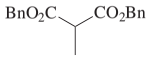


Catalyst (10 mol %),
La(O*i*-Pr)$_3$ (10 mol %),
THF/DME (9:1), rt



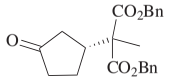
dr 1:1 655

| R | Catalyst | Time (h) | | er |
|---|---|---|---|---|
| Me | **333b** | 42 | (83) | 96.0:4.0 |
| Et | **333a** | 24 | (88) | 94.5:5.5 |

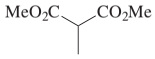




**202a** (10 mol %),
La(O*i*-Pr)$_3$ (3.33 mol %),
*t*-BuONa(10 mol %),
THF, –40°, 36 h

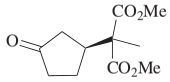


(89) er 86.0:14.0 50

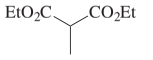




**288a** (1–2 mol %),
toluene, 30°, 48 h

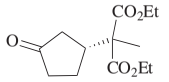


(51) er 98.5:1.5 34





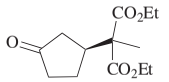
**301** (10 mol %),
THF, 0° to rt, 72 h



(84) er 95.5:4.5 112

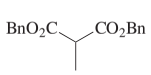
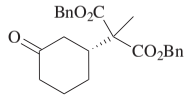
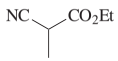
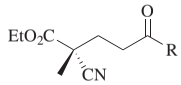
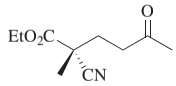


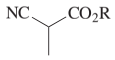
**318** (10 mol %),
THF, 0°, 0.25 h



(88) er 78.0:22.0 620

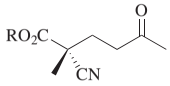
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **202a** (10 mol %), La(O*i*-Pr)$_3$ (3.33 mol %), *t*-BuONa (10 mol %), THF, rt, 12 h |  (96) er 95.0:5.0 | 50 |
|  |  | *ent*-**164b** (10 mol %), toluene, 4 Å MS, –60°, 96 h |  | 188 |
| | | | R (91) er<br>2-$C_4H_3S$ (91) 98.0:2.0<br>Ph (76) 95.5:4.5<br>4-$BrC_6H_4$ (67) 92.5:7.5<br>4-$MeOC_6H_4$ (61) 92.5:7.5 | |
| |  | **329** (1 mol %), *i*-Pr$_2$NEt (10 mol %), syringe pump, toluene, 20°, 16 h |  (84) er 62.5:37.5 | 657 |



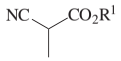


**334** (1 mol %), Rh(acac)$(CO)_2$ (1 mol %), solvent



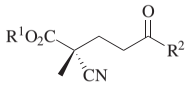
658

| R | Solvent | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Et | benzene | 30 | 40 | (90) | 77.5:22.5 |
| Et | toluene | 0 | 13 | (86) | 86.5:13.5 |
| *i*-Pr | benzene | 0 | 6 | (93) | 86.0:14.0 |
| *i*-Pr | toluene | 0 | 11 | (95) | 83.0:17.0 |



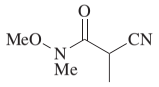


**335** (*x* mol %), *i*-$Pr_2NEt$, toluene or benzene, rt



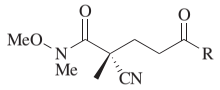
659

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Et | Me | 0.5 | 4 | (89) | 90.5:9.5 |
| *i*-Pr | Me | 0.5 | 4 | (90) | 90.0:10.0 |
| *i*-Pr | Et | 0.5 | 4 | (91) | 91.5:8.5 |
| *i*-Bu | Me | 1.0 | 24 | (93) | 90.0:10.0 |





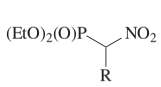
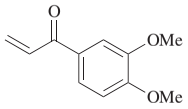
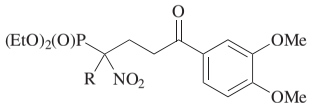
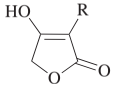
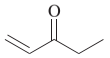
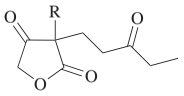
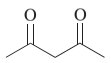
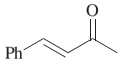
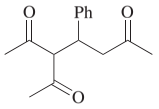
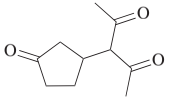
**336** (1 mol %), Rh(acac)$(CO)_2$ (0.95 mol %), benzene, 3°



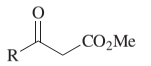
98

| R | Time (h) | | er |
|---|---|---|---|
| Me | 22 | (98) | 96.5:3.5 |
| Ph | 18 | (99) | 97.0:3.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

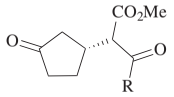
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{4–8}$  |  | **280** (10 mol %), mesitylene/xylene (85:15), –65°, 32–40 h |  | 590 |
| | | | R (95) er<br>*n*-Pr (95) 96.0:4.0<br>*c*-$C_3H_5$ (90) 93.5:6.5<br>*n*-Bu (97) 96.0:4.0<br>*i*-Bu (88) 96.0:4.0<br>*n*-$C_5H_{11}$ (94) 97.0:3.0<br>*c*-$C_6H_{11}$ (87) 93.5:6.5<br>Bn (85) 93.0:7.0 | |
| $C_{4–10}$  |  | **1** (30 mol %), DMSO, rt, 48 h |  | R (95) er<br>Me (95) <52.5:47.5<br>Bn (80) <52.5:47.5 | 660 |
| $C_5$  |  | **1** (12 mol %), $Yb(OTf)_3$ (12 mol %), NaOH (20 mol %), $H_2O$, 90°, 24 h |  | (70) er 59.5:40.5 | 584 |
| |  | **1** (12 mol %), $Yb(OTf)_3$ (12 mol %), NaOH (20 mol %), $H_2O$, 90°, 21 h |  | (61) er 80.5:19.5 | 584 |

$C_{5-7}$





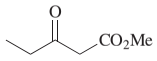
Catalyst (2 mol %),
toluene, rt



654

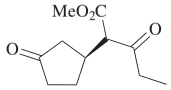
| R | Catalyst | | dr | er |
|---|---|---|---|---|
| Et | **288a** | (92) | 1:1 | 90.0:10.0 |
| Et | **288b** | (99) | 1:1 | 94.5:5.5 |
| *i*-Pr | **288a** | (97) | 1:1 | 94.0:6.0 |
| *t*-Bu | **288a** | (100) | 1:1 | 98.5:1.5 |
| *t*-Bu | **288b** | (92) | 1:1 | 93.5:6.5 |

$C_5$



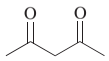


**333b** (10 mol %),
La(O*i*-Pr)$_3$ (10 mol %),
THF/DME (9:1), rt, 24 h



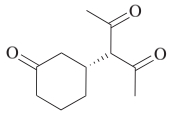
(85) dr 1:1
er 90.0:10.0

655



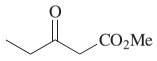


**1** (12 mol %),
Yb(OTf)$_3$ (12 mol %),
NaOH (20 mol %),
$H_2O$, 90°, 24 h



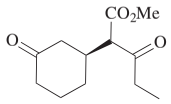
(94) er 89.5:10.5

584





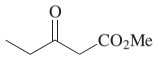
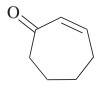
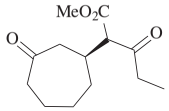
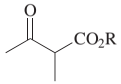
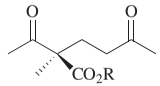
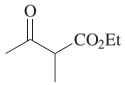
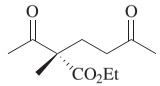
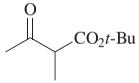
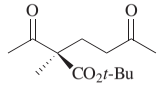
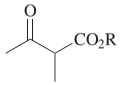
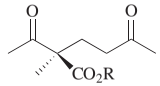
**333b** (10 mol %),
La(O*i*-Pr)$_3$ (10 mol %),
THF/DME (9:1), rt, 24 h



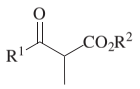
(71) dr 1:1
er 95.5:4.5

655

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

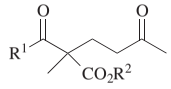
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **333a** (10 mol %), La(O*i*-Pr)$_3$ (10 mol %), THF/DME (9:1), rt, 24 h |  (91) dr 1:1, er 95.0:5.0 | 655 |
|  |  | ***ent*-202a** (15 mol %), La(O*i*-Pr)$_3$ (5 mol %), *t*-BuONa (15 mol %), $CH_2Cl_2$, –50° |  | 51 |
| | | | R: Et, Time (h): 20, (94), er: 87.0:13.0 | |
| | | | R: Bn, Time (h): 16, (93), er: 91.5:8.5 | |
|  |  | **288b** (1 mol %), $CH_2Cl_2$, –30°, 72 h |  (73) er 55.0:45.0 | 661 |
|  |  | **339a** (5 mol %), [hmim][$BF_4$], 0°, 36 h |  (63) er 93.5:6.5 | 95 |
|  |  | Catalyst (10 mol %), *x* M in THF, 0° |  | |
| | | R: *t*-Bu, Catalyst: **339a**, *x*: 4–5, Time (h): 72, (88), er: 95.0:5.0 | | 32, 31 |
| | | R: Ph, Catalyst: **339b**, *x*: 4–5, Time (h): 72, (69), er: 96.5:3.5 | | 32, 31 |
| | | R: 2-Br$C_6H_4$, Catalyst: **339a**, *x*: 4, Time (h): 36, (82), er: 97.0:3.0 | | 32 |

$C_{5-10}$





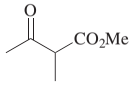
**340** (5 mol %),
$Et_3O\ PF_6$ (10 mol %),
$CH_2Cl_2$, rt



662

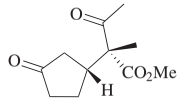
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Et | 24 | (59) | 55.0:45.0 |
| Me | Bn | 24 | (49) | 64.5:35.5 |
| Ph | Et | 72 | (26) | 80.0:20.0 |

$C_5$





**333c** (10 mol %),
$La(Oi\text{-}Pr)_3$ (5 mol %),
1 M in DME, rt, 24 h

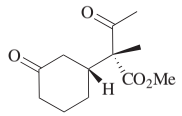


(100) dr 76:24
er (major) 89.5:10.5
er (minor) 86.5:13.5

656

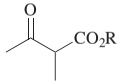


**333c** (10 mol %),
$La(Oi\text{-}Pr)_3$ (5 mol %),
1 M in DME, rt, 24 h



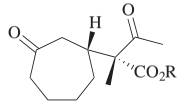
(92) dr 86:14
er (major) 93.0:7.0
er (minor) 90.0:10.0

656





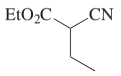
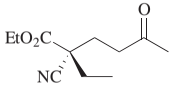
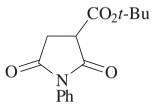
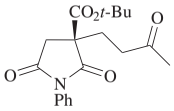
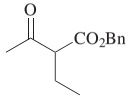
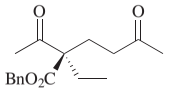
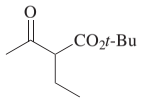
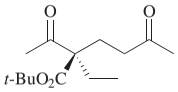
**333c** (10 mol %),
$La(Oi\text{-}Pr)_3$ (5 mol %),
1 M in DME, rt, 24 h



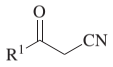
656

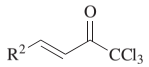
| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| Me | (89) | 86:14 | 91.0:9.0 | 91.0:9.0 |
| Et | (86) | 83:17 | 87.5:12.5 | 90.5:9.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

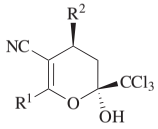
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | **334** (1 mol %), $Rh(acac)(CO)_2$ (1 mol %), benzene, 30°, 13 h |  | (89) er 57.0:43.0 | 658 |
|  |  | **342** (5 mol %), *i*-$Pr_2NEt$ (30 mol %), $CH_2Cl_2$, –40°, 0.3 d |  | (98) er 85.0:15.0 | 663 |
| $C_6$ | | | | | |
|  |  | *ent*-**202a** (15 mol %), La(O*i*-Pr)$_3$ (5 mol %), *t*-BuONa (15 mol %), $CH_2Cl_2$, –50°, 16 h |  | (98) er 94.5:5.5 | 51 |
|  |  | **339a** (10 mol %), 4 M in THF, rt, 7 d |  | (41) er 82.5:17.5 | 32 |

$C_{6-9}$





**350** (2 mol %), xylene, –10°

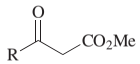
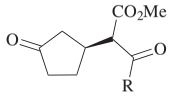


single diastereomer

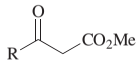
664

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| *n*-Pr | Ph | 168 | (64) | 93.5:6.5 |
| Ph | *n*-Pr | 96 | (96) | 86.0:14.0 |
| Ph | 2-$C_4H_3O$ | 96 | (87) | 93.0:7.0 |
| Ph | Ph | 67 | (94) | 95.0:5.0 |
| Ph | 4-$BrC_6H_4$ | 36 | (99) | 95.0:5.0 |
| Ph | 2-$ClC_6H_4$ | 40 | (98) | 91.0:9.0 |
| Ph | 3-$ClC_6H_4$ | 35 | (99) | 95.0:5.0 |
| Ph | 4-$ClC_6H_4$ | 60 | (95) | 95.0:5.0 |
| Ph | 2,4-$Cl_2C_6H_3$ | 36 | (97) | 92.0:8.0 |
| Ph | 4-$FC_6H_4$ | 66 | (92) | 95.0:5.0 |
| Ph | 4-$O_2NC_6H_4$ | 36 | (98) | 97.5:2.5 |
| Ph | 4-$MeC_6H_4$ | 96 | (93) | 95.0:5.0 |
| Ph | 1-Np | 48 | (97) | 95.0:5.0 |
| 4-$BrC_6H_4$ | Ph | 96 | (84) | 94.0:6.0 |
| 4-$FC_6H_4$ | Ph | 96 | (94) | 94.5:5.5 |
| 4-$MeOC_6H_4$ | Ph | 144 | (66) | 95.0:5.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

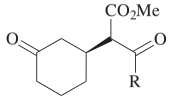
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | | Refs. |
|---|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | | |
| $C_{6-7}$  |  | **333a** (10 mol %), La(O*i*-Pr)$_3$ (10 mol %), THF, rt |  | dr 1:1 | 655 |

| R | Time (h) | | er |
|---|---|---|---|
| *n*-Pr | 24 | (75) | 87.5:12.5 |
| $CH_2$=$CH(CH_2)_2$ | 48 | (84) | 86.9:13.1 |

$C_{6-10}$ 



Catalyst (10 mol %), La(O*i*-Pr)$_3$ (10 mol %), solvent, rt

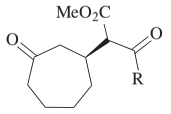


dr 1:1 655

| R | Catalyst | Solvent | Time (h) | | er |
|---|---|---|---|---|---|
| *n*-Pr | **333b** | THF/DME (9:1) | 36 | (81) | 93.5:6.5 |
| $CH_2$=$CH(CH_2)_2$ | **333a** | THF | 48 | (73) | 90.0:10.0 |
| HC≡$C(CH_2)_2$ | **333a** | THF/HFIP (19:1) | 48 | (65) | 86.5:13.5 |
| *c*-$C_6H_{11}CH_2$ | **333a** | THF | 48 | (67) | 86.5:13.5 |



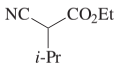
**333a** (10 mol %), La(O*i*-Pr)$_3$ (10 mol %), solvent, rt



dr 1:1 655

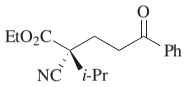
| R | Solvent | Time (h) | | er |
|---|---|---|---|---|
| *n*-Pr | THF/DME (9:1) | 24 | (87) | 94.0:6.0 |
| $CH_2$=$CH(CH_2)_2$ | THF/HFIP (19:1) | 48 | (83) | 91.5:8.5 |
| HC≡$C(CH_2)_2$ | THF | 48 | (74) | 88.5:11.5 |
| *c*-$C_6H_{11}CH_2$ | THF | 48 | (66) | 84.5:15.5 |

$C_6$



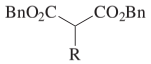


*ent*-**164b** (10 mol %),
toluene, 4 Å MS, –20°, 120 h



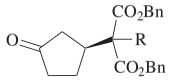
(66) er 96.5:3.5 188

$C_{6-8}$





**301** (10 mol %),
1 M in solvent, 4°



618

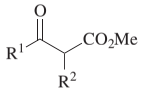
| R | Solvent | Time (h) | | er |
|---|---|---|---|---|
| allyl | DME | 86 | (86) | 99.5:0.5 |
| allyl | DME/HFIP (10:1) | 87 | (93) | 99.5:0.5 |
| $MeO_2C(CH_2)_2$ | DME | 88 | (69) | 99.5:0.5 |
| $MeO_2C(CH_2)_2$ | DME/HFIP (10:1) | 87 | (83) | 99.0:1.0 |
| $EtO_2C(CH_2)_2$ | DME | 92 | (62) | 99.0:1.0 |
| $EtO_2C(CH_2)_2$ | DME/HFIP (10:1) | 92 | (75) | 98.0:2.0 |
| $EtO_2C(CH_2)_3$ | DME | 89 | (55) | 97.5:2.5 |
| $EtO_2C(CH_2)_3$ | DME/HFIP (10:1) | 89 | (71) | 97.5:2.5 |
| $AcOCH_2CH{=}CHCH_2$ | DME | 84 | (77) | 99.5:0.5 |
| $AcOCH_2CH{=}CHCH_2$ | DME/HFIP (10:1) | 83 | (87) | 99.0:1.0 |
| $CH_2{=}CH(CH_2)_2$ | DME | 88 | (65) | 99.5:0.5 |
| $CH_2{=}CH(CH_2)_2$ | DME/HFIP (10:1) | 85 | (80) | 99.0:1.0 |
| $CH_2{=}CH(CH_2)_3$ | DME | 106 | (66) | 98.0:2.0 |
| $CH_2{=}CH(CH_2)_3$ | DME/HFIP (10:1) | 88 | (84) | 98.0:2.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

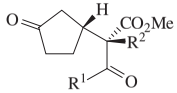
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{6-13}$





**333c** (10 mol %),
La(O*i*-Pr)$_3$ (5 mol %),
1 M in DME, rt

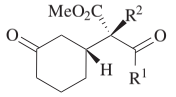


656

| $R^1$ | $R^2$ | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| Et | Me | 38 | (93) | 80:20 | 82.0:18.0 | 80.0:20.0 |
| Me | allyl | 70 | (86) | 77:23 | 78.0:22.0 | 81.5:18.5 |
| Me | HC≡CCH$_2$ | 70 | (76) | 73:27 | 80.5:19.5 | 75.0:25.0 |
| *i*-Pr | Me | 36 | (71) | 86:14 | 81.5:18.5 | 58.0:42.0 |
| Me | Ph(CH$_2$)$_3$ | 48 | (80) | 73:27 | 70.5:29.5 | 90.5:9.5 |



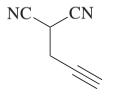
**333c** (10 mol %),
La(O*i*-Pr)$_3$ (5 mol %),
1 M in DME, rt



656

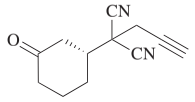
| $R^1$ | $R^2$ | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| Me | Et | 48 | (65) | 77:23 | 83.5:16.5 | 89.0:11.0 |
| Et | Me | 38 | (83) | 80:20 | 92.5:7.5 | 77.5:22.5 |
| Me | allyl | 48 | (75) | 72:28 | 81.0:19.0 | 92.0:8.0 |
| Me | HC≡CCH$_2$ | 48 | (64) | 79:21 | 83.0:17.0 | 71.0:29.0 |
| *i*-Pr | Me | 96 | (42) | 84:16 | 90.0:10.0 | 67.5:32.5 |
| Me | Ph(CH$_2$)$_3$ | 70 | (37) | 68:32 | 78.0:22.0 | 93.0:7.0 |

$C_6$

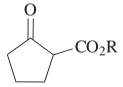




**152** (5 mol %),
**345** (10 mol %),
$Et_2O$, rt, 18 h

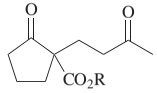


(95) er 96.0:4.0 665





**1** (12 mol %),
$Yb(OTf)_3$ (12 mol %),
NaOH (20 mol %),
$H_2O$, 60°

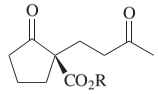


584

| R | Time (h) | | er |
|---|---|---|---|
| Et | 5 | (95) | <52.5:47.5 |
| *t*-Bu | 10 | (99) | <52.5:47.5 |

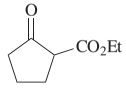


**125** (37.5 mol %),
$Ni(OAc)_2 \cdot 4H_2O$ (5 mol %),
$CH_2Cl_2$, rt, 18 h



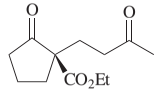
| R | | er |
|---|---|---|
| Me | (36) | 65.5:34.5 |
| Et | (40) | 70.0:30.0 |
| *i*-Pr | (53) | 53.0:47.0 |
| *i*-Bu | (31) | 87.0:13.0 |
| Bn | (78) | 60.5:39.5 |

666





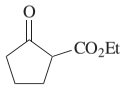
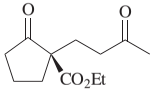
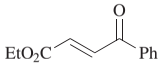
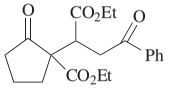
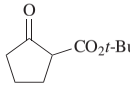
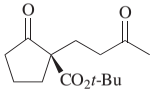
*ent*-**202a** (*x* mol %),
$La(Oi\text{-}Pr)_3$ (10–20 mol %),
*t*-BuONa (30–60 mol %),
$CH_2Cl_2$, –50°



51

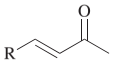
| *x* | Time (h) | | er |
|---|---|---|---|
| 10 | 17 | (95) | 87.5:12.5 |
| 20 | 18 | (97) | 92.0:8.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

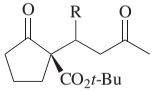
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_6$  |  | **288b** (1 mol %), $CH_2Cl_2$, –30°, 3 h |  (>99) er 83.5:16.5 | 661 |
| |  | **299**/$Sc(OTf)_2$ (1:1.1) (1.5 mol %), EtOH, 4 Å MS, rt, 30 h |  (83) dr 67:33<br>er (major) 97.5:2.5<br>er (minor) 97.5:2.5 | 648 |
|  |  | **339a** (5 mol %), [hmim][$BF_4$], –20°, 15 h |  (97) er 94.0:6.0 | 95 |

Catalyst Recycling

| Run | Time (h) | | er |
|---|---|---|---|
| 1 | 8 | (98) | 91.5:8.5 |
| 2 | 8 | (98) | 92.0:8.0 |
| 3 | 8 | (92) | 91.5:8.5 |
| 4 | 8 | (91) | 92.0:8.0 |
| 5 | 15 | (94) | 92.0:8.0 |

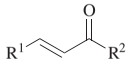


**339a** (5 mol %), THF

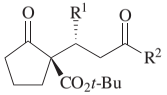


31

| R | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Me | –20 | 24 | (89) | 8:1 | 99.5:0.5 |
| Ph | 0 | — | (83) | 3.6:1 | 98.5:1.5 |



**339a** (*x* mol %), 2–4 M in THF

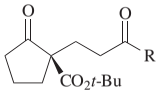


32

| $R^1$ | $R^2$ | *x* | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|
| H | Me | 2 | –20 | 40 | (93) | — | 96.5:3.5 |
| H | Et | 5 | –20 | 20 | (84) | — | 94.0:6.0 |
| Me | Me | 5 | –20 | 24 | (89) | 8:1 | 99.5:0.5 |
| Ph | Me | 5 | 0 | 36 | (83) | 3.6:1 | 98.5:1.5 |

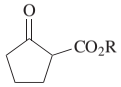


Catalyst (*x* mol %),
5 M in THF, –20°



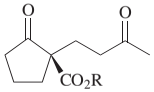
31

| R | Catalyst | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Me | **339b** | 2 | 40 | (93) | 96.5:3.5 |
| Me | **339b** | 5 | 24 | (92) | 96.0:4.0 |
| Et | **339a** | 5 | 20 | (84) | 94.0:6.0 |





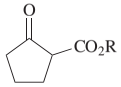
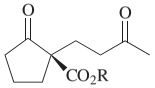
**340** (5 mol %),
$Et_3O\,PF_6$ (10 mol %),
additive, solvent, rt



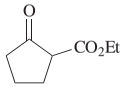
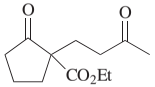
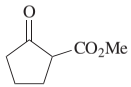
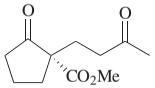
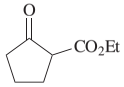
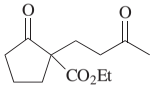
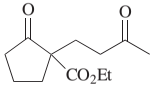
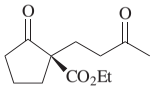
662

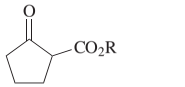
| R | Additive | Solvent | Time (h) | | er |
|---|---|---|---|---|---|
| Et | — | $CH_2Cl_2$ | 18 | (95) | 70.0:30.0 |
| *t*-Bu | $AgBF_4$ | $CH_2Cl_2/Et_2O$ (1:1) | 24 | (>99) | 96.5:3.5 |
| Bn | — | $CH_2Cl_2$ | 24 | (100) | 72.0:28.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_6$ | | | | |
|  |  | **341a** (12.5 mol %), $Yb(OTf)_3$ (10 mol %), solvent, 4 Å MS |  | 667 |

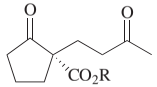
| Solvent | Temp | | er |
|---|---|---|---|
| $CH_2Cl_2$ | –41° to rt | (85) | 93.0:7.0 |
| MeCN | –41° | (96) | 98.0:2.0 |

| | | | | | |
|---|---|---|---|---|---|
|  |  | **342** (5 mol %), *i*-$Pr_2NEt$ (30 mol %), $CH_2Cl_2$, –40°, 5 h |  | (98) er 72.5:27.5 | 663 |
|  |  | **344** (2 or 10 mol %), 4-xylene, 50°, 48 h |  | (88) er 89.0:11.0 | 204 |
|  |  | **346** (7.5 mol %), $NiCl_2•6H_2O$ (5 mol %), $CH_2Cl_2$, rt, overnight |  | 76% conv. er 58.5:41.5 | 668 |
| |  | **347** (6 mol %), $Sc(OTf)_3$ (5 mol %), 0.02 M in $ClCH_2CH_2Cl$, 40°, 36 h |  | (69) er 80.5:19.5 | 669 |
| |  | **348** (10 mol %), PhI, rt, 21 h |  | (>99) er 87.0:13.0 | 670 |



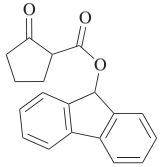


**351** (10 mol %),
toluene, –40°, 12 h



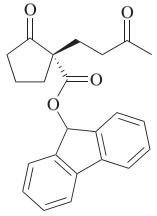
| R | | er |
|---|---|---|
| Me | (88) | 90.0:10.0 |
| Et | (82) | 89.0:11.0 |

671



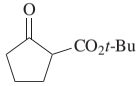


**358** (2 mol %),
$K_2CO_3$ (10 mol %),
*i*-Pr$C_6H_5$, –78 to –40°, 8 h



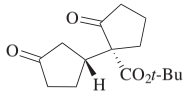
(>99) er 98.5:1.5

214





**339a** (2–5 mol %),
2–4 M in THF, rt, 12 h

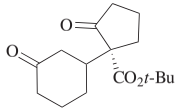


(85) dr 1.2:1
er (major) 96.5:3.5
er (minor) 93.0:7.0

32



**339a** (2–5 mol %),
2–4 M in THF, rt 12 h



(98) dr 1.6:1
er (major) 98.0:2.0
er (minor) 98.5:1.5

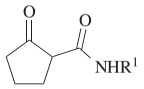
32

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

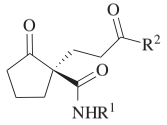
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$



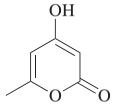


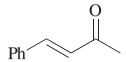
*ent*-**164b** (10 mol %), toluene, rt



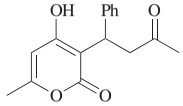
672

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | Me | 48 | (100) | 93.5:6.5 |
| 3-$MeOC_6H_4$ | Me | 48 | (64) | 91.5:8.5 |
| 4-$MeOC_6H_4$ | Me | 40 | (98) | 91.5:8.5 |
| 4-$O_2NC_6H_4$ | Me | 72 | (62) | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | Et | — | (78) | 92.0:8.0 |
| Ts | Me | 72 | (88) | 99.5:4.5 |
| Ts | Et | — | (96) | 96.5:3.5 |
| 1-Np | Me | 48 | (90) | 95.5:4.5 |
| 1-Np | Et | — | (90) | 95.5:4.5 |
| 1-anthracenyl | Me | 48 | (90) | 95.5:4.5 |





**337** (10 mol %), $CH_2Cl_2$, rt, 150 h

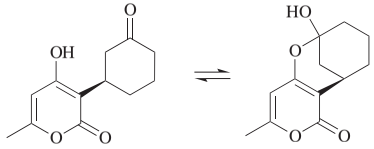


(76) er 92.5:7.5

172

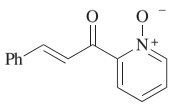


**343** (10 mol %), *n*-$C_5H_{11}CO_2H$ (10 eq), THF, rt, 36 h

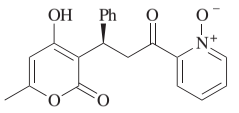


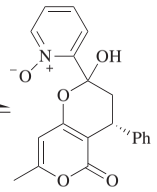
(88) er 97.5:2.5

673



**341** (6 mol %),
$Zn(OTf)_2$ (5 mol %),
DBU (10 mol %),
$CH_2Cl_2$, rt, 1.5 h

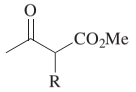




(90) er 98.0:2.0

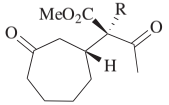
674

$C_{7-13}$



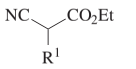


**333c** (10 mol %),
$La(Oi\text{-}Pr)_3$ (5 mol %),
1 M in DME, rt, 96 h



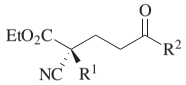
656

| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| allyl | (69) | 74:26 | 71.0:29.0 | 86.0:14.0 |
| $HC{\equiv}CCH_2$ | (58) | 84:16 | 85.0:15.0 | 92.0:8.0 |
| $Ph(CH_2)_3$ | (45) | 81:19 | 69.5:30.5 | 83.5:16.5 |





*ent*-**164b** (10 mol %),
toluene, 4 Å MS, –60°, 96 h



188

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| *n*-Bu | Ph | (72) | 96.0:4.0 |
| 2-$C_4H_3S$ | Me | (93) | 91.0:9.0 |
| Ph | Me | (95) | 95.5:4.5 |
| Ph | 2-$C_4H_3S$ | (99) | 96.5:3.5 |
| Ph | Ph | (94) | 93.0:7.0 |
| 4-$BrC_6H_4$ | Me | (86) | 94.0:6.0 |
| 4-$BrC_6H_4$ | Ph | (93) | 92.5:7.5 |
| 4-$ClC_6H_4$ | Me | (87) | 93.5:6.5 |
| 2-$FC_6H_4$ | Me | (95) | 97.5:2.5 |
| 2-$FC_6H_4$ | 2-$C_4H_3S$ | (97) | 98.5:1.5 |
| 2-$FC_6H_4$ | Ph | (90) | 98.5:1.5 |
| 2-$FC_6H_4$ | 4-$BrC_6H_4$ | (99) | 96.0:4.0 |
| 2-$FC_6H_4$ | 4-$MeOC_6H_4$ | (97) | 95.5:4.5 |
| 4-$FC_6H_4$ | Me | (94) | 96.0:4.0 |

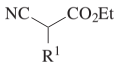
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

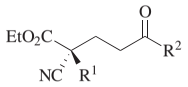
*Continued from previous page*

$C_{7-13}$





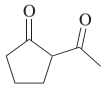
*ent*-**164b** (10 mol %),
toluene, 4 Å MS, –60°, 96 h



| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 4-$MeOC_6H_4$ | Me | (95) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | Ph | (95) | 94.5:5.5 |
| 3,4-$(OCH_2O)C_6H_3$ | Me | (88) | 97.5:2.5 |
| 3-$CF_3C_6H_4$ | Me | (95) | 92.5:7.5 |
| Bn | 2-$C_4H_3S$ | (98) | 98.5:1.5 |
| Bn | Ph | (90) | 96.0:4.0 |
| 1-Np | Ph | (97) | 95.5:4.5 |

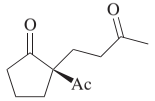
188

$C_7$



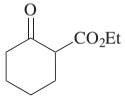


**125** (37.5 mol %),
$Ni(OAc)_2 \cdot 4H_2O$ (5 mol %),
$CH_2Cl_2$, rt, 18 h



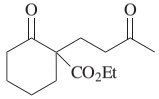
(41) er 78.5:21.5

666





**1** (12 mol %),
$Yb(OTf)_3$ (12 mol %),
NaOH (20 mol %),
$H_2O$, 60°, 6 h

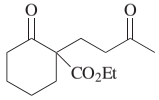


(95) er <52.5:47.5

584

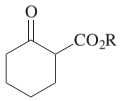


**125** (37.5 mol %),
$Cu(OAc)_2 \cdot H_2O$ (5 mol %),
[bmim][$BF_4$], rt, 24 h



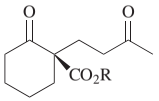
(67) er 92.0:8.0

675





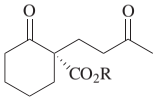
**125** (37.5 mol %),
$Ni(OAc)_2 \cdot 4H_2O$ (5 mol %),
$CH_2Cl_2$, rt, 18 h



(37) er 95.5:4.5 666



**144c** (5.6 mol %),
50% NaOH,
toluene, 20°

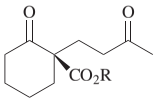


| R | | er |
|---|---|---|
| Et | (55) | 52.0:48.0 |
| Bn | (25) | 60.0:40.0 |

386

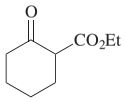


*ent*-**202a** (*x* mol %),
$La(Oi\text{-}Pr)_3$ (5–10 mol %),
*t*-BuONa (15–30 mol %),
$CH_2Cl_2$, –50°



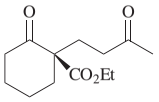
51

| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| Et | 5 | 19 | (89) | 95.5:4.5 |
| Et | 10 | 19 | (85) | 96.5:3.5 |
| Bn | 10 | 12 | (73) | 95.5:4.5 |





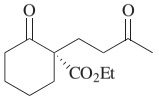
**288b** (1 mol %),
$CH_2Cl_2$, –30°, 72 h



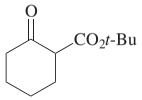
(30) er 67.0:33.0 661



**291a** (10 mol %),
toluene, –30°, 36 h

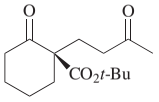


(97) er 87.5:12.5 104





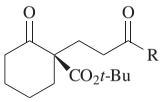
**339a** (5 mol %),
[hmim][$BF_4$], 0°, 36 h



(92) er 93.0:7.0 95



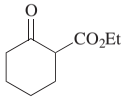
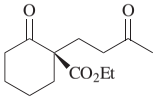
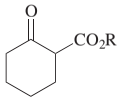
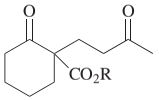
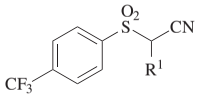
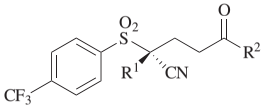
**339a** (5 mol %),
1–5 M in THF, 0°, 72 h



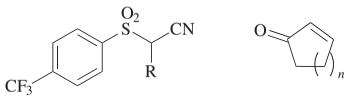
| R | | er |
|---|---|---|
| Me | (92) | 95.0:5.0 |
| Et | (89) | 93.0:7.0 |

32, 31

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

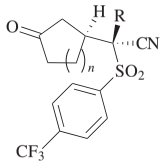
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_7$ | | | | |
|  |  | **348** (10 mol %), PhI, rt, 6–16 h |  (91) er 94.0:6.0 | 670 |
|  |  | **351** (10 mol %), toluene, –40°, 12 h |  R: Me (80), Et (76) | 671 |
| $C_8$ | | | | |
|  |  | **352** (*x* mol %), 0.14 M in toluene, –40° |  | 676 |

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | Me | 1 | 3 | (97) | 85.0:15.0 |
| Ph | Et | 5 | 5 | (98) | 86.0:14.0 |
| Ph | *n*-$C_5H_{11}$ | 5 | 5 | (98) | 86.0:14.0 |
| 2-$ClC_6H_4$ | Me | 1 | 48 | (97) | 87.0:13.0 |
| 4-$ClC_6H_4$ | Me | 1 | 3 | (93) | 85.0:15.0 |
| 4-$FC_6H_4$ | Me | 1 | 1.5 | (90) | 66.0:34.0 |
| 4-$MeOC_6H_4$ | Me | 1 | 24 | (85) | 89.0:11.0 |



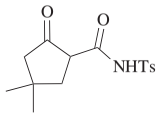


**352** (10 mol %),
0.14 M in toluene, –40°



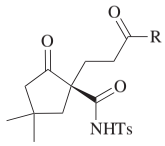
588

| R | *n* | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Ph | 1 | 22 | (75)[a] | 80:20 | 90.0:10.0 |
| 4-$ClC_6H_4$ | 1 | 20 | (62)[a] | 72.28 | 85.0:15.0 |
| 4-$MeOC_6H_4$ | 1 | 68 | (81)[a] | 90:10 | 88.0:12.0 |
| Ph | 2 | 87 | (79)[a] | 80:20 | 89.0:11.0 |
| Ph | 3 | 240 | (58)[a] | 65:35 | 80.0:20.0 |

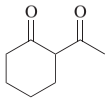




*ent*-**164b** (10 mol %),
toluene, rt

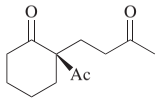


| R | | er | |
|---|---|---|---|
| Me | (98) | 99.5:0.5 | 672 |
| Et | (93) | 95.0:5.0 | |





**125** (37.5 mol %),
$Ni(OAc)_2 \cdot 4H_2O$ (5 mol %),
$CH_2Cl_2$, rt, 18 h



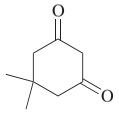
(57) er 70.5:29.5 666

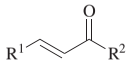
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

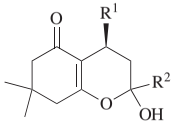
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_8$



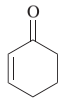


**70** (*x* mol %), $PhCO_2H$ (*x* mol %), $NaB[3,5\text{-}(CF_3)_2(C_6H_3)_4]$ (*x* mol %), $MeOC_6H_5$, –20°, 96 h

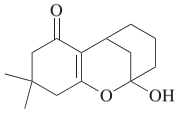


677

| $R^1$ | $R^2$ | *x* | | er |
|---|---|---|---|---|
| *n*-Pr | Me | 10 | (73) | 91.0:9.0 |
| *i*-Pr | Me | 10 | (62) | 93.0:7.0 |
| 2-$C_4H_3O$ | Me | 10 | (86) | 97.0:3.0 |
| Ph | Me | 20 | (94) | 97.5:2.5 |
| 4-$BrC_6H_4$ | Me | 20 | (91) | 97.0:3.0 |
| 3-$ClC_6H_4$ | Me | 20 | (98) | 97.0:3.0 |
| 4-$ClC_6H_4$ | Me | 20 | (95) | 97.5:2.5 |
| 4-$FC_6H_4$ | Me | 20 | (96) | 96.5:3.5 |
| 3-$HOC_6H_4$ | Me | 20 | (66) | 97.0:3.0 |
| 2-$MeOC_6H_4$ | Me | 20 | (70) | 97.0:3.0 |
| 3-$MeOC_6H_4$ | Me | 20 | (90) | 96.5:3.5 |
| 4-$MeOC_6H_4$ | Me | 20 | (78) | 97.5:2.5 |
| 2,3-$(MeO)_2C_6H_3$ | Me | 20 | (70) | 98.5:1.5 |
| 3,4-$(OCH_2O)C_6H_3$ | Me | 20 | (80) | 97.0:3.0 |
| 4-$BnOC_6H_4$ | Me | 20 | (80) | 97.5:2.5 |
| 3-$O_2NC_6H_4$ | Me | 20 | (90) | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | Me | 20 | (86) | 98.5:1.5 |
| Ph | Et | 20 | (65) | 97.0:3.0 |
| 3-$MeC_6H_4$ | Me | 20 | (92) | 96.5:3.5 |
| 3-$CF_3C_6H_4$ | Me | 20 | (96) | 96.5:3.5 |
| 4-$NCC_6H_4$ | Me | 20 | (90) | 97.0:3.0 |
| 2-Np | Me | 20 | (93) | 97.5:2.5 |
| 4-$PhC_6H_4$ | Me | 20 | (89) | 95.5:4.5 |

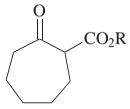


**70** (20 mol %), $PhCO_2H$ (20 mol %), $NaB[3,5\text{-}(CF_3)_2(C_6H_3)_4]$ (20 mol %), $MeOC_6H_5$, –20°



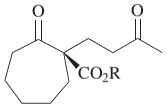
(70) er 95.0:5.0

677





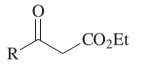
**125** (37.5 mol %), $Ni(OAc)_2 \cdot 4H_2O$ (5 mol %), $CH_2Cl_2$, rt, 18 h



(14) er 51.0:49.0

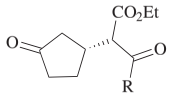
666

$C_{9–10}$





**160b** (20 mol %), solvent, –20°

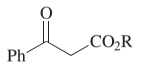


dr 1:1

612

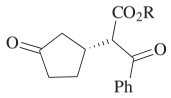
| R | Solvent | Time (h) | | er | er |
|---|---|---|---|---|---|
| Ph | $Et_3N$ | 72 | (98) | 95.0:5.0 | 96.5:3.5 |
| 3-$ClC_6H_4$ | $Et_3N$ | 48 | (99) | 96.5:3.5 | 96.5:3.5 |
| 3-$ClC_6H_4$ | toluene | 144 | (99) | 95.0:5.0 | 95.0:5.0 |
| 4-$ClC_6H_4$ | $Et_3N$ | 48 | (99) | 97.0:3.0 | 97.5:2.5 |
| 4-$ClC_6H_4$ | toluene | 144 | (99) | 96.0:4.0 | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | $Et_3N$ | 72 | (99) | 89.0:11.0 | 90.0:10.0 |
| 4-$O_2NC_6H_4$ | toluene | 120 | (91) | 96.6:3.4 | 97.0:3.0 |
| 3-$MeC_6H_4$ | $Et_3N$ | 60 | (89) | 93.0:7.0 | 98.5:1.5 |
| 3-$MeC_6H_4$ | toluene | 192 | (85) | 95.5:4.5 | 95.0:5.0 |
| 4-$CF_3C_6H_4$ | $Et_3N$ | 72 | (91) | 95.5:4.5 | 96.0:4.0 |
| 4-$CF_3C_6H_4$ | toluene | 144 | (90) | 96.0:4.0 | 98.0:2.0 |

$C_9$



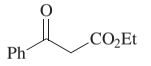


**288b** (2 mol %), toluene, rt



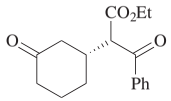
dr 1:1

| R | | er | |
|---|---|---|---|
| Me | (91) | 98.0:2.0 | 654 |
| Et | (99) | 98.5:1.5 | |





**221a** (5 mol %), $PhCO_2H$ (5 mol %), toluene, 50°, 20 h



(84) dr 1:1
er 97.5:2.5
er 97.5:2.5

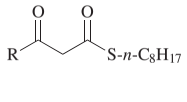
587

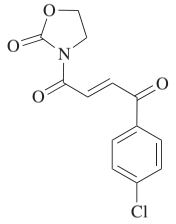
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

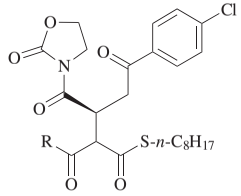
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_9$





**160b** (20 mol %), toluene

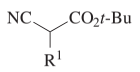


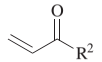
dr 1:1

647

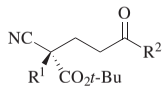
| R | Temp (°) | Time (h) | | er | er |
|---|---|---|---|---|---|
| Ph | –50 | 48 | (99) | 96.5:3.5 | 98.5:1.5 |
| Ph | –20 | 18 | (99) | 95.0:5.0 | 96.5:3.5 |
| 4-MeOC$_6$H$_4$ | –20 | 24 | (87) | 95.0:5.0 | 96.0:4.0 |

$C_{9-10}$





**362** (*x* mol %),
$AgO_3S$-2,4,6-$iPr_3C_6H_2$ (6 eq[b]),
AcOH (20 mol %), diglyme



678

| $R^1$ | $R^2$ | *x* | Temp | Time (h) | | er |
|---|---|---|---|---|---|---|
| Ph | Me | 0.2 | rt | 24 | (>99) | 95.0:5.0 |
| Ph | Et | 0.75 | rt | 24 | (>99) | 94.0:6.0 |
| Ph | *n*-Pr | 1.0 | rt | 24 | (90) | 93.0:7.0 |
| Ph | *n*-$C_5H_{11}$ | 1.0 | rt | 24 | (98) | 94.5:5.5 |
| Ph | Ph | 1.0 | rt | 24 | (95) | 88.5:11.5 |
| Ph | 4-MeOC$_6$H$_4$ | 1.0 | rt | 24 | (80) | 88.0:12.0 |
| 3-BrC$_6$H$_4$ | Me | 0.5 | rt | 24 | (>99) | 95.5:4.5 |
| 4-BrC$_6$H$_4$ | Me | 0.05 | rt | 48 | (>99) | 94.5:5.5 |
| 4-BrC$_6$H$_4$ | Me | 0.1 | rt | 24 | (>99) | 97.0:3.0 |
| 3-ClC$_6$H$_4$ | Me | 0.5 | rt | 24 | (>99) | 95.5:4.5 |

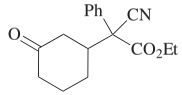
| | | | | | | |
|---|---|---|---|---|---|---|
| 4-$ClC_6H_4$ | Me | 0.02 | 40° | 48 | (98) | 92.5:7.5 |
| 4-$ClC_6H_4$ | Me | 0.05 | 40° | 24 | (99) | 95.5:4.5 |
| 4-$ClC_6H_4$ | Me | 0.1 | rt | 24 | (>99) | 97.5:2.5 |
| 4-$ClC_6H_4$ | Et | 0.5 | rt | 24 | (>99) | 97.0:3.0 |
| 4-$FC_6H_4$ | Me | 0.2 | rt | 24 | (>99) | 96.5:3.5 |
| 4-$FC_6H_4$ | Me | 0.5 | rt | 24 | (>99) | 97.5:2.5 |
| 3-$MeOC_6H_4$ | Me | 1.0 | rt | 24 | (>99) | 90.0:10.0 |
| 3-$MeC_6H_4$ | Me | 0.5 | rt | 24 | (>99) | 95.0:5.0 |
| 4-$MeC_6H_4$ | Me | 0.25 | rt | 24 | (>99) | 95.5:4.5 |
| 3-$CF_3C_6H_4$ | Me | 0.5 | rt | 24 | (>99) | 95.5:4.5 |

$C_9$





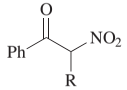
**253** (5 mol %),
$C_6H_5OLi$ (5 mol %),
$CHCl_3$, rt, 48 h



(90) dr 1.2:1
er (minor) 68.0:32.0
er (major) 71.5:28.5

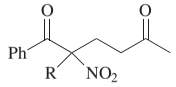
546

$C_{9-11}$





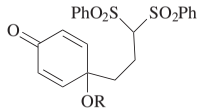
**330** (2 mol %),
100 mM in toluene, 4°



| R | | er |
|---|---|---|
| Me | (82) | 76.0:24.0 |
| Et | (64) | 87.0:13.0 |
| *n*-Pr | (29) | 80.0:20.0 |

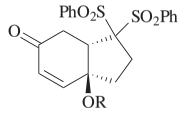
653

$C_9$



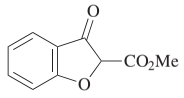
Intramolecular

**361** (10 mol %),
DCE, rt, 48 h



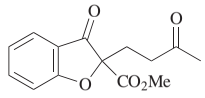
| R | | er |
|---|---|---|
| H | (85) | 92.5:7.5 |
| Me | (97) | 95.0:5.0 |
| Et | (97) | 95.0:5.0 |
| Ac | (94) | 92.5:7.5 |
| $HO(CH_2)_2$ | (92) | 93.0:7.0 |
| $HO(CH_2)_3$ | (83) | 93.5:6.5 |

679





**347** (6 mol %),
$Sc(OTf)_3$ (5 mol %),
0.02 M in DCE, 40°, 24 h



(72) er 97.0:3.0

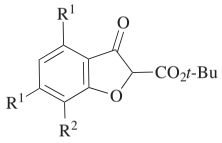
669

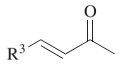
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

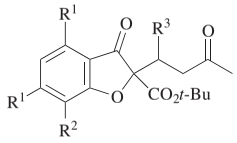
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_9$





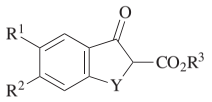
**355** (5 mol %), $Sc(OTf)_3$ (5 mol %), $CH_2Cl_2$, rt, 2 h



680

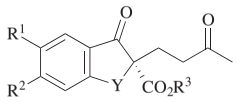
| $R^1$ | $R^2$ | $R^3$ | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| H | H | H | (89) | — | 88.5:11.5 | — |
| H | H | Me | (86) | 2:1 | 88.0:12.0 | 54.5:45.5 |
| MeO | Cl | Me | (81) | 1:1 | <55.0:45.0 | <55.0:45.0 |

$C_{9-10}$





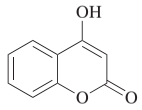
**344** (*x* mol %), 3-xylene

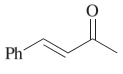


204

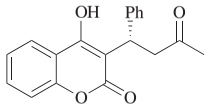
| Y | $R^1$ | $R^2$ | $R^3$ | *x* | Temp (°) | | er |
|---|---|---|---|---|---|---|---|
| O | H | H | Me | 2 | 20 | (99) | 91.5:8.5 |
| O | H | Br | Me | 1 | 40 | (79) | 87.5:12.5 |
| O | H | Cl | Me | 10 | 40 | (99) | 89.0:11.0 |
| O | H | Me | Me | 2 | 20 | (87) | 85.0:15.0 |
| $CH_2$ | H | H | Me | 10 | 40 | (99) | 89.0:11.0 |
| $CH_2$ | H | H | Bn | 10 | 40 | (99) | 90.0:10.0 |
| $CH_2$ | Br | H | Me | 10 | 40 | (89) | 89.0:11.0 |
| $CH_2$ | Cl | H | Me | 10 | 40 | (99) | 90.5:9.5 |

$C_9$



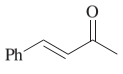


**70** (*x* mol %), additive (4–20 mol %), $H_2O$, rt, ultrasound

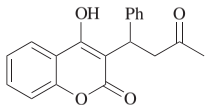


681

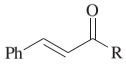
| *x* | Additive | Time (h) | | er |
|---|---|---|---|---|
| 10 | AcOH | 10 | (98) | 84.0:16.0 |
| 10 | $PhCO_2H$ | 10 | (93) | 86.0:14.0 |
| 10 | $PhCO_2H$ | 2 | (66) | 87.5:12.5 |
| 5 | $PhCO_2H$ | 10 | (87) | 84.0:16.0 |
| 2 | $PhCO_2H$ | 10 | (78) | 85.0:15.0 |



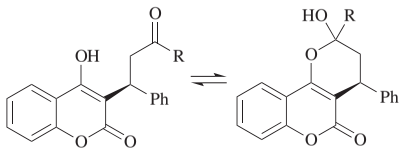
**134** (20 mol %), $CHCl_3$, rt



(99) er 67.0:33.0 376



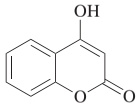
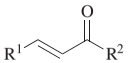
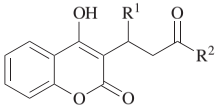
**343** (10 mol %), *n*-$C_5H_{11}CO_2H$ (10 eq), THF, rt, 36 h



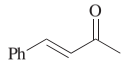
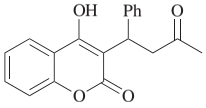
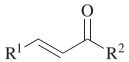
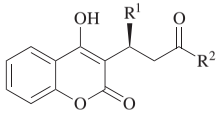
673

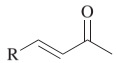
| R | | er |
|---|---|---|
| Me | (96) | 95.5:4.5 |
| Ph | (61) | 97.0:3.0 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_9$  |  | **349** (20 mol %), 1,4-dioxane, rt, 55 h |  | 682 |

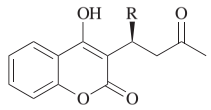
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | Me | (87) | 94.0:6.0 |
| 2-$C_4H_3S$ | Me | (88) | 93.0:7.0 |
| Ph | Me | (97) | 97.5:2.5 |
| Ph | Et | (96) | 94.0:6.0 |
| 4-$BrC_6H_4$ | Me | (93) | 96.5:3.5 |
| 2-$ClC_6H_4$ | Me | (95) | 94.0:6.0 |
| 4-$ClC_6H_4$ | Me | (92) | 96.0:4.0 |
| 3-$FC_6H_4$ | Me | (92) | 95.5:4.5 |
| 4-$FC_6H_4$ | Me | (89) | 95.5:4.5 |
| 2-$MeOC_6H_4$ | Me | (87) | 96.5:3.5 |
| 4-$MeOC_6H_4$ | Me | (80) | 95.0:5.0 |
| 3-$O_2NC_6H_4$ | Me | (89) | 94.5:5.5 |
| 4-$O_2NC_6H_4$ | Me | (96) | 95.5:4.5 |
| 4-$MeC_6H_4$ | Me | (90) | 96.0:4.0 |
| 1-Np | Me | (83) | 94.5:5.5 |

| | | | | |
|---|---|---|---|---|
| |  | **353** (20 mol %), AcOH (10 eq), THF, rt, 96 h |  (93) er 85.0:15.0 | 683 |
| |  | **354** (10 mol %), 4-$MeC_6H_4CO_2H$ (20 mol %), toluene, rt, 72 h |  | 684 |



**359** (20 mol %), succinic acid (10 mol %), *n*-BuOH, $H_2O$ (50 μL), 40°, 12 h

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | Me | (14) | 99.5:0.5 |
| Ph | Me | (99) | 97.0:3.0 |
| 2-$BrC_6H_4$ | Me | (97) | 96.5:3.5 |
| 4-$BrC_6H_4$ | Me | (97) | 98.0:2.0 |
| 4-$ClC_6H_4$ | Me | (99) | 97.0:3.0 |
| 2-$MeOC_6H_4$ | Me | (82) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | Me | (91) | 97.0:3.0 |
| 3-$O_2NC_6H_4$ | Me | (88) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | Me | (98) | 95.5:4.5 |
| 4-$Me_2NC_6H_4$ | Me | (65) | 93.0:7.0 |
| 4-$MeC_6H_4$ | Me | (58) | 98.0:2.0 |
| 1-Np | Me | (86) | 97.5:2.5 |
| Ph | *c*-$C_6H_{11}$ | (12) | 91.5:8.5 |



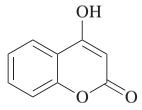
| R | | er |
|---|---|---|
| *n*-Pr | (96) | 77.5:22.5 |
| *i*-Pr | (88) | 78.5:21.5 |
| Ph | (99) | 91.5:8.5 |
| 2-$ClC_6H_4$ | (90) | 89.5:10.5 |
| 3-$ClC_6H_4$ | (97) | 87.5:12.5 |
| 4-$ClC_6H_4$ | (92) | 89.5:10.5 |
| 4-$FC_6H_4$ | (90) | 90.0:10.0 |
| 3-$HOC_6H_4$ | (95) | 94.0:6.0 |
| 2-$MeOC_6H_4$ | (91) | 94.5:5.5 |
| 3-$MeOC_6H_4$ | (98) | 90.5:9.5 |
| 4-$MeOC_6H_4$ | (90) | 93.5:6.5 |
| 3,4-$(OCH_2O)C_6H_3$ | (97) | 92.5:7.5 |
| 3-$MeC_6H_4$ | (84) | 90.5:9.5 |
| 4-$MeC_6H_4$ | (80) | 93.5:6.5 |
| 3-$CF_3C_6H_4$ | (89) | 89.0:11.0 |
| 2-Np | (99) | 91.5:8.5 |

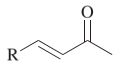
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

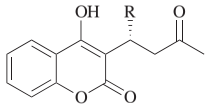
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_9$





**360** (20 mol %),
AcOH (5 eq),
THF, rt, 45 h

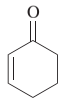


686

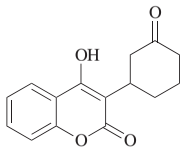
Catalyst Recycling (R = Ph)

| Run | Time (h) | | er |
|---|---|---|---|
| 1 | 45 | (97) | 89.0:11.0 |
| 2 | 45 | (94) | 89.0:11.0 |
| 3 | 45 | (93) | 88.5:11.5 |
| 4 | 45 | (61) | 88.0:12.0 |
| 5 | 45 | (42) | 88.0:12.0 |
| 6 | 100 | (51) | 86.5:13.5 |

| R | | er |
|---|---|---|
| Ph | (96) | 90.0:10.0 |
| 4-$ClC_6H_4$ | (70) | 88.5:11.5 |
| 4-$MeOC_6H_4$ | (81) | 88.5:11.5 |

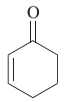


**225c** (20 mol %),
TFA (40 mol %),
$CH_2Cl_2$, 0°, 6 d

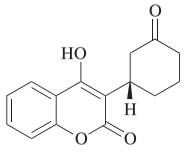


(78) er 97.0:3.0

687

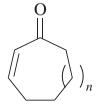


**360** (20 mol %),
AcOH (5 eq),
THF, rt, 45 h

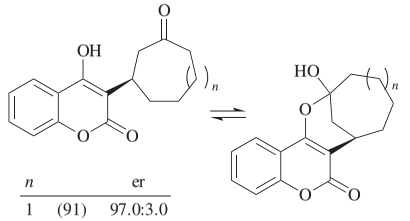


(91) er 75.0:25.0

686

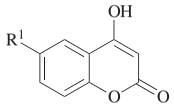


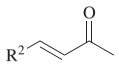
**343** (10 mol %),
*n*-$C_5H_{11}CO_2H$ (10 eq),
THF, rt, 36 h



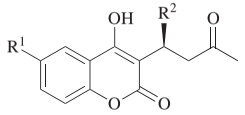
673

| *n* | | er |
|---|---|---|
| 1 | (91) | 97.0:3.0 |
| 2 | (88) | 97.5:2.5 |





**70** (5 mol %),
$LiClO_4$ (5 mol %),
AcOH (10 eq),
1,4-dioxane, rt, 24 h



688

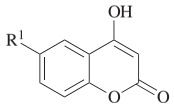
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| H | Ph | (61) | 96.0:4.0 |
| H | 4-$ClC_6H_4$ | (74) | 95.0:5.0 |
| H | 2-$MeOC_6H_4$ | (52) | 95.5:4.5 |
| H | 3-$MeOC_6H_4$ | (64) | 95.0:5.0 |
| H | 4-$MeC_6H_4$ | (75) | 95.0:5.0 |
| Cl | Ph | (61) | 97.0:3.0 |
| Cl | 4-$MeOC_6H_4$ | (69) | 96.0:4.0 |
| Cl | 2-$MeC_6H_4$ | (62) | 95.5:4.5 |
| Br | 2-$MeOC_6H_4$ | (50) | 96.0:4.0 |

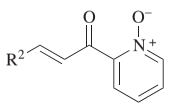
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

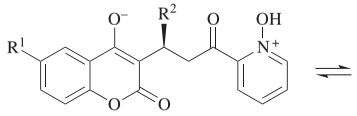
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{9–10}$

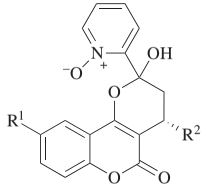




**341** (6 mol %),
$Zn(OTf)_2$ (5 mol %),
DBU (10 mol %),
$CH_2Cl_2$, rt

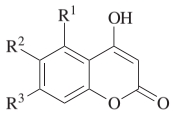


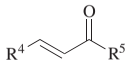
674



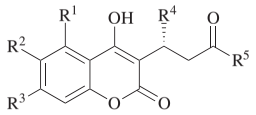
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| H | $EtO_2C$ | 7 | (80) | 89.5:10.5 |
| H | 2-$C_4H_3O$ | 5 | (99) | 89.0:11.0 |
| H | Ph | 2 | (99) | 94.0:6.0 |
| H | 3-$ClC_6H_4$ | 2 | (98) | 94.0:6.0 |
| H | 4-$MeOC_6H_4$ | 3 | (87) | 83.5:16.5 |
| H | 2-$O_2NC_6H_4$ | 3 | (95) | 95.5:4.5 |
| H | 3-$O_2NC_6H_4$ | 1 | (66) | 94.5:5.5 |
| H | 4-$O_2NC_6H_4$ | 1 | (98) | 94.5:5.5 |
| H | PhCH=CH | 2 | (85) | 84.5:15.5 |
| H | 1-Np | 9 | (95) | 76.5:23.5 |
| $O_2N$ | Ph | 2 | (97) | 92.5:7.5 |
| Me | Ph | 2 | (93) | 90.0:10.0 |

$C_{9-11}$





**225c** (20 mol %),
TFA (40 mol %),
$CH_2Cl_2$, 0°



687

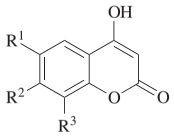
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | Time (d) | | er |
|---|---|---|---|---|---|---|---|
| H | H | H | *n*-Pr | Me | 6 | (93) | 97.5:2.5 |
| H | H | H | *i*-Pr | Me | 6 | (88) | 99.0:1.0 |
| H | H | H | *n*-Pr | Et | 6 | (55) | 95.0:5.0 |
| H | H | H | 2-$C_4H_3O$ | Me | 4 | (81) | 97.0:3.0 |
| H | H | H | 2-$C_4H_3S$ | Me | 4 | (83) | 96.5:3.5 |
| H | H | H | Ph | Me | 4 | (88) | 98.0:2.0 |
| H | H | H | 4-$ClC_6H_4$ | Me | 4 | (87) | 98.5:1.5 |
| H | H | H | 4-$MeOC_6H_4$ | Me | 4 | (81) | 97.5:2.5 |
| H | H | H | Ph | Et | 6 | (90) | 99.5:0.5 |
| H | H | H | Ph | *n*-Pr | 6 | (82) | 98.5:1.5 |
| H | Br | H | Ph | Me | 4 | (82) | 99.0:1.0 |
| H | Me | H | Ph | Me | 4 | (87) | 99.5:0.5 |
| Me | H | Me | Ph | Me | 4 | (80) | 99.0:1.0 |

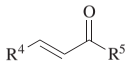
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

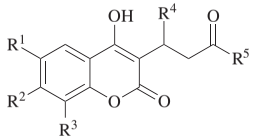
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{9–11}$





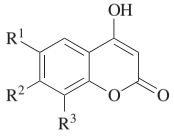
Catalyst (10 mol %), $CH_2Cl_2$, rt

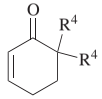


172

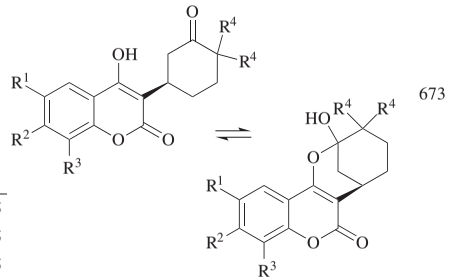
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | Catalyst | Time (h) | | er | Config. |
|---|---|---|---|---|---|---|---|---|---|
| H | H | H | *i*-Pr | Me | **337** | 180 | (71) | 92.5:7.5 | (*S*) |
| H | H | H | *n*-Bu | Me | **338** | 60 | (99) | 92.0:8.0 | (*S*) |
| H | H | H | 2-$C_4H_3O$ | Me | **338** | 150 | (75) | 87.5:12.5 | (*R*) |
| H | H | H | 2-$C_4H_3S$ | Me | **338** | 150 | (78) | 89.5:10.5 | (*R*) |
| H | H | H | Ph | Me | **338** | 150 | (96) | 91.0:9.0 | (*S*) |
| H | H | H | 4-$ClC_6H_4$ | Me | **337** | 130 | (86) | 91.0:9.0 | (*S*) |
| H | H | H | 4-$MeOC_6H_4$ | Me | **337** | 160 | (91) | 91.0:9.0 | (*S*) |
| H | H | H | 4-$O_2NC_6H_4$ | Me | **337** | 130 | (81) | 91.5:8.5 | (*S*) |
| H | H | H | Ph | Et | **337** | 130 | (84) | 94.0:6.0 | (*S*) |
| H | H | H | Ph | *i*-Pr | **337** | 180 | (71) | 92.5:7.5 | (*S*) |
| H | H | H | 2-Np | Me | **337** | 130 | (81) | 91.5:8.5 | (*S*) |
| H | F | H | Ph | Me | **337** | 150 | (68) | 91.5:8.5 | (*S*) |
| H | MeO | H | Ph | Me | **337** | 150 | (81) | 92.5:7.5 | (*S*) |
| Cl | H | Cl | Ph | Me | **337** | 150 | (65) | 89.5:10.5 | (*S*) |
| Me | Me | H | Ph | Me | **337** | 150 | (84) | 92.5:7.5 | (*S*) |

$C_{9-17}$





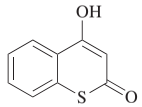
**343** (10 mol %),
*n*-$C_5H_{11}CO_2H$ (10 eq),
THF, rt, 36 h

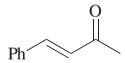


673

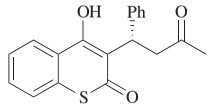
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | | er |
|---|---|---|---|---|---|
| H | H | H | H | (94) | 97.5:2.5 |
| H | H | H | Me | (94) | 97.5:2.5 |
| H | F | H | H | (93) | 97.5:2.5 |
| Br | H | H | H | (94) | 95.5:4.5 |
| Cl | H | H | H | (92) | 97.5:2.5 |
| MeO | H | H | H | (91) | 97.5:2.5 |
| H | H | Me | H | (91) | 98.5:1.5 |
| Me | H | H | H | (94) | 97.0:3.0 |
| *t*-Bu | H | H | H | (87) | 98.0:2.0 |
| *t*-Bu | *t*-Bu | H | H | (86) | 97.5:2.5 |

$C_9$

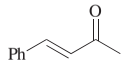




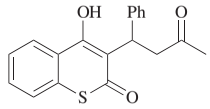
**225c** (20 mol %),
TFA (40 mol %),
$CH_2Cl_2$, 0°, 4 d



(68) er 94.5:5.5 687

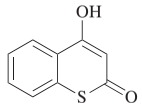
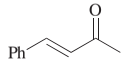
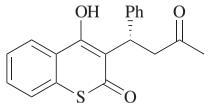
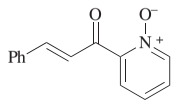
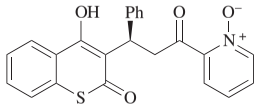
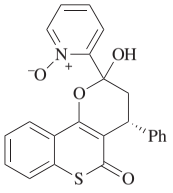
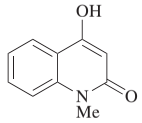
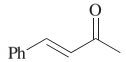
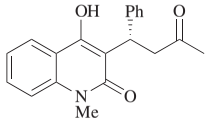
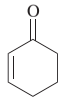
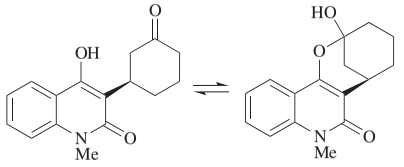


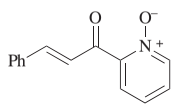
**337** (10 mol %),
$CH_2Cl_2$, rt, 150 h



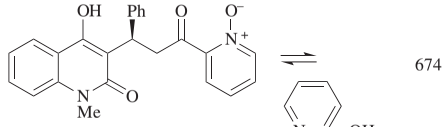
(84) er 89.0:11.0 172

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

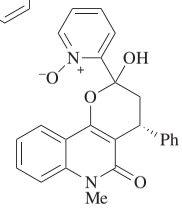
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_9$ | | | | |
|  |  | **360** (20 mol %), AcOH (5 eq), THF, rt, 45 h |  (51) er 88.0:12.0 | 686 |
| |  | **341** (6 mol %), $Zn(OTf)_2$ (5 mol %), DBU (10 mol %), $CH_2Cl_2$, rt, 4 h |   (87) er 85.0:15.0 | 674 |
|  |  | **225c** (20 mol %), TFA (40 mol %), $CH_2Cl_2$, 0°, 4 d |  (71) er 99.5:0.5 | 687 |
| |  | **343** (10 mol %), $n$-$C_5H_{11}CO_2H$ (10 eq), THF, rt, 36 h |  (83) er 94.0:6.0 | 673 |



**341** (6 mol %),
$Zn(OTf)_2$ (5 mol %),
DBU (10 mol %),
$CH_2Cl_2$, rt, 2 h

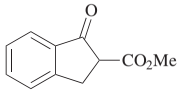


(93) er 98.5:1.5



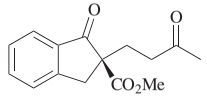
674

$C_{10}$



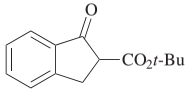


Catalyst (1 mol %),
$CH_2Cl_2$, –30°



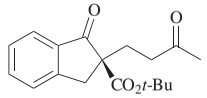
661

| Catalyst | Time (h) | | er |
|---|---|---|---|
| **288b** | 8 | (>99) | 83.5:16.5 |
| **365** | 10 | (>99) | 87.5:12.5 |





**339b** (10 mol %),
1 M in THF, –20°, 48 h



(88) er 94.5:5.5

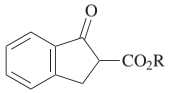
31, 32

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

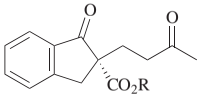
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{10}$

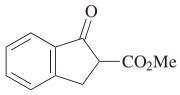




**355** (5 mol %), $Sc(OTf)_3$ (5 mol %), $CH_2Cl_2$

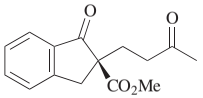


| R | Temp | Time (h) | | er | |
|---|---|---|---|---|---|
| Me | 20° | 0.5 | (98) | 69.5:30.5 | 689 |
| Me | rt | 5 | (98) | 69.5:30.5 | 680 |
| *i*-Pr | 20° | 0.5 | (94) | 73.5:26.5 | 689 |
| *i*-Pr | rt | 5 | (94) | 73.5:26.5 | 680 |
| *i*-Bu | 20° | 0.5 | (98) | 84.5:15.5 | 689 |
| *i*-Bu | rt | 5 | (89) | 92.0:8.0 | 680 |
| *t*-Bu | 20° | 0.5 | (93) | 90.0:10.0 | 689 |
| *i*-$Pr_2CH$ | rt | 5 | (98) | 84.5:15.5 | 680 |
| Bn | 20° | 0.5 | (85) | 69.0:31.0 | 689 |
| Bn | rt | 5 | (85) | 69.0:31.0 | 680 |





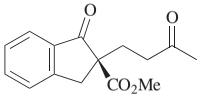
**356** (1 mol %), $CCl_4$, –20°, 3 d



(>99) er 87.5:12.5 690



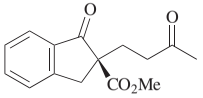
**357** (1.2 mol %), La complex with $Ca_{10}(PO_4)_6F_2$ (0.5 mol % in La) toluene rt, 6 h



(97) er 80.0:20.0 691



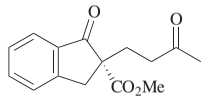
**363** (5 mol %), toluene, 50°, 3 h



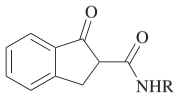
(96) er 74.0:26.0 692



**364** (10 mol %), $CH_2Cl_2$, 20°

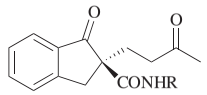


(85) er 93.5:6.5 693





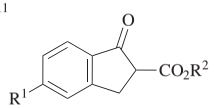
*ent*-**164b** (10 mol %), toluene, rt



| R | | er |
|---|---|---|
| Ph | (39) | 92.5:7.5 |
| 1-Np | (88) | 95.5:4.5 |

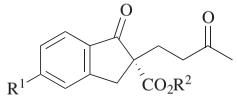
672

$C_{10-11}$





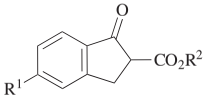
**342** (*x* mol %), *i*-$Pr_2NEt$ (30 mol %), $CH_2Cl_2$, –40°



694

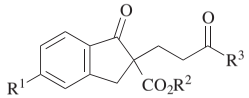
| $R^1$ | $R^2$ | *x* | Time (d) | | er |
|---|---|---|---|---|---|
| H | Me | 1 | 1 | (98) | 75.5:24.5 |
| H | *t*-Bu | 1 | 0.6 | (87) | 86.5:13.5 |
| Br | *t*-Bu | 1 | 0.7 | (98) | 84.0:16.0 |
| MeO | *t*-Bu | 5 | 3.5 | (98) | 91.5:8.5 |
| Me | *t*-Bu | 1 | 4 | (98) | 89.0:11.0 |

$C_{10}$





**347** (6 mol %), $Sc(OTf)_3$ (5 mol %), 0.02 M in DCE, 40°



669

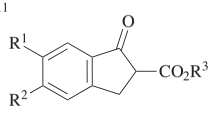
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| H | Me | Me | 50 | (94) | 96.0:4.0 |
| H | Me | Et | 48 | (98) | 96.5:3.5 |
| H | Et | Me | 60 | (81) | 95.0:5.0 |
| H | Et | Et | 38 | (95) | 96.5:3.5 |
| H | *t*-Bu | Me | 120 | (61) | 95.5:4.5 |
| Br | Et | Me | 28 | (85) | 92.5:7.5 |
| MeO | Et | Me | 13 | (88) | 97.5:2.5 |
| MeO | Et | Et | 20 | (81) | 97.5:2.5 |

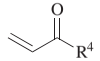
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

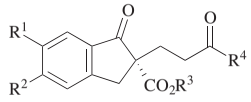
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{10-11}$





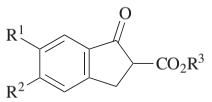
**42** (*x* mol %),
*i*-$Pr_2NEt$ (30 mol %),
$CH_2Cl_2$, –40°



663

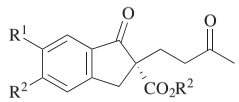
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | *x* | Time (d) | | er |
|---|---|---|---|---|---|---|---|
| H | H | Me | Me | 1 | 1 | (98) | 75.5:24.5 |
| H | H | *t*-Bu | Me | 1 | 0.6 | (87) | 86.5:13.5 |
| H | H | *t*-Bu | Et | 1 | 7 | (98) | 88.5:11.5 |
| H | Br | *t*-Bu | Me | 1 | 0.7 | (98) | 84.0:16.0 |
| H | Cl | *t*-Bu | Me | 1 | 1 | (98) | 83.0:17.0 |
| H | MeO | *t*-Bu | Me | 5 | 3.5 | (98) | 91.5:8.5 |
| MeO | MeO | Me | Me | 5 | 7 | (92) | 90.5:9.5 |
| H | Me | *t*-Bu | Me | 1 | 4 | (98) | 89.0:11.0 |

$C_{10}$



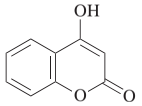


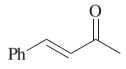
**351** (10 mol %),
solvent, –40°, 12 h



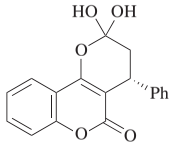
671

| $R^1$ | $R^2$ | $R^3$ | Solvent | | er |
|---|---|---|---|---|---|
| H | H | Me | toluene | (93) | 86.0:14.0 |
| H | H | *i*-Pr | $CCl_4$ | (91) | 84.0:16.0 |
| H | H | *t*-Bu | toluene | (86) | 81.0:19.0 |
| H | Br | Me | toluene | (82) | — |
| H | Cl | Me | toluene | (90) | — |
| MeO | H | Me | toluene | (80) | — |

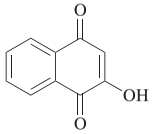


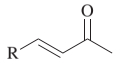


**70** (20 mol %),
$PhCO_2H$ (20 mol %),
$NaB[3,5\text{-}(CF_3)_2(C_6H_3)_4]F$
(20 mol %), $MeOC_6H_5$, –20°

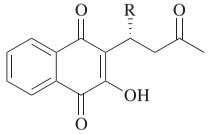


(95) er 98.0:2.0 677





**225a** (20 mol %),
TFA (40 mol %), THF, rt

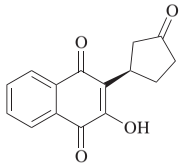


695

| R | Time (h) | | er |
|---|---|---|---|
| $2\text{-}C_4H_3O$ | 72 | (67) | 92.0:8.0 |
| Ph | 48 | (82) | 97.0:3.0 |
| $3\text{-}BrC_6H_4$ | 48 | (88) | 95.5:4.5 |
| $4\text{-}BrC_6H_4$ | 48 | (93) | 96.8:3.2 |
| $2\text{-}ClC_6H_4$ | 72 | (75) | 96.0:4.0 |
| $4\text{-}ClC_6H_4$ | 48 | (87) | 95.8:4.2 |
| $2,4\text{-}Cl_2C_6H_3$ | 72 | (78) | 98.0:2.0 |
| $3\text{-}MeOC_6H_4$ | 96 | (65) | 97.5:2.5 |
| $4\text{-}O_2NC_6H_4$ | 52 | (85) | 99.0:1.0 |



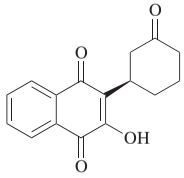
**225a** (20 mol %),
TFA (40 mol %),
THF, rt, 8 h



(93) er 96.0:4.0 695

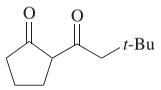
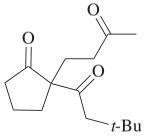
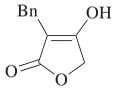
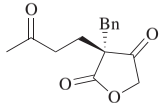
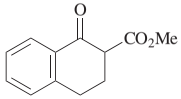
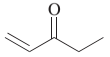
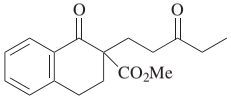
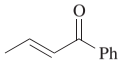
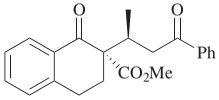
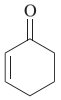
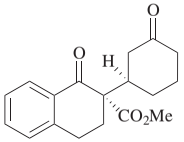
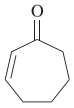
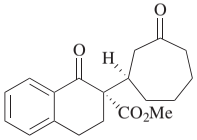


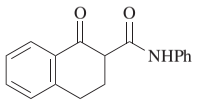
**225a** (20 mol %),
TFA (40 mol %),
THF, rt, 12 h



(92) er 97.0:3.0 695

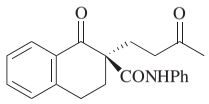
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_{11}$ | | | | |
|  |  | **339a** (10 mol %), 4 M in THF, −10°, 30 d |  (90) er 95.0:5.0 | 32 |
|  |  | **225c** (10 mol %), 40% $Cl_3CCO_2H$, 0.1 M in THF, rt, 8 h |  (60) er 54.0:46.0 | 660 |
|  |  | **347** (7.5 mol %), $Sc(OTf)_3$ (5 mol %), 0.02 M in DCE, 60°, 110 h |  (54) er 96.0:4.0 | 669 |
| |  | **297** (30 mol %), 1 M in toluene, rt, 72 h |  (85) dr 77:23 er (major) 57.5:42.5 er (minor) 91.0:9.0 | 696 |
| |  | **297** (10 mol %), 1 M in toluene, rt, 72 h |  (98) dr 57:43 er (major) 82.5:17.5 er (minor) 91.0:9.0 | 696 |
| |  | **297** (10 mol %), 1 M in toluene, rt, 72 h |  (90) dr 60:40 er (major) 97.0:3.0 er (minor) 96.0:4.0 | 696 |

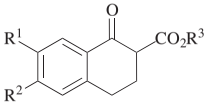


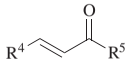


*ent*-**164b** (10 mol %),
toluene, rt

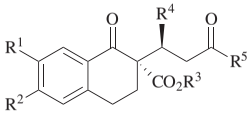


(73) er 93.5:6.5 672





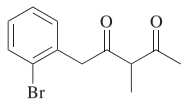
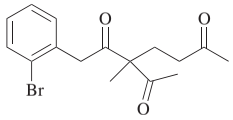
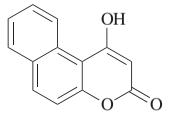
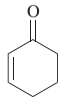
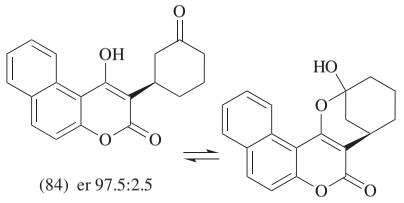
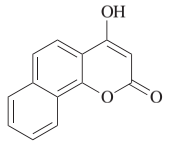
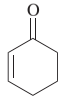
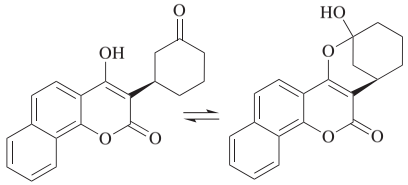
**297** (10 mol %),
1 M in toluene, rt, 72 h



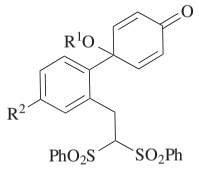
696

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | | dr | er |
|---|---|---|---|---|---|---|---|
| H | H | Me | Me | Me | (82) | 99:1 | 97.5:2.5 |
| H | H | Me | Me | Et | (95) | 99:1 | 98.0:2.0 |
| H | H | Me | *n*-Pr | Me | (95) | 98:2 | 97.0:3.0 |
| H | H | Me | Me | *n*-Bu | (80) | 98:2 | 97.5:2.5 |
| H | H | Me | *n*-Bu | Me | (86) | 98:2 | 98.0:2.0 |
| H | H | Me | *i*-Bu | Me | (75) | >99:1 | 93.0:7.0 |
| H | H | Me | $n$-$C_5H_{11}$ | Me | (97) | 98:2 | 95.5:4.5 |
| H | H | Me | $n$-$C_6H_{13}$ | Me | (97) | 98:2 | 98.0:2.0 |
| H | H | Me | $BnCH_2$ | Me | (95) | >99:1 | 95.5:4.5 |
| H | H | Et | Me | Me | (95) | 99:1 | 97.5:2.5 |
| H | H | Et | $n$-$C_6H_{13}$ | Me | (93) | 98:2 | 96.5:3.5 |
| H | Br | Me | Me | Et | (89) | >99:1 | 96.5:3.5 |
| H | Br | Me | *n*-Pr | Me | (87) | 98:2 | 96.0:4.0 |
| H | Br | Me | *n*-Bu | Me | (85) | 97:3 | 96.5:3.5 |
| H | Cl | Me | Me | Et | (93) | >99:1 | 97.5:2.5 |
| H | Cl | Me | Me | *n*-Bu | (75) | >99:1 | 96.0:4.0 |
| H | Cl | Me | $n$-$C_5H_{11}$ | Me | (92) | 98:2 | 93.5:6.5 |
| H | MeO | Me | Me | Me | (92) | 97:3 | 96.5:3.5 |
| H | MeO | Me | $n$-$C_6H_{13}$ | Me | (90) | 98:2 | 96.5:3.5 |
| MeO | H | Me | *n*-Bu | Me | (82) | 98:2 | 98.5:1.5 |
| MeO | H | Me | $n$-$C_5H_{11}$ | Me | (92) | 98:2 | 96.0:4.0 |

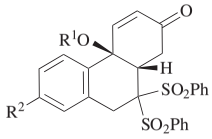
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{12}$  |  | **339a** (10 mol %), 4 M in THF, –10°, 36 h |  (84) er 95.0:5.0 | 32 |
| $C_{13}$  |  | **343** (10 mol %), *n*-$C_5H_{11}CO_2H$ (10 eq), THF, rt, 36 h |  (84) er 97.5:2.5 | 673 |
|  |  | **343** (10 mol %), *n*-$C_5H_{11}CO_2H$ (10 eq), THF, rt, 36 h |  (82) er 97.5:2.5 | 673 |

$C_{14}$



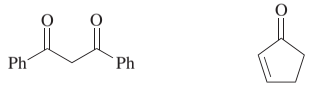
intramolecular **361** (20 mol %), $CH_2Cl_2$, rt



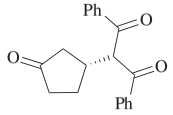
679

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| H | H | 48 | (96) | 92.0:8.0 |
| Me | H | 72 | (95) | 95.5:4.5 |
| Me | Cl | 48 | (89) | 94.0:6.0 |
| Me | F | 96 | (82) | 95.0:5.0 |

$C_{15}$



**160b** (20 mol %), solvent, –20°



612

| Solvent | Time (h) | | er |
|---|---|---|---|
| $Et_3N$ | 48 | (99) | 93.5:6.5 |
| toluene | 120 | (61) | 95.5:4.5 |

[a] The yield given is for the major diastereoisomer.

[b] The equivalents given are with respect to the catalyst.

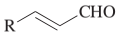
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

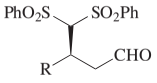
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_1$



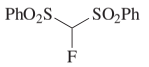


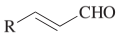
**145b** (10 mol %), toluene, 24–72 h



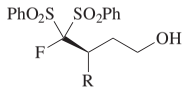
161

| R | Temp (°) | | er |
|---|---|---|---|
| Me | 4 | (90) | 96.5:3.5 |
| $EtO_2C$ | 4 | (74) | 97.0:3.0 |
| Et | 4 | (74) | 99.5:0.5 |
| *n*-Pr | 4 | (77) | 99.5:0.5 |
| $BzO(CH_2)_3$ | 4 | (72) | 98.5:1.5 |
| *n*-Bu | 4 | (79) | 95.0:5.0 |
| $CH_2{=}CH(CH_2)_2$ | 4 | (91) | 97.0:3.0 |
| $BnO_2C(CH_2)_3$ | –20 | (61) | 95.5:4.5 |





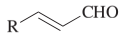
1. **145b** (20 mol %), $PhCO_2H$ (*x* mol %), toluene, 0°
2. $NaBH_4$, MeOH



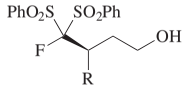
165

| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| Me | 20 | 48 | (66) | 97.0:3.0 |
| *n*-Pr | 20 | 96 | (17) | 99.0:1.0 |
| *n*-Pr | — | 79 | (81) | 96.0:4.0 |
| 2-$C_4H_3O$ | 20 | 58 | (79) | 93.0:7.0 |
| Ph | 20 | 72 | (71) | >99.5:0.5 |
| 4-$BrC_6H_4$ | 20 | 72 | (81) | >99.5:0.5 |
| 2-$FC_6H_4$ | 20 | 70 | (74) | >99.5:0.5 |
| 4-$MeOC_6H_4$ | 100 | 76 | (71) | 96.0:4.0 |
| 3-$O_2NC_6H_4$ | 20 | 59 | (75) | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | 20 | 72 | (83) | 99.5:0.5 |

| | | | | |
|---|---|---|---|---|
| 4-$CF_3C_6H_4$ | 20 | 70 | (80) | >99.5:0.5 |
| 4-$NCC_6H_4$ | 20 | 67 | (72) | 99.5:0.5 |
| PhCH=CH | 20 | 45 | (77) | 96.5:3.5 |
| 2-Np | 20 | 73 | (42) | 98.0:2.0 |

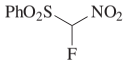


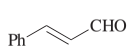
1. **145b** (20 mol %),
   $Et_3N$ (*x* mol %), toluene
2. $NaBH_4$, MeOH, 0°, 5 min



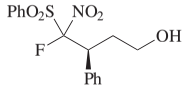
163

| R | *x* | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| Me | — | rt | 16 | (78) | 95.5:4.5 |
| Et | 10 | rt | 18 | (59) | 94.5:5.5 |
| *n*-Pr | 10 | 50° | 2 | (45) | 97.5:2.5 |
| $BnO_2C(CH_2)_2$ | 10 | 50° | 16 | (66) | 92.0:8.0 |
| *n*-Bu | 15 | rt | 20 | (57) | 95.0:5.0 |
| $CH_2{=}CH(CH_2)_2$ | 10 | 50° | 16 | (65) | 95.0:5.0 |
| Ph | 10 | 6° | 16 | (61) | 95.5:4.5 |
| $BnCH_2$ | 10 | 50° | 16 | (84) | 93.5:6.5 |





1. **145b** (20 mol %),
   EtOH, 0°, 16 h
2. $NaBH_4$, MeOH, 0°, 5 min



(94) dr 80:20
er (major) 94.5:5.5
er (minor) 92.0:8.0

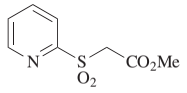
163

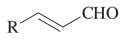
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

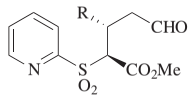
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_2$



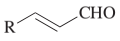


**145c** (10 mol %), toluene, 48 h

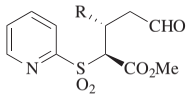


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| R | Temp | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 0° | (55) | 1.7:1 | 94.5:5.5 |
| Ph | rt | (90) | >30:1 | 100.0:0.0 |
| 2-$ClC_6H_4$ | rt | (80) | 7.7:1 | 100.0:0.0 |
| 4-$ClC_6H_4$ | rt | (92) | 2.1:1 | 100.0:0.0 |
| 2-$FC_6H_4$ | rt | (82) | 2.1:1 | 100.0:0.0 |
| 4-$MeOC_6H_4$ | rt | (83) | 3:1 | 100.0:0.0 |
| 4-$AcOC_6H_4$ | rt | (85) | 14.3:1 | 100.0:0.0 |
| 4-$O_2NC_6H_4$ | rt | (95) | 5.8:1 | 100.0:0.0 |
| 3-MeO-4-$AcOC_6H_3$ | rt | (76) | 3:1 | 98.5:1.5 |
| 4-$MeO_2CC_6H_4$ | rt | (88) | 1.5:1 | 100.0:0.0 |
| 4-$MeC_6H_4$ | rt | (88) | >30:1 | 100.0:0.0 |
| 4-$EtC_6H_4$ | rt | (87) | 6.3:1 | 100.0:0.0 |
| 1-Np | rt | (85) | >30:1 | 100.0:0.0 |
| 4-$PhC_6H_4$ | rt | (83) | 4.8:1 | 100.0:0.0 |



**145c** (20 mol %),
$K_2CO_3$ (10 mol %),
toluene, rt

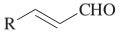


| R | Time (h) | | dr | er |
|---|---|---|---|---|
| *n*-Pr | 72 | (54) | 1.8:1 | 96.0:4.0 |
| *n*-Bu | 48 | (65) | 1.8:1 | 97.0:3.0 |
| *n*-$C_6H_{13}$ | 48 | (55) | 1.6:1 | 97.0:3.0 |
| *n*-$C_7H_{15}$ | 48 | (51) | 1.8:1 | 95.0:5.0 |

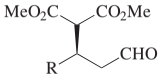
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$C_3$



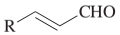


**145b** (10 mol %),
TPAP (5 mol %), NMO (1 eq),
$CH_2Cl_2$, rt, 24–48 h

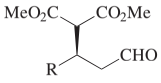


| R | | er |
|---|---|---|
| Ph | (61)[a] | 96.5:3.5 |
| 4-$BrC_6H_4$ | (63)[a] | 96.0:4.0 |
| 2-$O_2NC_6H_4$ | (73)[a] | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | (71)[a] | 93.0:7.0 |
| 4-$MeC_6H_4$ | (72)[a] | 88.5:11.5 |

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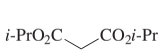
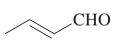
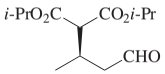
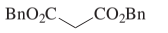
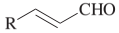
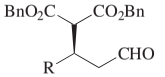
**166** (10 mol %),
LiOAc (30 mol %), $CH_2Cl_2$



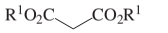
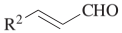
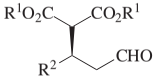
| R | | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| *n*-Bu | — | rt | 96 | (85) | 89.5:10.5 |
| *n*-Bu | MW (2W) | — | 6 | (76) | 91.5:8.5 |
| 2-$C_4H_3O$ | — | rt | 96 | (75) | 88.5:11.5 |
| 2-$C_4H_3O$ | MW (2W) | — | 6 | (82) | 89.0:11.0 |
| 4-$MeOC_6H_4$ | — | rt | 96 | (87) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | MW (2W) | — | 6 | (85) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | — | rt | 36 | (90) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | MW (2W) | — | 6 | (89) | 95.0:5.0 |

421

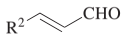
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **202** (15 mol %), *t*-BuOK (30 mol %), $CaCl_2$ (18 mol %), toluene, –15°, 24 h |  (60) er 65.6:34.4 | 594 |
|  |  | Catalyst (5 mol %), $PhCO_2H$ (5 mol %), $H_2O$ |  | 167 |

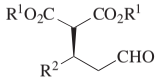
| R | Catalyst | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | **172** | rt | 36 | (77) | 98.0:2.0 |
| Ph | **207b** | 0° | 72 | (74) | 94.0:6.0 |
| Ph | **207b** | rt | 36 | (83) | 91.0:9.0 |
| 4-$MeOC_6H_4$ | **172** | rt | 36 | (74) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | **207b** | 0° | 72 | (69) | 96.0:4.0 |

| | | | | |
|---|---|---|---|---|
|  |  | **145b** (15 mol %), $PhCO_2H$ (15 mol %), EtOH, $H_2O$, 0° |  | 699 |

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | 2-$C_4H_3O$ | 6 | (92) | 99.5:0.5 |
| Me | Ph | 5 | (92) | >99.5:0.5 |
| Me | 4-$MeOC_6H_4$ | 8 | (95) | 99.5:0.5 |
| Me | 4-$O_2NC_6H_4$ | 8 | (96) | 99.5:0.5 |
| Et | Ph | 5 | (95) | >99.5:0.5 |
| Bn | *n*-Bu | 6 | (55) | 98.0:2.0 |
| Bn | Ph | 5 | (97) | 99.5:0.5 |
| Bn | 4-$EtC_6H_4$ | 6 | (90) | >99.5:0.5 |
| Bn | 4-*i*-$PrC_6H_4$ | 6 | (89) | >99.5:0.5 |



**145b** (*x* mol %),
4-$FC_6H_4CO_2Li$ (*y* mol %),
$CH_2Cl_2$/MeOH (9:1), rt





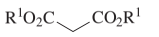
| $R^1$ | $R^2$ | *x* | *y* | Time (h) | | er |
|---|---|---|---|---|---|---|
| Me | Ph | 10 | 5 | 40 | (71) | 97.5:2.5 |
| Et | Me | 10 | 5 | 40 | (81) | 98.0:2.0 |
| Et | Et | 5 | 30 | 120 | (61) | 92.5:7.5 |
| Et | *n*-Pr | 5 | 30 | 60 | (67) | 94.0:6.0 |
| Et | 2-$C_4H_3O$ | 10 | 5 | 40 | (76) | 92.0:8.0 |
| Et | Ph | 10 | 5 | 40 | (81) | 98.0:2.0 |
| Et | 3-$ClC_6H_4$ | 10 | 5 | 48 | (76) | 96.0:4.0 |
| Et | 4-$ClC_6H_4$ | 10 | 5 | 36 | (73) | 97.5:2.5 |
| Et | 4-$FC_6H_4$ | 10 | 5 | 40 | (72) | 97.0:3.0 |
| Et | 2-$MeOC_6H_4$ | 10 | 5 | 60 | (65) | 97.0:3.0 |
| Et | 2-$O_2NC_6H_4$ | 10 | 5 | 36 | (85) | >99.5:0.5 |
| Et | 4-$O_2NC_6H_4$ | 10 | 5 | 36 | (81) | 97.5:2.5 |
| Et | 3-$MeC_6H_4$ | 10 | 5 | 36 | (76) | 95.0:5.0 |
| Et | 4-$MeC_6H_4$ | 10 | 5 | 36 | (75) | 95.5:4.5 |
| *i*-Pr | Ph | 10 | 5 | 40 | (82) | 97.5:2.5 |
| *t*-Bu | Ph | 10 | 5 | 72 | (45) | 98.5:1.5 |

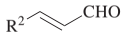
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

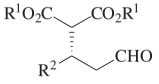
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$





*ent*-**145b** (5 mol %), AcOH (20 mol %), $H_2O$, 0° to rt



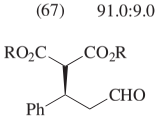
701

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | 2-$C_4H_3O$ | 3 | (92) | 94.0:6.0 |
| Me | Ph | 6 | (90) | 98.0:2.0 |
| Me | 2-$BrC_6H_4$ | 12 | (74) | 95.0:5.0 |
| Me | 4-$BrC_6H_4$ | 4 | (75) | 97.0:3.0 |
| Me | 4-$FC_6H_4$ | 2 | (78) | 98.5:1.5 |
| Me | 4-$MeOC_6H_4$ | 4 | (81) | 95.5:4.5 |
| Me | 4-$O_2NC_6H_4$ | 3 | (78) | 96.0:4.0 |
| Bn | Me | 27 | (55) | 89.5:10.5 |
| Bn | *i*-Pr | 48 | (70) | 97.5:2.5 |
| Bn | MeCH=CH | 20 | (62) | 91.0:9.0 |
| Bn | 2-$C_4H_3O$ | 3 | (85) | 95.0:5.0 |
| Bn | $EtCH=CH(CH_2)_2$ | 27 | (62) | 91.5:8.5 |
| Bn | Ph | 5 | (93) | 97.5:2.5 |
| Bn | 4-$BrC_6H_4$ | 4 | (95) | 96.0.4.0 |
| Bn | 4-$MeOC_6H_4$ | 4 | (88) | 98.0:2.0 |
| Bn | *n*-$C_5H_{11}CH=CH$ | 20 | (67) | 91.0:9.0 |





**166** (10 mol %), LiOAc (30 mol %), $CH_2Cl_2$



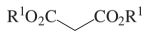
421

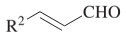
Catalyst Recycling (R = Et)

| Run | Time (h) | er | Conv. (%) |
|---|---|---|---|
| 1 | 6 | 95.0:5.0 | 93 |
| 2 | 6 | 95.0:5.0 | 73 |
| 3 | 6 | 95.0:5.0 | 53 |
| 4 | 6 | 95.0:5.0 | 77 |

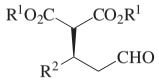
| R | | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| Me | — | rt | 36 | (86) | 99.5:0.5 |
| Me | MW (2W) | — | 6 | (80) | 99.5:0.5 |
| Et | — | rt | 36 | (81) | 95.5:4.5 |
| Et | MW (2W) | — | 6 | (88) | 95.0:5.0 |
| *i*-Pr | — | rt | 72 | (85) | 95.0:5.0 |
| *i*-Pr | MW (2W) | — | 6 | (63) | 95.0:5.0 |

$C_3$





**168a** (10 mol %),
$PhCO_2H$ (40 mol %),
*i*-PrOH/$H_2O$ (3:2), rt





Catalyst Recycling ($R^1$ = Me; $R^2$ = Ph)

| Run | Time (h) | | er |
|---|---|---|---|
| 1 | 38 | (95) | 97.0:3.0 |
| 2 | 50 | (88) | 97.0:3.0 |
| 3 | 65 | (70) | 93.0:7.0 |
| 4 | 80 | (44) | 88.0:12.0 |

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | 2-$C_4H_3O$ | 50 | (91) | 94.5:5.5 |
| Me | Ph | 50 | (82) | 97.0:3.0 |
| Me | 4-$FC_6H_4$ | 60 | (85) | 97.5:2.5 |
| Me | 4-$MeOC_6H_4$ | 60 | (88) | 95.5:4.5 |
| Me | 4-$O_2NC_6H_4$ | 48 | (86) | 95.5:4.5 |
| Et | Ph | 60 | (96) | 98.5:1.5 |
| Bn | Me | 60 | (80) | 92.5:7.5 |
| Bn | Ph | 48 | (94) | 97.5:2.5 |
| Bn | 4-$BrC_6H_4$ | 60 | (73) | 95.5:4.5 |
| Bn | 4-$MeOC_6H_4$ | 60 | (92) | 97.5:2.5 |
| Bn | 4-$O_2NC_6H_4$ | 50 | (95) | 96.5:3.5 |

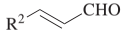
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

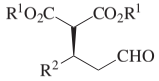
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





**366** (10 mol %), EtOH, 4°

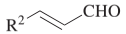


703

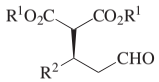
Catalyst Recycling ($R^1$ = Me; $R^2$ = Ph)

| Run | Time (h) | er | Conv. (%) |
|---|---|---|---|
| 1 | 24 | 97.5:2.5 | >99 |
| 2 | 24 | 97.0:3.0 | >99 |
| 3 | 24 | 97.0:3.0 | >99 |
| 4 | 24 | 97.5:2.5 | 96 |
| 5 | 24 | 99.0:1.0 | 70 |
| 6 | 96 | 99.0:1.0 | 70 |

| $R^1$ | $R^2$ | Time (d) | | er |
|---|---|---|---|---|
| Me | Ph | 1 | (93) | 98.0:2.0 |
| Me | 4-$ClC_6H_4$ | 2 | (97) | 95.5:4.5 |
| Me | 4-$FC_6H_4$ | 2 | (95) | 96.0:4.0 |
| Me | 4-$MeOC_6H_4$ | 2 | (97) | 88.0:12.0 |
| Et | Ph | 2 | (98) | 97.5:2.5 |
| Bn | Ph | 3 | (81) | 96.0:4.0 |
| Bn | 4-$ClC_6H_4$ | 3 | (95) | 94.0:6.0 |
| Bn | 4-$FC_6H_4$ | 3 | (94) | 98.0:2.0 |
| Bn | 4-$MeOC_6H_4$ | 3 | (97) | 94.5:5.5 |
| Bn | 4-$O_2NC_6H_4$ | 3 | (97) | 91.0:9.0 |



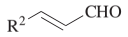
**368** (10 mol %), MeOH, rt



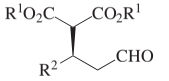
704

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | 2-$C_4H_3O$ | 13 | (30) | 91.0:9.0 |
| Me | Ph | 3 | (97) | 97.0:3.0 |
| Me | 2-$MeOC_6H_4$ | 6 | (86) | 93.5:6.5 |
| Me | 2-$O_2NC_6H_4$ | 6 | (88) | 97.5:2.5 |
| Et | Ph | 3 | (98) | 98.5:1.5 |
| Et | 2-$MeOC_6H_4$ | 4 | (73) | 97.5:2.5 |

| | | | | |
|---|---|---|---|---|
| Et | 4-$MeOC_6H_4$ | 6 | (87) | 95.5:4.5 |
| Et | 2-$O_2NC_6H_4$ | 6 | (73) | 97.5:2.5 |
| Bn | Me | 48 | (42) | 89.5:10.5 |
| Bn | Ph | 3 | (87) | 97.0:3.0 |
| Bn | 2-$MeOC_6H_4$ | 6 | (85) | 96.0:4.0 |
| Bn | 2-$O_2NC_6H_4$ | 6 | (77) | 97.5:2.5 |



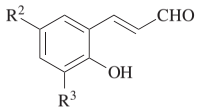
**371** (10 mol %), EtOH, 4°, 48 h



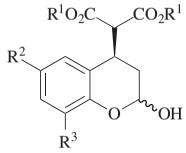
| $R^1$ | $R^2$ | | er | |
|---|---|---|---|---|
| Me | Ph | (99) | 96.5:35 | 705 |
| Me | 4-$FC_6H_4$ | (93) | 96.0:4.0 | |
| Bn | Ph | (94) | 93.5:6.5 | |

$C_3$





**370** (20 mol %), $CHCl_3$, rt



706

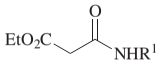
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| Me | H | H | 24 | (89) | 60:40 | 98.0:2.0 |
| Me | H | MeO | 30 | (77) | 58:42 | 99.0:1.0 |
| Me | Br | H | 28 | (71) | 59:41 | >99.5:0.5 |
| Me | Br | Br | 48 | (64) | 60:40 | 99.5:0.5 |
| Me | Cl | H | 28 | (74) | 58:42 | 94.5:5.5 |
| Me | Cl | Cl | 48 | (62) | 59:41 | >99.5:0.5 |
| Me | MeO | H | 28 | (72) | 59:41 | 98.5:1.5 |
| Me | $O_2N$ | H | 48 | (70) | 62:38 | 97.0:3.0 |
| Me | Me | H | 28 | (77) | 62:38 | 99.0:1.0 |
| Et | H | H | 30 | (76) | 59:41 | 98.0:2.0 |
| *i*-Pr | H | H | 48 | (77) | 64:36 | 97.5:2.5 |
| Bn | H | H | 28 | (85) | 62:38 | 98.5:1.5 |

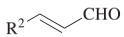
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

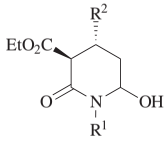
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$





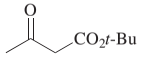
**145b** (10 mol %),
AcOK (1 eq),
$CF_3CH_2OH$, rt, overnight

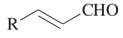


707

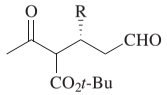
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| Me | Ph | (66) | 19:1 | 97.5:2.5 |
| Me | 4-$BrC_6H_4$ | (68) | 9:1 | 97.0:3.0 |
| Me | 4-$ClC_6H_4$ | (82) | 9:1 | 97.0:3.0 |
| Me | 4-$FC_6H_4$ | (52) | 9:1 | 84.5:15.5 |
| Me | 4-$O_2NC_6H_4$ | (95) | 19:1 | 97.5:2.5 |
| Me | 4-$MeC_6H_4$ | (66) | 9:1 | 96.0:4.0 |
| Et | Ph | (14) | 19:1 | 94.5:5.5 |
| $HOCH_2CH_2$ | Ph | (73) | 9:1 | 99.0:1.0 |
| $HOCH_2CH_2$ | 4-$BrC_6H_4$ | (44) | 9:1 | 95.0:5.0 |
| $HOCH_2CH_2$ | 4-$O_2NC_6H_4$ | (56) | 9:1 | 97.5:2.5 |
| *i*-Pr | Ph | (10) | 10:7 | 95.5:4.5 |
| Bn | Ph | (90) | 3:1 | 99.0:1.0 |
| Bn | 2-$BrC_6H_4$ | (71) | 5:1 | 98.0:2.0 |
| Bn | 4-$BrC_6H_4$ | (93) | 5:1 | 97.0:3.0 |
| Bn | 4-$ClC_6H_4$ | (84) | 4:1 | 95.0:5.0 |
| Bn | 4-$FC_6H_4$ | (84) | 5:1 | 95.0:5.0 |
| Bn | 4-$O_2NC_6H_4$ | (92) | 5:1 | 97.5:2.5 |
| Bn | 4-$NCC_6H_4$ | (94) | 5:1 | 97.0:3.0 |
| Bn | 2-Np | (86) | 3:1 | 99.5:0.5 |

$C_4$





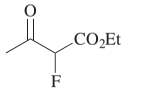
**207c** (10 mol %), $H_2O$, rt, 5 h

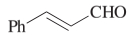


dr 1:1–6:1

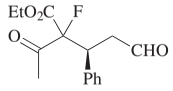
| R | | er |
|---|---|---|
| Me | (82) | 92.0:8.0 |
| Et | (95) | 95.0:5.0 |
| *n*-Bu | (71) | 96.5:3.5 |
| Ph | (97) | 97.0:3.0 |

708



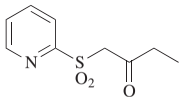


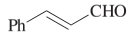
**145b** (20 mol %), toluene, rt, 16 h



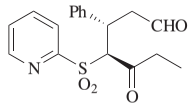
(72) dr 77:23
er (major) 94.0:6.0
er (minor) 94.0:6.0

163



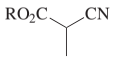


**145c** (10 mol %), toluene, rt, 48 h



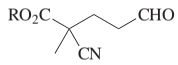
(94) dr >30:1
er 100.0:0.0

697





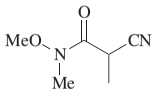
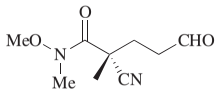
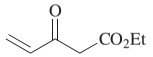
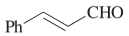
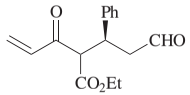
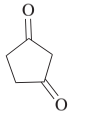
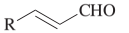
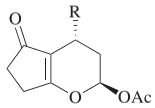
**367** (2 mol %), $[RhCl(cyclooctene)_2]_2$ (1 mol %), toluene, rt



709

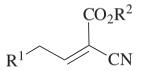
| R | Time (h) | | er |
|---|---|---|---|
| Et | 1 | (96) | 84.5:15.5 |
| *i*-Pr | 1 | (97) | 86.5:13.5 |
| *i*-$Pr_2CH$ | 2 | (82) | 90.0:10.0 |
| *t*-$Bu_2CH$ | 2 | (82) | 93.0:7.0 |
| 2,4,6-$Me_3C_6H_2$ | 0.5 | (93) | 87.5:12.5 |
| 2,6-*i*-$Pr_2C_6H_3$ | 0.5 | (95) | 92.5:7.5 |
| $Ph_2CH$ | 1 | (97) | 89.5:10.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **336** (*x* mol %), Rh(acac)$(CO)_2$ (0.95 mol %), benzene, 3° |  | 98 |
| | | | *x* Time (h) (94) er<br>0.1 2 (94) 94.5:5.5<br>1 17 (89) 94.5:5.5 | |
| $C_5$ | | | | |
|  |  | **145b** (10 mol %), $PhCO_2H$ (10 mol %), toluene, 18 h, rt |  63% conv., dr 1:1, er 97.0:3.0 | 710 |
|  |  | 1. **207c** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, –35°, 4 h<br>2. $Ac_2O$, $Et_3N$, DMAP, $CH_2Cl_2$, rt, 2 h |  | 711 |

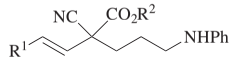
| R | | dr | er |
|---|---|---|---|
| Me | (74) | 7:2 | 92.0:8.0 |
| $EtO_2C$ | (48) | >20:1 | 94.0:6.0 |
| Et | (74) | 5:2 | 96.5:3.5 |
| *i*-Pr | (74) | 5:2 | 97.0:3.0 |
| 2-$C_4H_3O$ | (85) | 9:2 | 91.0:9.0 |
| 2-$C_4H_3S$ | (95) | 5:1 | 96.5:3.5 |
| $EtCH{=}CH(CH_2)_2$ | (81) | 2:1 | 98.0:2.0 |
| Ph | (85) | 3:1 | 95.0:5.0 |
| 2-$BrC_6H_4$ | (59) | 3:1 | 96.0:4.0 |
| 4-$FC_6H_4$ | (82) | 7:2 | 94.0:6.0 |
| 2-$O_2NC_6H_4$ | (65) | 2:1 | 96.0:4.0 |
| 2-$CF_3C_6H_4$ | (69) | 5:2 | 95.5:4.5 |
| Bn | (85) | 2:1 | 97.5:2.5 |

$C_{6-12}$





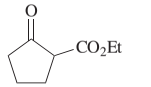
1. **394** (10 mol %), $CH_2Cl_2$, –20°, times
2. $PhNH_2$, $NaBH(OAc)_3$, DCE, rt



712

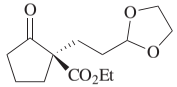
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Me | 23 | (44) | 78.0:22.0 |
| Me | *i*-Pr | 70 | (63) | 75.0:25.0 |
| Et | *t*-Bu | 73 | (45) | 70.0:30.0 |
| Et | Bn | 24 | (39) | 76.5:23.5 |
| *i*-Pr | Me | 70 | (63) | 75.0:25.0 |
| $TBSO(CH_2)_3$ | Me | 24 | (55) | 76.5:23.5 |
| allyl | Me | 26 | (54) | 75.5:24.5 |
| *t*-Bu | Me | 192 | (59) | 70.0:30.0 |
| *n*-$C_6H_{13}$ | Me | 26 | (52) | 78.0:22.0 |
| Bn | Me | 18 | (39) | 69.5:30.5 |

$C_6$



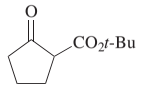


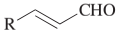
1. **348** (10 mol %), PhI, rt, 21 h
2.  , PTSA



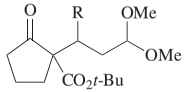
(87) er 96.5:3.5

670





**339a** (5 mol %), solvent, 0°



32

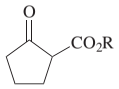
| R | Solvent | Time (h) | | dr | er |
|---|---|---|---|---|---|
| H | MeOH | 48 | (73) | — | 93.5:6.5 |
| H | THF; then MeOH | 26 | (10) | — | 95.0:5.0 |
| Me | THF; then MeOH | 30 | (90) | 3.8:1 | 99.5:0.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

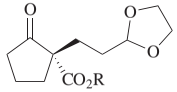
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_6$



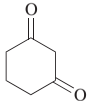


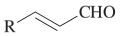
1. **358** (2 mol %),
$K_2CO_3$ (10 mol %),
*i*-$PrC_6H_5$
2. 4-TsOH,  , rt



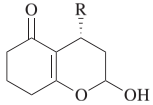
214

| R | Temp (°) | Time (h) | | er |
|---|---|---|---|---|
| *t*-Bu | –40 | 2 | (84) | 89.5:10.5 |
| 9-fluorenyl | –35 | 0.5 | (92) | 95.0:5.0 |



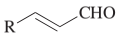


Catalyst (10 mol %),
TPAP (5 mol %),
NMO (1 eq), $CH_2Cl_2$

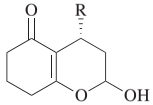


698

| R | Catalyst | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| *n*-Pr | **207c** | rt | 48 | (59)[a] | 97.0:3.0 |
| 2-$BrC_6H_4$ | **145b** | 10° | 96 | (53)[a] | 90.0:10.0 |
| 2-$ClC_6H_4$ | **145b** | 10° | 48 | (66)[a] | 96.0:4.0 |
| *n*-$C_7H_{15}$ | **207c** | rt | 48 | (51)[a] | 98.0:2.0 |

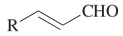


**146** (20 mol %), $CH_2Cl_2$

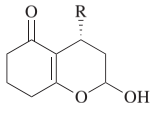


713

| R | Temp (°) | | er |
|---|---|---|---|
| 2-$BrC_6H_4$ | 0 | (78) | 98.0:2.0 |
| 3-$BrC_6H_4$ | 0 | (95) | 93.5:6.5 |
| 4-$BrC_6H_4$ | 0 | (76) | 98.5:1.5 |
| 2-$ClC_6H_4$ | rt | (51) | 96.5:3.5 |
| 2-$O_2NC_6H_4$ | 0 | (77) | 97.0:3.0 |

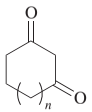


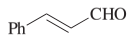
**207c** (10 mol %), $CH_2Cl_2$, 0°



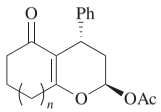
| R | | er | |
|---|---|---|---|
| *n*-Pr | (78) | 98.0:2.0 | 713 |
| *n*-$C_7H_{15}$ | (66) | 98.0:2.0 | |
| *n*-$C_{10}H_{21}$ | (67) | 98.0:2.0 | |

$C_{6-7}$



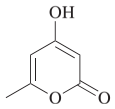


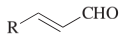
1. **207c** (10 mol %), $PhCO_2H$ (10 mol %), $CH_2Cl_2$, –35°, 4 h
2. $Ac_2O$, $Et_3N$, DMAP, $CH_2Cl_2$, rt, 2 h



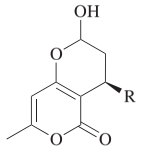
| *n* | | dr | er | |
|---|---|---|---|---|
| 1 | (48) | 4:1 | 98.0:1.5 | 711 |
| 2 | (77) | >8:1 | 98.5:1.5 | |

$C_6$





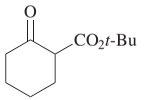
**207c** (20 mol %), $CH_2Cl_2$



156

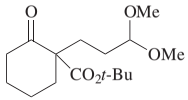
| R | Temp | Time (h) | | er |
|---|---|---|---|---|
| Et | 0° | 60 | (82) | 96.0:4.0 |
| *n*-Pr | 0° | 60 | (86) | 95.5:4.5 |
| *n*-Bu | 0° | 60 | (74) | 95.5:4.5 |
| Ph | rt | 96 | (56) | 91.5:8.5 |
| 4-$BrC_6H_4$ | rt | 48 | (55) | 92.0:8.0 |
| 2-$ClC_6H_4$ | rt | 48 | (48) | 90.0:10.0 |
| 4-$MeOC_6H_4$ | rt | 48 | (43) | 92.5:7.5 |
| *n*-$C_7H_{15}$ | 0° | 60 | (96) | 95.0:5.0 |
| *n*-$C_{10}H_{21}$ | 0° | 60 | (59) | 95.5:4.5 |

$C_7$





**339a** (5 mol %), 1 M in MeOH, rt, 120 h



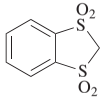
(31) er 90.0:10.0 32

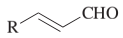
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

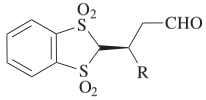
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_7$





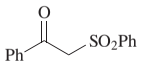
Catalyst (*x* mol %),
$PhCO_2H$ (*y* mol %),
solvent, rt

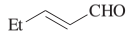


714

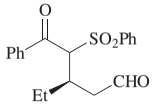
| R | Catalyst | *x* | *y* | Solvent | Time (h) | | er |
|---|---|---|---|---|---|---|---|
| Me | **145b** | 20 | — | toluene/THF | 35 | (95) | 94.0:6.0 |
| Et | **145b** | 20 | — | toluene/THF | 135 | (73) | 96.0:4.0 |
| 2-$C_4H_3O$ | **145d** | 20 | — | toluene | 72 | (76) | 92.0:8.0 |
| Ph | **145b** | 10 | 10 | *t*-BuOMe | 72 | (95) | 98.5:1.5 |
| 4-$BrC_6H_4$ | **145b** | 10 | 10 | *t*-BuOMe | 72 | (90) | 97.0:3.0 |
| 4-$ClC_6H_4$ | **145b** | 10 | 10 | *t*-BuOMe | 72 | (68) | 98.0:2.0 |
| 2-$FC_6H_4$ | **145d** | 20 | 10 | *t*-BuOMe | 72 | (63) | 97.0:3.0 |
| 3-$FC_6H_4$ | **145b** | 20 | 10 | toluene | 120 | (72) | 97.5:2.5 |
| 4-$FC_6H_4$ | **145b** | 10 | 10 | toluene | 120 | (70) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | **145b** | 10 | — | toluene | 34 | (98) | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | **145b** | 10 | 10 | toluene | 115 | (76) | 99.0:1.0 |
| 4-$O_2NC_6H_4$ | **145b** | 10 | 10 | toluene | 43 | (85) | 99.0:1.0 |
| 4-$MeC_6H_4$ | **145d** | 20 | 10 | toluene | 68 | (71) | 96.5:3.5 |
| 4-$NCC_6H_4$ | **145b** | 10 | 10 | toluene | 96 | (87) | 99.0:1.0 |

$C_8$



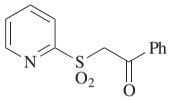


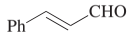
**207c** (20 mol %),
$PhCO_2H$ (20 mol %),
THF, rt, 20 h



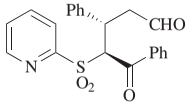
(81) dr 1:1
er 95.0:5.0

715



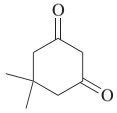


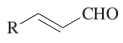
**145c** (10 mol %),
toluene, rt, 48 h



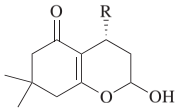
(76) dr >30:1
er 100.0:0.0

697



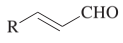


**145b** (20 mol %), $CH_2Cl_2$

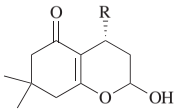


713

| R | Temp (°) | | er |
|---|---|---|---|
| Ph | 0 | (89) | 97.0:3.0 |
| 2-$BrC_6H_4$ | rt | (63) | 96.0:4.0 |
| 2-$ClC_6H_4$ | rt | (64) | 96.0:4.0 |
| 2-$O_2NC_6H_4$ | 0 | (49) | 94.0:6.0 |
| 2-$MeC_6H_4$ | 0 | (69) | 94.0:6.0 |
| 2,4-$Me_2C_6H_3$ | 0 | (76) | 93.5:6.5 |

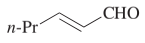


**207c** (*x* mol %), $CH_2Cl_2$, 10°

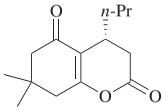


713

| R | *x* | | er |
|---|---|---|---|
| Et | 10 | (62) | 97.0:3.0 |
| *n*-Pr | 10 | (63) | 97.5:2.5 |
| *n*-Bu | 10 | (68) | 98.0:2.0 |
| 3-$BrC_6H_4$ | 20 | (48) | 96.0:4.0 |
| *n*-$C_7H_{15}$ | 10 | (67) | 98.0:2.0 |
| *n*-$C_{10}H_{21}$ | 10 | (67) | 98.0:2.0 |



**207c** (10 mol %), TPAP (5 mol %), NMO (1 eq), $CH_2Cl_2$, 10°, 96 h



(50)[a] er 95.0:5.0

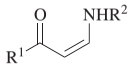
698

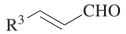
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

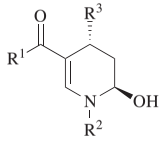
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{9–10}$





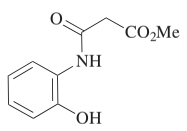
**145b** (20 mol %),
$PhCO_2H$ (10 mol %),
EtOAc or EtOAc/$Et_2O$ (2:1),
0°, 4 d

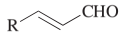


716

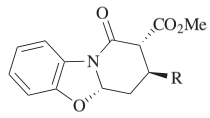
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| Ph | Ph | Ph | (60) | 6:1 | >99.0:1.0 |
| Ph | Ph | 2-$MeOC_6H_4$ | (52) | 2.7:1 | 86.0:14.0 |
| Ph | Ph | 4-$MeOC_6H_4$ | (22) | 6:1 | 85.0:15.0 |
| Ph | 4-$MeC_6H_4$ | Ph | (48) | 5.4:1 | 87.0:13.0 |
| Ph | 4-*c*-$C_6H_{11}C_6H_4$ | Ph | (44) | 3.4:1 | 92.0:8.0 |
| Ph | 4-*c*-$C_6H_{11}C_6H_4$ | 4-$MeOC_6H_4$ | (20) | 4.1:1 | 98.0:2.0 |
| 4-$FC_6H_4$ | Ph | Ph | (30) | 3.5:1 | 89.0:11.0 |
| 4-$MeOC_6H_4$ | 2-Cl-5-$C_5H_3N$ | Ph | (44) | 10:1 | >99.0:1.0 |
| 4-$MeOC_6H_4$ | Ph | Ph | (57) | 3.4:1 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | Ph | 4-$ClC_6H_4$ | (63) | 2.5:1 | 89.0:11.0 |
| 4-$MeOC_6H_4$ | 4-$ClC_6H_4$ | Ph | (42) | 7.8:1 | 91.0:9.0 |
| 4-$MeOC_6H_4$ | 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | (60) | 4.1:1 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 4-$MeC_6H_4$ | Ph | (72) | 4:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 4-*c*-$C_6H_{11}C_6H_4$ | Ph | (57) | 5.9:1 | 90.0:10.0 |
| 4-$MeC_6H_4$ | 4-$ClC_6H_4$ | 2-$MeOC_6H_4$ | (33) | 2.4:1 | 85.0:15.0 |

$C_9$




1. *ent*-**145b** (10 mol %), $CH_2Cl_2$, –20°
2. $TsOH•H_2O$ (2 eq), $CH_2Cl_2$, rt, 12 h



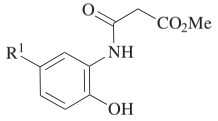

| R | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| Me | 11 | (93) | 73:27 | 96.0:4.0 | 93.5:6.5 |
| Et | 72 | (60) | 67:33 | 98.0:2.0 | 97.5:2.5 |
| *n*-Pr | 120 | (50) | 69:31 | 98.5:1.5 | 95.5:4.5 |
| *i*-Pr | 120 | (72) | 55:45 | 99.5:0.5 | 99.5:0.5 |
| Ph | 4.5 | (90) | 92:8 | 98.0:2.0 | — |
| 2-$BrC_6H_4$ | 14 | (69) | 95:5 | 98.5:1.5 | — |
| 4-$BrC_6H_4$ | 5.5 | (76) | 85:15 | 95.0:5.0 | — |
| 2-$ClC_6H_4$ | 24 | (70) | 96:4 | 98.5:1.5 | — |
| 3-$ClC_6H_4$ | 72 | (65) | 93:7 | 98.5:1.5 | — |
| 4-$ClC_6H_4$ | 3.5 | (53) | 85:15 | 96.0:4.0 | — |
| 2-$FC_6H_4$ | 72 | (89) | 93:7 | 99.0:1.0 | — |
| 4-$FC_6H_4$ | 72 | (64) | 95:5 | 99.0:1.0 | — |
| 2-$MeOC_6H_4$ | 14 | (87) | 93:7 | 98.0:2.0 | — |
| 4-$MeOC_6H_4$ | 48 | (82) | 92:8 | 92.5:7.5 | — |
| 4-$O_2NC_6H_4$ | 4.5 | (55) | 93:7 | 97.0:3.0 | — |
| *n*-$C_7H_{15}$ | 120 | (27) | 54:46 | 99.0:1.0 | 99.0:1.0 |
| 4-$MeC_6H_4$ | 9 | (83) | 92:8 | 95.0:5.0 | — |

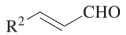
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

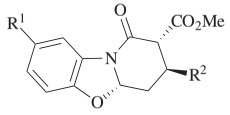
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{9-10}$





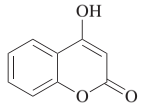
1. *ent*-**145b** (10 mol %), $CH_2Cl_2$, –20°
2. $TsOH•H_2O$ (2 eq), $CH_2Cl_2$, rt, 12 h

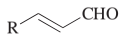


717

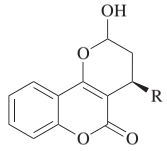
| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Cl | 2-$ClC_6H_4$ | 72 | (53) | 93:7 | 99.5:0.5 |
| Cl | 3-$MeC_6H_4$ | 12 | (54) | 95:5 | 98.0:2.0 |
| Me | 4-$ClC_6H_4$ | 8.5 | (81) | 94:6 | 98.0:2.0 |
| Me | 4-$MeC_6H_4$ | 9.5 | (86) | 93:7 | 97.0:3.0 |

$C_9$

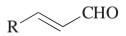




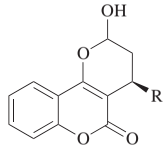
**145b** (20 mol %), toluene, –20°, 50 h



| R | | er | Refs. |
|---|---|---|---|
| *n*-Pr | (83) | 97.5:2.5 | 156 |
| *n*-Bu | (63) | 97.0:3.0 | |
| *n*-$C_{10}H_{21}$ | (76) | 96.0:4.0 | |



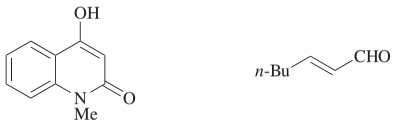
**207c** (20 mol %), solvent, 10°, 48–96 h



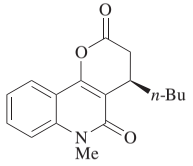
156

| R | Solvent | | er |
|---|---|---|---|
| Et | $CH_2Cl_2$ | (83) | 96.5:3.5 |
| *n*-Pr | $CH_2Cl_2$ | (85) | 96.0:4.0 |
| *n*-Bu | $CH_2Cl_2$ | (81) | 96.5:3.5 |
| Ph | MeCN | (41) | 94.5:5.5 |
| 2-$BrC_6H_4$ | $CH_2Cl_2$ | (82) | 96.0:4.0 |

| | | | |
|---|---|---|---|
| 4-$BrC_6H_4$ | MeCN | (45) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | MeCN | (57) | 97.0:3.0 |
| *n*-$C_7H_{15}$ | $CH_2Cl_2$ | (89) | 95.5:4.5 |
| *n*-$C_{10}H_{21}$ | $CH_2Cl_2$ | (80) | 97.5:2.5 |




1. **207c** (20 mol %), $CH_2Cl_2$, rt
2. PCC, $CH_2Cl_2$, rt

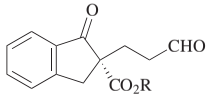



(43) er 94.5:5.5 156

$C_{10}$

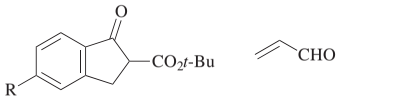



**355** (5 mol %), $Sc(OTf)_3$ (5 mol %), $CH_2Cl_2$

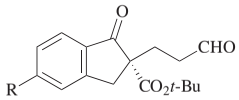



(73) er 87.5:12.5

| R | Temp | Time (h) | |
|---|---|---|---|
| *i*-Bu | rt | 5 | 680 |
| *t*-Bu | 20° | 0.5 | 689 |



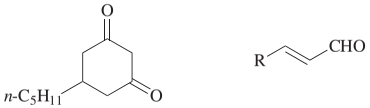

**342** (*x* mol %), *i*-PrNEt (30 mol %), $CH_2Cl_2$, –40°



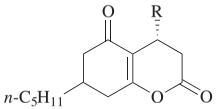

694, 663

| R | *x* | Time (d) | | er |
|---|---|---|---|---|
| H | 1 | 0.2 | (86) | 89.5:10.5 |
| MeO | 5 | 2 | (98) | 92.5:7.5 |

$C_{11}$




1. **207c** (10 mol %), TPAP (5 mol %), NMO (1 eq), $CH_2Cl_2$, rt, 72 h
2. TPAP (5 mol %), NMO (1 eq), $CH_2Cl_2$, rt, 0.33 h




698

| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| *n*-Pr | (51)[a] | 1:1 | 98.5:1.5 | 98.5:1.5 |
| *n*-$C_7H_{15}$ | (50)[a] | 1:1 | 98.5:1.5 | 98.5:1.5 |

[a] The aldehyde is generated in situ.

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

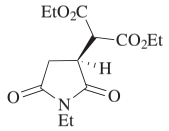
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_3$



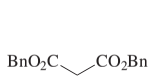


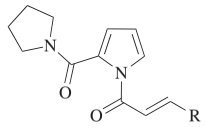
**160b** (20 mol %), $Et_3N$, –50°, 96 h



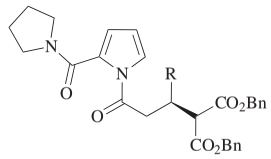
(90) er 85.5:14.5

612



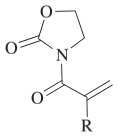


**369** (*x* mol %), La(O*i*-Pr)$_3$ (10–20 mol %), HFIP (10 mol %), DME, –20°, 40 h

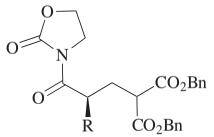


718

| R | *x* | | er |
|---|---|---|---|
| Me | 10 | (85) | 95.0:5.0 |
| *n*-Pr | 10 | (78) | 90.0:10.0 |
| MeCH=CH | 20 | (80) | 98.0:2.0 |
| *n*-PrCH=CH | 10 | (83) | 96.0:4.0 |
| *c*-$C_6H_{11}$ | 20 | (87) | 94.0:6.0 |
| Ph | 20 | (76) | 89.0:11.0 |
| 4-$ClC_6H_4$ | 20 | (80) | 93.0:7.0 |



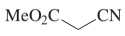
**372** (11 mol %), $Ca(OEt)_2$ (10 mol %), 2-(2-$MeOC_6H_4$)$C_6H_4OH$ (10 mol %), EtOH (2 eq), solvent, –20°

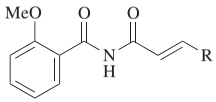


719

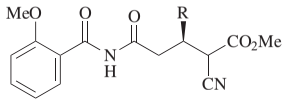
| R | Solvent | Time (h) | | er |
|---|---|---|---|---|
| Me | CPME | 48 | (90) | 97.5:2.5 |
| (Z)-CH(Cl)=$CH_2$ | CPME | 48 | (96) | 97.5:2.5 |
| allyl | CPME | 48 | (86) | 98.0:2.0 |
| $BnOCH_2C{\equiv}CCH_2$ | CPME | 48 | (77) | 96.5:3.5 |
| prenyl | CPME | 72 | (85) | 96.5:3.5 |
| Ph | toluene/$CH_2Cl_2$ (4:1) | 48 | (72) | 74.0:26.0 |
| (*n*-Bu)$C{\equiv}CCH_2$ | CPME | 48 | (91) | 97.0:3.0 |
| PhCH=CH | CPME/THF (2:1) | 72 | (85) | 97.0:3.0 |
| $PhC{\equiv}CCH_2$ | CPME/toluene (4:1) | 48 | (88) | 97.0:3.0 |







*ent*-**164b** (10 mol %), toluene



182

mixture of 2 diasteromers

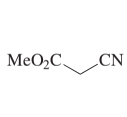
| R | Temp | Time (h) | | er |
|---|---|---|---|---|
| Me | rt | 87 | (90) | 96.0:4.0 |
| $TBSO(CH_2)_5$ | rt | 137 | (96) | 96.0:4.0 |
| Ph | 80° | 52 | (94) | 91.0:9.0 |
| 4-$FC_6H_4$ | 80° | 48 | (91) | 92.5:7.5 |

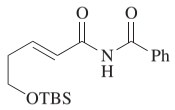
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

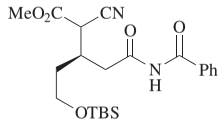
*Please refer to the preceding chart for structures indicated by the **bold** numbers.*

$C_3$



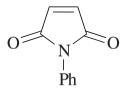




**378** (5 mol %), *t*-BuOH, cyclohexane, rt

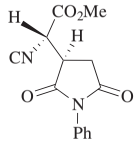



(91) er 96.0:4.0

225



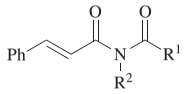

**383** (20 mol %), 4-xylene, –15°, 72 h



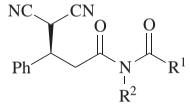

(65) dr 55:45
er (major) 77.0:23.0
er (minor) 58.0:42.0

720



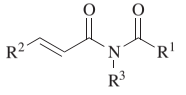




*ent*-**164b** (10 mol %), toluene, rt, 8 h

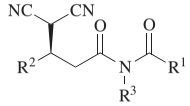



181

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Me | 216 | (27) | 78.0:22.0 |
| Ph | H | 8 | (94) | 92.0:8.0 |



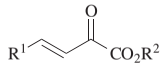

*ent*-**164b** (10 mol %), toluene, rt



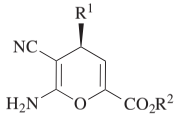

182

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Ph | Me | 216 | (27) | 78.0:22.0 |
| 2-$MeOC_6H_4$ | Me | H | 3 | (96) | 95.0:5.0 |
| 2-$MeOC_6H_4$ | $TBSO(CH_2)_5$ | H | 5 | (95) | 96.5:3.5 |
| Ph | Ph | H | 26 | (84) | 94.0:6.0 |
| 2-$MeOC_6H_4$ | Ph | H | 14 | (95) | 95.5:4.5 |

| | | | | | |
|---|---|---|---|---|---|
| 2,6-$(MeO)_2C_6H_3$ | Ph | H | 75 | (90) | 81.0:19.0 |
| 2-$MeOC_6H_4$ | 4-$FC_6H_4$ | H | 7 | (92) | 95.0:5.0 |
| 2-$MeOC_6H_4$ | 4-$MeOC_6H_4$ | H | 24 | (96) | 95.0:5.0 |
| 2-$MeC_6H_4$ | Ph | H | 24 | (93) | 94.5:5.5 |
| 3,5-$(CF_3)_2C_6H_3$ | Ph | H | 216 | (27) | 78.0:22.0 |



*ent*-**164b** (5 mol %),
toluene, –30°, 12 h



| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Me | (64) | 89.0:11.0 |
| Ph | *i*-Pr | (57) | 87.5:12.5 |
| Ph | allyl | (60) | 88.5:11.5 |
| Ph | Bn | (63) | 90.0:10.0 |
| Ph | 4-$BrC_6H_4CH_2$ | (58) | 90.0:10.0 |
| 2-$BrC_6H_4$ | Me | (65) | 91.5:8.5 |
| 4-$BrC_6H_4$ | Me | (68) | 94.0:6.0 |
| 4-$ClC_6H_4$ | Me | (64) | 91.0:9.0 |
| 2,4-$Cl_2C_6H_3$ | Me | (62) | 94.0:6.0 |
| 4-$FC_6H_4$ | Me | (66) | 90.5:9.5 |
| 4-$EtOC_6H_4$ | Me | (61) | 92.5:7.5 |
| 2,5-$(MeO)_2C_6H_3$ | Me | (65) | 90.0:10.0 |
| 4-$O_2NC_6H_4$ | Me | (50) | 86.0:14.0 |

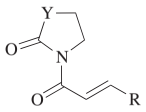
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

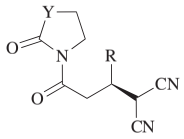
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_3$



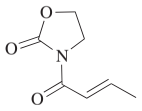


*ent*-**164b** (10 mol %), toluene, rt

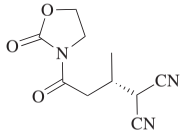


| Y | R | Time (h) | | er |
|---|---|---|---|---|
| O | Ph | 96 | (89) | 91.5:8.5 |
| MeN | Ph | 120 | (59) | 90.5:9.5 |
| $CH_2$ | Me | 168 | (82) | 92.0:8.0 |
| $CH_2$ | *t*-Bu | 192 | (78) | 96.0:4.0 |
| $CH_2$ | 2-$C_4H_3O$ | 24 | (79) | 92.5:7.5 |
| $CH_2$ | Ph | 60 | (93) | 93.5:6.5 |
| $CH_2$ | 4-$ClC_6H_4$ | 72 | (85) | 94.5:5.5 |
| $CH_2$ | 4-$FC_6H_4$ | 48 | (99) | 94.0:6.0 |
| $CH_2$ | 4-$MeOC_6H_4$ | 216 | (77) | 92.5:7.5 |
| $CH_2$ | $BnCH_2$ | 24 | (96) | 94.0:6.0 |
| $CH_2$ | 1-Np | 48 | (93) | 94.0:6.0 |
| $(CH_2)_2$ | Ph | 140 | (42) | 79.5:20.5 |

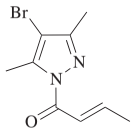
Refs.: 181, 182 | 181, 182 | 181 | 181 | 181 | 181, 182 | 181 | 181 | 181 | 181 | 181 | 181, 182



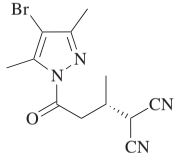
**373** (10 mol %), $Ni(ClO_4)_2•6H_2O$ (10 mol %), MeOH/THF (1:1), rt, 7 h



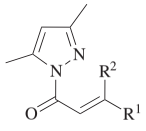
(81) er 92.0:8.0 — 722



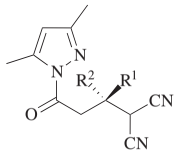
**373** (10 mol %), $Ni(OAc)_2•4H_2O$ (10 mol %), *t*-BuOH/THF (10:1), rt, 4 h



(98) er 96.0:4.0 — 723

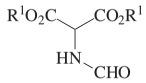


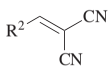
**373** (10 mol %), $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), *t*-BuOH/THF (1:1), rt



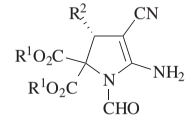
722

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | H | 4 | (69) | 93.5:6.5 |
| $EtO_2C$ | Me | 36 | (94) | 92.5:7.5 |





**376** (10 mol %), toluene, rt, 12 h



724

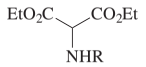
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | Ph | (85) | 93.5:6.5 |
| Et | 2-$C_4H_3O$ | (79) | 89.0:11.0 |
| Et | *c*-$C_6H_{11}$ | (62) | 64.0:36.0 |
| Et | Ph | (92) | 98.0:2.0 |
| Et | 2-$BrC_6H_4$ | (96) | 97.0:3.0 |
| Et | 3-$BrC_6H_4$ | (95) | 95.0:5.0 |
| Et | 4-$BrC_6H_4$ | (90) | 93.0:7.0 |
| Et | 2-$ClC_6H_4$ | (92) | 94.5:5.5 |
| Et | 3-$ClC_6H_4$ | (94) | 96.0:4.0 |
| Et | 4-$ClC_6H_4$ | (91) | 98.5:1.5 |
| Et | 2-$MeOC_6H_4$ | (83) | 92.5:7.5 |
| Et | 4-$MeOC_6H_4$ | (80) | 98.0:2.0 |
| Et | 2,5-$(MeO)_2C_6H_3$ | (81) | 96.0:4.0 |
| Et | 4-$MeC_6H_4$ | (84) | 95.0:5.0 |
| Et | 4-$NCC_6H_4$ | (82) | 91.5:8.5 |
| Bn | Ph | (97) | 97.0:3.0 |
| Bn | 4-$BrC_6H_4$ | (90) | 93.0:7.0 |
| Bn | 4-$ClC_6H_4$ | (94) | 95.0:5.0 |
| Bn | 4-$FC_6H_4$ | (93) | 94.5:5.5 |

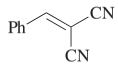
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

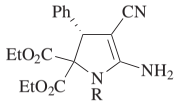
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_3$

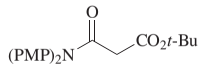


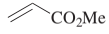


**376** (10 mol %), toluene, rt, 12 h

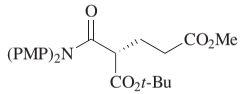


| R | | er | |
|---|---|---|---|
| Ac | (<10) | — | 724 |
| Boc | (74) | — | |
| Ts | (70) | — | |
| Cbz | (62) | 72.5:27.5 | |



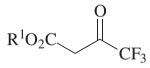


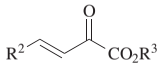
**377** (1 mol %), CsOH (1 eq), toluene, –40°, 12 h



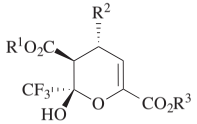
(60) er 65.0:35.0 725

$C_4$





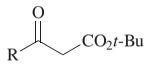
**69b** (10 mol %), $CH_2Cl_2$, rt

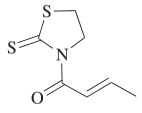


726

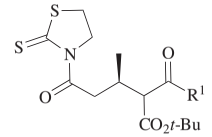
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| Me | Ph | Me | 14 | (96) | 22:1 | 98.5:1.5 |
| Me | 4-$BrC_6H_4$ | Me | 14 | (93) | 28:1 | 96.0:4.0 |
| Et | *i*-Pr | Me | 18 | (95) | 18:1 | 93.5:6.5 |
| Et | 2-$C_4H_3S$ | Me | 20 | (76) | >30:1 | 95.0:5.0 |
| Et | Ph | Me | 15 | (93) | >30:1 | 98.0:2.0 |
| Et | Ph | Et | 15 | (90) | >30:1 | 98.0:2.0 |
| Et | Ph | *i*-Pr | 18 | (85) | 27:1 | 97.0:3.0 |
| Et | Ph | allyl | 16 | (88) | >30:1 | 97.5:2.5 |
| Et | 4-$BrC_6H_4$ | Me | 14 | (91) | 23:1 | 96.5:3.5 |
| Et | 3-$ClC_6H_4$ | Me | 15 | (90) | >30:1 | 97.0:3.0 |
| Et | 4-$ClC_6H_4$ | Me | 15 | (85) | >30:1 | 97.5:2.5 |
| Et | 4-$FC_6H_4$ | Me | 16 | (82) | >30:1 | 98.5:1.5 |
| Et | 4-$MeOC_6H_4$ | Me | 17 | (82) | >30:1 | 96.5:3.5 |
| Et | 4-$MeC_6H_4$ | Me | 16 | (84) | >30:1 | 97.0:3.0 |

$C_{4-9}$



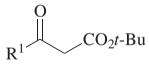


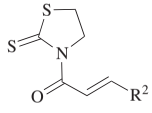
**375a** (10 mol %),
0.2 M in EtOAc, 0°



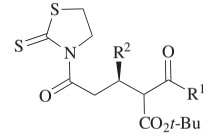
101

| R | Time (h) | | er |
|---|---|---|---|
| Me | 12 | (89) | 96.5:3.5 |
| Et | 14 | (92) | 97.0:3.0 |
| *n*-Pr | 14 | (86) | 96.5:3.5 |
| *i*-Bu | 24 | (78) | 95.5:4.5 |
| *n*-$C_6H_{13}$ | 24 | (97) | 95.0:5.0 |
| Ph | 24 | (85) | 91.5:8.5 |





**375b** (10 mol %),
0.2–0.8 M in EtOAc, 0°

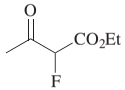
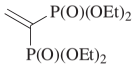
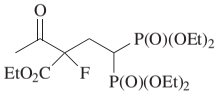
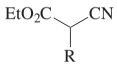
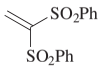
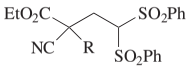
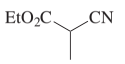
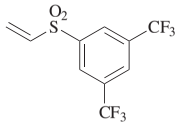
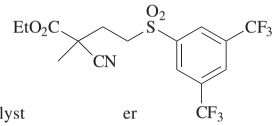
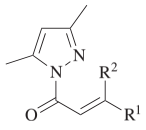
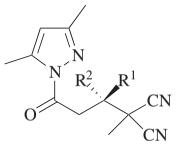


dr 1:1

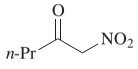
101

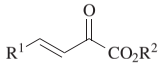
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Me | 12 | (95) | 96.5:3.5 |
| Me | $EtO_2C$ | 12 | (87) | 98.5:1.5 |
| Me | Et | 14 | (88) | 97.5:2.5 |
| Me | *n*-Pr | 14 | (91) | 97.5:2.5 |
| Me | *i*-Bu | 24 | (67) | 92.0:8.0 |
| Ph | Me | 12 | (95) | 95.5:4.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

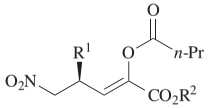
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the preceding chart for structures indicated by the **bold** numbers.* | | | | |
| $C_4$  |  | **374** (20 mol %), 0.1 M in toluene, –60°, 0.25 h |  (72) er 77.0:23.0 | 727 |
| $C_{4–10}$  |  | *ent*-**252b** (20 mol %), toluene, 4 Å MS |  | 728 |
| | | R: Me; Temp (°): –40; Time (h): 48; (96); er: 86.5:13.5 | | |
| | | R: $(EtO)_2CHCH_2$; Temp (°): –50; Time (h): 96; (52); er: 98.0:2.0 | | |
| | | R: *n*-Bu; Temp (°): –40; Time (h): 48; (98); er: 91.0:9.0 | | |
| | | R: Bn; Temp (°): –40; Time (h): 48; (98); er: 86.0:14.0 | | |
| $C_4$  |  | Catalyst (20 mol %), toluene, 0°, 96 h |  | 729 |
| | | Catalyst: **240**; (83); er: 94.0:6.0 | | |
| | | Catalyst: **267**; (85); er: 96.0:4.0 | | |
|  |  | **373** (10 mol %), $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), *t*-BuOH/THF (1:1), rt |  | 722 |
| | | $R^1$: Me; $R^2$: H; Time (h): 12; (92); er: 97.5:2.5 | | |
| | | $R^1$: $EtO_2C$; $R^2$: Me; Time (h): 48; (77); 88.0:12.0 | | |

$C_5$



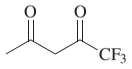


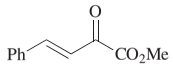
**69b** (15 mol %), $Et_2O$, 20°, 12 h



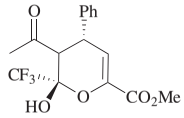
730

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Me | (51) | 98.0:2.0 |
| Ph | Et | (50) | 91.5:8.5 |
| 3-$BrC_6H_4$ | Et | (43) | 95.0:5.0 |
| 4-$BrC_6H_4$ | Et | (50) | 97.0:3.0 |
| 3-$ClC_6H_4$ | Et | (45) | 94.5:5.5 |
| 4-$ClC_6H_4$ | Et | (55) | 94.0:6.0 |
| 4-$FC_6H_4$ | Et | (69) | 92.0:8.0 |
| 3-$MeOC_6H_4$ | Et | (63) | 86.5:13.5 |
| 3-$O_2NC_6H_4$ | Et | (61) | 91.0:9.0 |
| 4-$MeC_6H_4$ | Et | (54) | 89.0:11.0 |



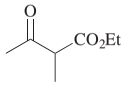


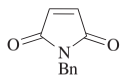
**69b** (10 mol %), $CH_2Cl_2$, rt, 24 h



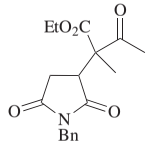
(77) dr >30:1
er 96.0:4.0

726





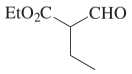
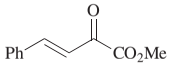
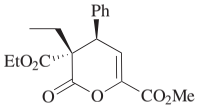
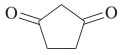
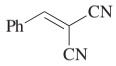
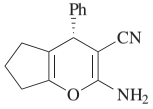
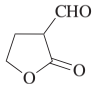
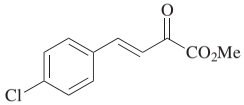
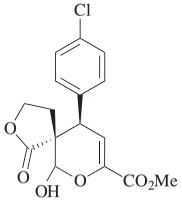
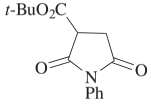
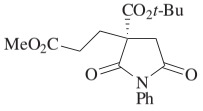
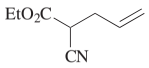
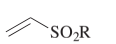
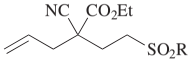
**379** (10 mol %), $Et_3N$, 1.5 M in toluene, rt, 6 d



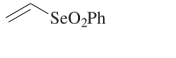
(72) dr 88:12
er 87.5:12.5

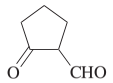
731

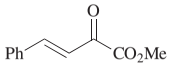
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the preceding chart for structures indicated by the **bold** numbers.* | | | | |
| $C_5$ | | | | |
|  |  | 1. **384** (10 mol %), toluene/*t*-BuOH (10:1), –20°, 24 h<br>2. PCC, $CH_2Cl_2$, reflux |  (97) er 94.5:5.5 | 732 |
|  |  | **232a** (5 mol %), THF, 4 Å MS, 0°, 5 h |  (89) er 66.0:34.0 | 733 |
|  |  | 1. **384** (1 mol %), toluene/*t*-BuOH (10:1), –20°, 48 h<br>2. PCC, $CH_2Cl_2$, reflux |  (98) dr 94:6<br>er (major) 87.5:12.5<br>er (minor) 96.5:3.5 | 732 |
|  |  | **342** (10 mol %), *i*-PrNEt (30 mol %), $CH_2Cl_2$, –40°, 7 d |  (27) er 70.0:30.0 | 663 |
| $C_6$ | | | | |
|  |  | **240** (20 mol %), toluene |  | 729 |

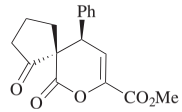
| R | Temp | Time (h) | Conv. (%) | | er | Abs. config. |
|---|---|---|---|---|---|---|
| Ph | rt | 17 | 17 | (—) | 93.5:6.5 | — |
| 3,5-$(CF_3)_2C_6H_3$ | 0° | 96 | 88 | (76) | 97.0:3.0 | (*S*) |
| 3,5-$(CF_3)_2C_6H_3$ | rt | 17 | 100 | (—) | 92.0:6.0 | (*S*) |





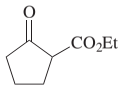


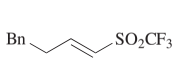
1. **384** (*x* mol %),
toluene/*t*-BuOH (10:1),
–20°, times
2. PCC, $CH_2Cl_2$, reflux



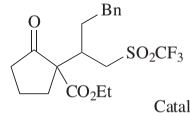
732

| *x* | Time (h) | | er |
|---|---|---|---|
| 5 | 72 | (79) | 95.0:5.0 |
| 10 | 12 | (96) | 83.0:17.0 |



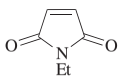


Catalyst (20 mol %),
$CH_2Cl_2$, –20°, 48 h

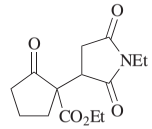


729

| Catalyst | | dr | er |
|---|---|---|---|
| **240** | (91) | 49:1 | 97.5:2.5 |
| **267** | (80) | 49:1 | 94.5:5.5 |



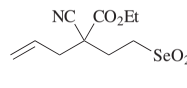
**379** (10 mol %),
$Et_3N$, 1.5 M in toluene, rt



731

Catalyst Recycling

| Run | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| 1 | 7 | (83) | 75:25 | 90.5:9.5 |
| 2 | 8 | (80) | 78:22 | 91.5:8.5 |
| 3 | 6 | (78) | 76:24 | 89.0:11.0 |
| 4 | 8 | (85) | 75:25 | 89.5:10.5 |
| 5 | 8 | (75) | 71:29 | 90.0:10.0 |
| 6 | 8 | (82) | 75:25 | 90.0:10.0 |



*ent*-**252b** (20 mol %),
toluene, 4 Å MS, –40°, 90 h



(53) er 85.0:15.0

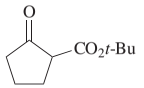
734

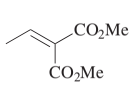
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

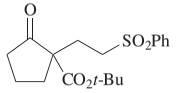
*Please refer to the preceding chart for structures indicated by the **bold** numbers.*

$C_6$





Catalyst (20 mol %), toluene, 48 h

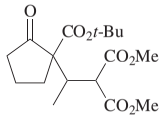


| Catalyst | | er |
|---|---|---|
| **240** | (93) | 98.0:2.0 |
| **267** | (96) | 98.0:2.0 |

729



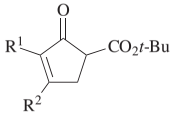
**339a** (5 mol %), 2–4 M in THF, 0° to rt, 72 h

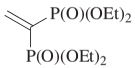


(79) dr 2.9:1, er 98.0:2.0

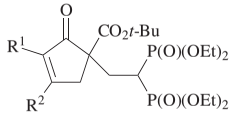
32

$C_{6-7}$





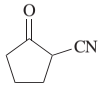
**374** (20 mol %), 0.1 M in toluene



727

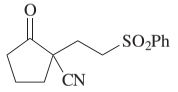
| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| H | MeO | –30 | 8 | (98) | >99.5:0.5 |
| MeO | Me | –60 | 2 | (95 | >99.5:0.5 |
| Me | H | –60 | 1 | (93) | 99.5:0.5 |

$C_6$



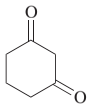


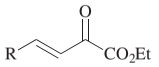
Catalyst (20 mol %), toluene, 24 h

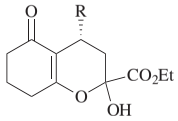


| Catalyst | | er |
|---|---|---|
| **240** | (96) | 97.5:2.5 |
| **267** | (90) | 98.5:1.5 |

729

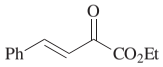


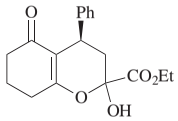


**381** (2.5 mol %), $CHCl_3$, rt 

735

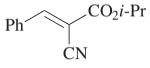
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3S$ | 12 | (87) | 99.0:1.0 |
| Ph | 3 | (93) | 99.0:1.0 |
| 3-$BrC_6H_4$ | 9 | (81) | 98.0:2.0 |
| 4-$BrC_6H_4$ | 6 | (87) | 98.0:2.0 |
| 2-$ClC_6H_4$ | 9 | (82) | 97.5:2.5 |
| 4-$ClC_6H_4$ | 6 | (91) | 98.5:1.5 |
| 2,4-$Cl_2C_6H_3$ | 9 | (86) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 12 | (82) | 99.0:1.0 |
| 4-$O_2NC_6H_4$ | 9 | (79) | 96.5:3.5 |
| 4-$MeC_6H_4$ | 12 | (75) | 97.5:2.5 |
| 4-$CF_3C_6H_4$ | 6 | (92) | 98.0:2.0 |
| 2-Np | 12 | (84) | 96.5:3.5 |

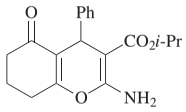


**385** (10 mol %), toluene, 0° 

(89) er 98.5:1.5

736



**69b** (10 mol %), toluene, 0°, 4.5 h 

(83) er 85.0:15.0

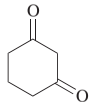
737

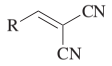
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

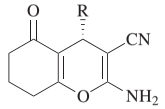
*Please refer to the preceding chart for structures indicated by the **bold** numbers.*

$C_6$





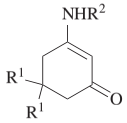
**232a** (5 mol %), THF, 4 Å MS, 0°, 5 h

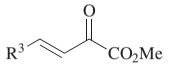


733

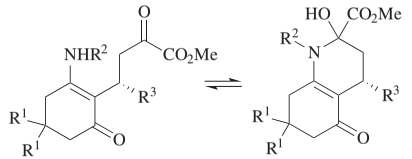
| R | | er |
|---|---|---|
| Ph | (84) | 77.5:22.5 |
| 4-$BrC_6H_4$ | (94) | 74.5:25.5 |
| 2-$ClC_6H_4$ | (93) | 74.5:25.5 |
| 4-$ClC_6H_4$ | (98) | 76.5:23.5 |
| 4-$FC_6H_4$ | (91) | 71.0:29.0 |
| 3,4-$(MeO)_2C_6H_3$ | (94) | 76.0:24.0 |
| 4-$O_2NC_6H_4$ | (91) | 65.5:34.5 |
| 2-$MeC_6H_4$ | (99) | 74.5:25.5 |
| 4-$MeC_6H_4$ | (99) | 77.0:23.0 |
| 2-Np | (99) | 73.0:27.0 |

$C_{6-8}$





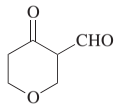
**143** (11 mol %), $Cu(OTf)_2$ (10 mol %), $Et_2O$, reflux, 60 h

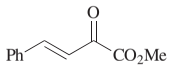


38

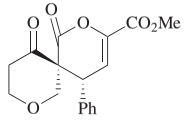
| $R^1$ | $R^2$ | $R^3$ | | dr | er | er |
|---|---|---|---|---|---|---|
| H | Ph | Ph | (88) | 1:1 | 99.0:1.0 | 96.0:4.0 |
| H | Ph | 4-$ClC_6H_4$ | (98) | 1:1 | 97.5:2.5 | 95.5:4.5 |
| Me | Me | 4-$ClC_6H_4$ | (34) | — | 73.5:26.5[a] | 73.5:26.5[a] |

$C_6$

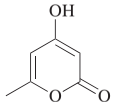


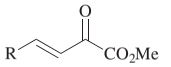


1. **384** (10 mol %), toluene/*t*-BuOH (10:1), –20°, 48 h
2. PCC, $CH_2Cl_2$, reflux

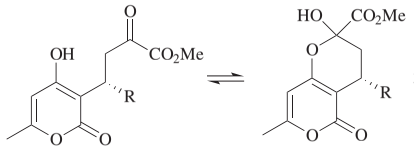


(94) er 96.0:4.0 732



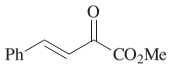


**143** (11 mol %), $Cu(OTf)_2$ (10 mol %), $Et_2O$, reflux

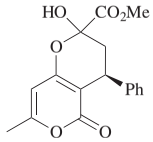


38

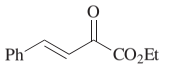
| R | | er |
|---|---|---|
| Ph | (85) | 91.0:9.0 |
| 4-$ClC_6H_4$ | (88) | 88.5:11.5 |



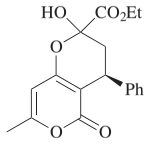
**380** (1 mol %), $Ni(acac)_2$ (1.5 mol %), DCE, 4 Å MS, 0°



(95) er 90.5:9.5 738



**381** (2.5 mol %), $CHCl_3$, rt, 12 h



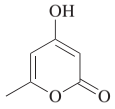
(87) er 96.0:4.0 735

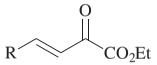
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

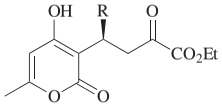
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_6$



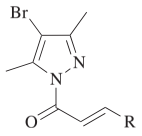


**386** (2.5 mol %), DCE, rt

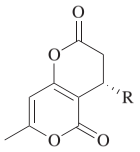


739

| R | Time (h) | | er |
|---|---|---|---|
| Me | 12 | (67) | 95.0:5.0 |
| *n*-Pr | 12 | (71) | 96.5:3.5 |
| 2-$C_4H_3O$ | 12 | (79) | 95.5:4.5 |
| 2-$C_4H_3S$ | 12 | (75) | 96.0:4.0 |
| Ph | 12 | (85) | 97.0:3.0 |
| 3-$BrC_6H_4$ | 8 | (82) | 97.5:2.5 |
| 4-$BrC_6H_4$ | 1 | (90) | 98.0:2.0 |
| 4-$ClC_6H_4$ | 1 | (89) | 98.0:2.0 |
| 2,4-$Cl_2C_6H_3$ | 8 | (82) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 12 | (80) | 98.0:2.0 |
| 4-$O_2NC_6H_4$ | 24 | (68) | 97.0:3.0 |
| 4-$MeC_6H_4$ | 12 | (86) | 97.5:2.5 |
| 4-$CF_3C_6H_4$ | 1 | (88) | 98.0:2.0 |
| 2-Np | 8 | (83) | 96.5:3.5 |



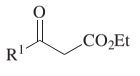
**373** (10 mol %),
$Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %),
TMP (10 mol %),
$Ac_2O$ (2 eq),
0.1 M in THF, rt

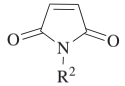


740

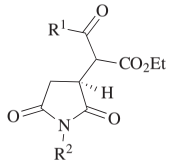
| R | Time (h) | | er |
|---|---|---|---|
| Me | 12 | (85) | 99.0:1.0 |
| 3,5-$Br_2C_6H_3$ | 24 | (60) | 98.0:2.0 |
| 2-MeO-5-$BrC_6H_3$ | 166 | (23) | 92.0:8.0 |

$C_{7-10}$





**160b** (20 mol %),
–50°, 5 min

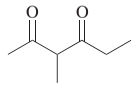


dr 1:1

612

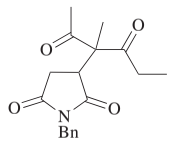
| $R^1$ | $R^2$ | | er (major) | er (minor) |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Et | (99) | 93.0:7.0 | 93.0:7.0 |
| Ph | Me | (93) | 96.5:3.5 | 96.5:3.5 |
| Ph | Et | (99) | 96.6:3.5 | 96.5:3.5 |
| Ph | *n*-$C_6H_{13}$ | (90) | 95.0:5.0 | 95.5:4.5 |
| Ph | *c*-$C_6H_{11}$ | (99) | 96.5:3.5 | 96.5:3.5 |
| 4-$ClC_6H_4$ | Et | (99) | 95.0:5.0 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | Et | (91) | 94.5:5.5 | 94.5:5.5 |
| 3-$MeC_6H_4$ | Et | (88) | 96.0:4.0 | 96.5:3.5 |

$C_7$





**379** (10 mol %),
1.5 M in $Et_3N$, toluene,
rt, 12 d



(70) dr 87:13
er 84.5:15.5

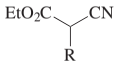
731

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

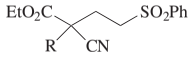
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_{7–13}$





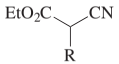
Catalyst (20 mol %), toluene



| R | Catalyst | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| 2-$C_4H_3S$ | **240** | –25 | 48 | (95) | 96.5:3.5 |
| 2-$C_4H_3S$ | **267** | –25 | 48 | (91) | 94.0:6.0 |
| Ph | **240** | –25 | 72 | (89) | 97.5:2.5 |
| Ph | **267** | –25 | 72 | (80) | 95.5:4.5 |
| 4-$BrC_6H_4$ | **240** | –25 | 69 | (95) | 97.0:3.0 |
| 4-$BrC_6H_4$ | **267** | –25 | 72 | (95) | 94.0:6.0 |
| 3-$ClC_6H_4$ | **240** | –25 | 60 | (96) | 96.5:3.5 |
| 4-$ClC_6H_4$ | **240** | –25 | 69 | (95) | 97.0:3.0 |
| 4-$ClC_6H_4$ | **267** | –25 | 72 | (94) | 94.5:5.5 |
| 4-$FC_6H_4$ | **240** | –25 | 72 | (90) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | **240** | 0 | 70 | (92) | 96.5:3.5 |
| 4-$MeC_6H_4$ | **240** | 0 | 48 | (96) | 96.5:3.5 |
| 2-Np | **240** | –25 | 60 | (96) | 98.5:1.5 |
| 2-Np | **267** | –25 | 60 | (95) | 95.0:5.0 |

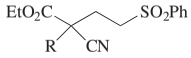
729

$C_{7–10}$





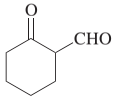
*ent*-**252b** (20 mol %), toluene, 4 Å MS, –40°, 96 h

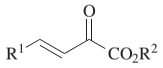


| R | | er |
|---|---|---|
| 2-$C_4H_3S$ | (96) | 97.5:2.5 |
| Ph | (83) | 97.0:3.0 |
| 4-$BrC_6H_4$ | (93) | 98.0:2.0 |
| 4-$ClC_6H_4$ | (90) | 97.5:2.5 |
| 4-$FC_6H_4$ | (92) | 96.5:3.5 |
| 4-$MeOC_6H_4$ | (73) | 97.0:3.0 |
| 3-$CF_3C_6H_4$ | (92) | 95.5:4.5 |

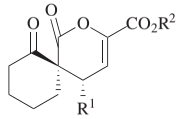
728

$C_7$



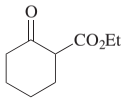


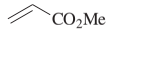
1. **384** (10 mol %), toluene/*t*-BuOH (5:1 or 10:1), –20°
2. PCC, $CH_2Cl_2$, reflux



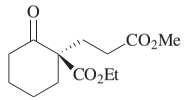
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | Et | 72 | (76) | 96.0:4.0 |
| Ph | Me | 48 | (89) | 97.5:2.5 |
| 4-$ClC_6H_4$ | Et | 42 | (94) | 94.0:6.0 |
| 4-$FC_6H_4$ | Me | 42 | (99) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | Me | 72 | (71) | 95.0:5.0 |
| 3-$O_2NC_6H_4$ | Me | 36 | (99) | 95.0:5.0 |
| 4-$MeC_6H_4$ | Me | 48 | (97) | 94.0:6.0 |
| *N*-Ts-3-indolyl | Et | 108 | (67) | 98.5:1.5 |

732



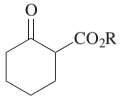


*ent*-**202a** (30 mol %), La(O*i*-Pr)$_3$ (10 mol %), *t*-BuONa (30 mol %), $CH_2Cl_2$, 0° to rt, 17 h



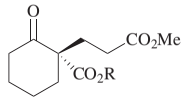
(60) er 88.0:12.0

51



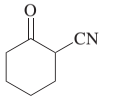


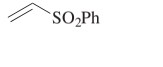
**144a** (5.6 mol %), 50% of NaOH, toluene, 20°



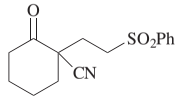
| R | | er |
|---|---|---|
| Et | (5) | 53.0:47.0 |
| Bn | (9) | 64.0:36.0 |

386





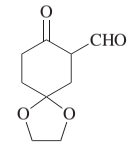
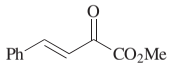
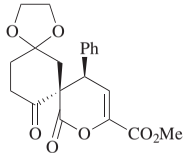
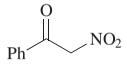
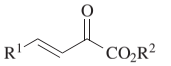
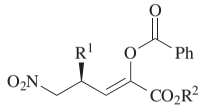
Catalyst (20 mol %), toluene, 24 h



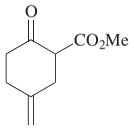
| R | | er |
|---|---|---|
| **240** | (96) | 97.5:2.5 |
| **267** | (98) | 97.5:2.5 |

729

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

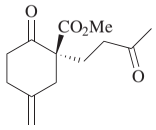
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_7$  |  | 1. **450** (10 mol %), toluene/*t*-BuOH (10:1), –20°, 48 h<br>2. PCC, $CH_2Cl_2$, reflux |  (80) er 95.5:4.5 | 732 |
| $C_8$  |  | **69b** (15 mol %), $Et_2O$, 20°, 12 h |  | 730 |

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 5-Me-2-$C_4H_2S$ | Et | (94) | 84.0:16.0 |
| Ph | Me | (56) | 97.0:3.0 |
| Ph | Et | (50) | 92.0:8.0 |
| Ph | *i*-Pr | (61) | 86.0:14.0 |
| 2-$BrC_6H_4$ | Et | (71) | 93.0:7.0 |
| 3-$BrC_6H_4$ | Et | (58) | 95.5:4.5 |
| 4-$BrC_6H_4$ | Et | (70) | 96.0:4.0 |
| 2-$ClC_6H_4$ | Et | (50) | 91.0:9.0 |
| 3-$ClC_6H_4$ | Et | (62) | 92.0:8.0 |
| 4-$ClC_6H_4$ | Et | (47) | 94.0:6.0 |
| 4-$FC_6H_4$ | Et | (56) | 94.0:6.0 |
| 3-$MeOC_6H_4$ | Et | (47) | 93.0:7.0 |
| 4-$MeOC_6H_4$ | Et | (63) | 86.5:13.5 |
| 3-$O_2NC_6H_4$ | Me | (56) | 93.0:7.0 |
| 3-$O_2NC_6H_4$ | Et | (49) | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | Et | (58) | 92.0:8.0 |
| 3-$MeC_6H_4$ | Et | (50) | 91.0:9.0 |
| 4-$MeC_6H_4$ | Et | (56) | 91.0:9.0 |

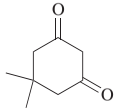


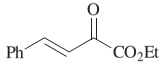


*ent*-**202a** (60 mol %), La(O*i*-Pr)$_3$ (20 mol %), *t*-BuONa (60 mol %), $CH_2Cl_2$, 0° to rt, 93 h

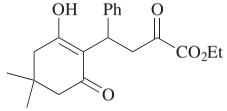


(69) er 94.5:5.5 51

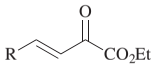




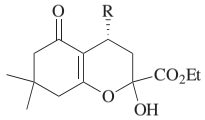
**143** (11 mol %), $Cu(OTf)_2$ (10 mol %), $Et_2O$, reflux



(85) er 72.5:27.5 38



**381** (2.5 mol %), $CHCl_3$, rt



735

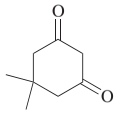
| R | Time (h) | | er |
|---|---|---|---|
| Et | 12 | (78) | 99.0:1.0 |
| *n*-Pr | 12 | (82) | 98.5:1.5 |
| *n*-Bu | 12 | (75) | 89.5:10.5 |
| 2-$C_4H_3S$ | 6 | (88) | 98.5:1.5 |
| Ph | 2 | (95) | 99.5:0.5 |
| 3-$BrC_6H_4$ | 6 | (83) | 99.0:1.0 |
| 4-$ClC_6H_4$ | 3 | (92) | 99.5:0.5 |
| 2,4-$Cl_2C_6H_3$ | 6 | (89) | 99.0:1.0 |
| 4-$MeOC_6H_4$ | 12 | (86) | 97.5:2.5 |
| 4-$CF_3C_6H_4$ | 4 | (94) | 99.5:0.5 |
| 2-Np | 12 | (85) | 97.5:2.5 |

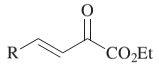
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

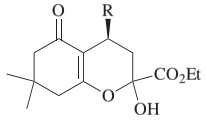
*Please refer to the preceding chart for structures indicated by the **bold** numbers.*

$C_8$



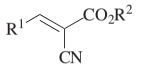


**385** (10 mol %), toluene, 0°

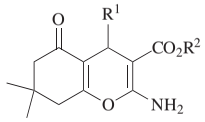


| R | | er |
|---|---|---|
| *i*-Pr | (64) | 97.0:3.0 |
| *n*-$C_6H_{13}$ | (74) | 97.5:2.5 |
| Ph | (89) | 96.0:4.0 |
| 4-$BrC_6H_4$ | (99) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | (95) | 98.0:2.0 |
| 4-$O_2NC_6H_4$ | (96) | 99.5:0.5 |

736



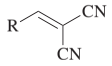
**69b** (10 mol %), toluene, 0°



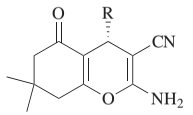
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | *i*-Pr | 11 | (67) | 88.0:12.0 |
| Ph | Me | 4 | (90) | 84.5:15.5 |
| Ph | Et | 4.5 | (92) | 89.5:10.5 |
| Ph | *i*-Pr | 4.5 | (85) | 90.0:10.0 |
| 2-$BrC_6H_4$ | *i*-Pr | 3.5 | (85) | 60.0:40.0 |
| 3-$BrC_6H_4$ | *i*-Pr | 4.5 | (90) | 87.0:13.0 |
| 4-$BrC_6H_4$ | *i*-Pr | 4.5 | (91) | 87.5:12.5 |
| 4-$ClC_6H_4$ | *i*-Pr | 4 | (85) | 88.0:12.0 |
| 4-$FC_6H_4$ | *i*-Pr | 4 | (88) | 87.0:13.0 |
| 2-$MeOC_6H_4$ | *i*-Pr | 6.5 | (82) | 75.5:24.5 |
| 3-$MeOC_6H_4$ | *i*-Pr | 6.5 | (86) | 87.0:13.0 |
| 4-$MeOC_6H_4$ | *i*-Pr | 6.5 | (84) | 90.0:10.0 |

737

| | | | | |
|---|---|---|---|---|
| 4-$O_2NC_6H_4$ | *i*-Pr | 2.5 | (72) | 82.5:17.5 |
| 4-$MeC_6H_4$ | *i*-Pr | 4.5 | (85) | 91.0:9.0 |
| 4-$NCC_6H_4$ | *i*-Pr | 3 | (75) | 83.0:17.0 |
| 1-Np | *i*-Pr | 7.5 | (81) | 82.5:17.5 |

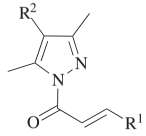


**232a** (5 mol %),
THF, 4 Å MS, 0°, 5 h

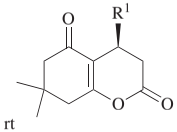


733

| R | | er |
|---|---|---|
| Ph | (99) | 83.5:16.5 |
| 4-$BrC_6H_4$ | (96) | 91.5:8.5 |
| 2-$ClC_6H_4$ | (99) | 75.5:24.5 |
| 4-$ClC_6H_4$ | (97) | 77.5:22.5 |
| 4-$FC_6H_4$ | (95) | 79.0:21.0 |
| 3,4-$(MeO)_2C_6H_3$ | (90) | 79.5:20.5 |
| 4-$O_2NC_6H_4$ | (94) | 71.0:29.0 |
| 2-$MeC_6H_4$ | (98) | 82.5:17.5 |
| 4-$MeC_6H_4$ | (97) | 84.0:16.0 |
| 2-Np | (94) | 77.0:23.0 |



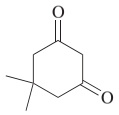
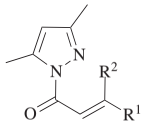
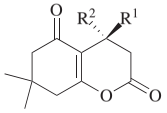
**373** (10 mol %),
$Ni(ClO_4)_2 \cdot 6H_2O$
(10 mol %),
TMP (10 mol %),
$Ac_2O$ (2 eq), 0.1 M in THF, rt



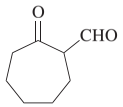
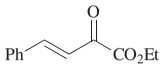
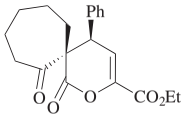
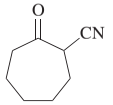
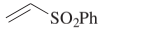
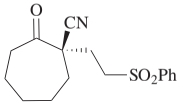
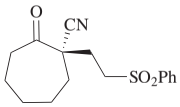
740

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | Br | 5 | (93) | 98.0:2.0 |
| Me | I | 6 | (62) | 99.0:1.0 |
| $MeO_2C$ | Br | 3 | (77) | — |
| Et | Br | 8 | (73) | 96.5:3.5 |
| *n*-Pr | Br | 24 | (94) | 96.0:4.0 |
| *i*-Pr | Br | 96 | (71) | 98.0:2.0 |
| allyl | Br | 48 | (85) | 95.0:5.0 |
| 2-$C_4H_3O$ | Br | 168 | (73) | 94.5:5.5 |
| *c*-$C_6H_{11}$ | Br | 96 | (53) | 97.5:2.5 |
| Ph | Br | 12 | (94) | 99.5:0.5 |
| 4-$BrC_6H_4$ | Br | 12 | (99) | 98.0:2.0 |

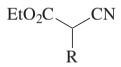
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

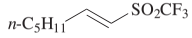
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_8$  |  | **373** (10 mol %), $Ni(ClO_4)_2•6H_2O$ (10 mol %), solvent. rt |  | 722 |

| $R^1$ | $R^2$ | Solvent | Time (h) | | er |
|---|---|---|---|---|---|
| Me | H | *i*-PrOH/THF (1:1) | 29 | (78) | 97.0:3.0 |
| $EtO_2C$ | Me | *t*-BuOH/THF (1:1) | 48 | (35) | 79.5:20.5 |

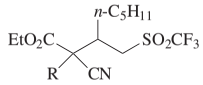
| | | | | | |
|---|---|---|---|---|---|
|  |  | 1. **384** (10 mol %), toluene/*t*-BuOH (10:1), –20°, 48 h<br>2. PCC, $CH_2Cl_2$, reflux |  single diasteromer | (62) er 92.0:8.0 | 732 |
|  |  | **240** (20 mol %), toluene, 24 h |  | (91) er 98.0:2.0 | 729 |
| |  | **267** (20 mol %), toluene, 24 h |  | (91) er 98.5:1.5 | 729 |

$C_9$





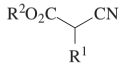
Catalyst (20 mol %),
$CH_2Cl_2$, –50°, 96 h



729

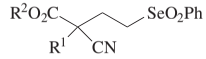
| R | Catalyst | | dr | er |
|---|---|---|---|---|
| Ph | **240** | (87) | 5.6:1 | 96.5:3.5 |
| Ph | **267** | (76) | 4.6:1 | 93.5:6.5 |
| 4-$BrC_6H_4$ | **240** | (92) | 49:1 | 90.5:9.5 |
| 4-$BrC_6H_4$ | **267** | (92) | 26:1 | 93.0:7.0 |
| 4-$FC_6H_4$ | **240** | (94) | 26:1 | 96.0:4.0 |
| 4-$FC_6H_4$ | **267** | (91) | 12:1 | 92.0:8.0 |

$C_{9–13}$





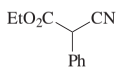
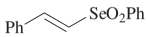
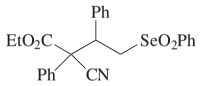
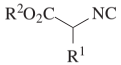
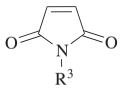
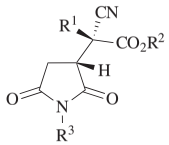
*ent*-**252a** (20 mol %),
toluene, 4 Å MS, –70°, 66 h



734

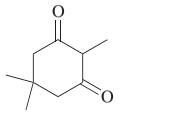
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Et | (90) | 90.0:10.0 |
| Ph | *i*-Pr | (99) | 85.0:15.0 |
| Ph | Bn | (97) | 81.0:19.0 |
| 4-$BrC_6H_4$ | Et | (90) | 90.0:10.0 |
| 4-$ClC_6H_4$ | Et | (93) | 90.0:10.0 |
| 4-$FC_6H_4$ | Et | (97) | 91.0:9.0 |
| 4-$MeOC_6H_4$ | Et | (88) | 95.0:5.0 |
| 3-$MeC_6H_4$ | Et | (75) | 88.0:12.0 |
| 4-$MeC_6H_4$ | Et | (80) | 95.0:5.0 |
| 2-Np | Et | (93) | 91.0:9.0 |

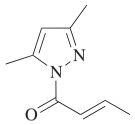
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_9$  |  | **387** (20 mol %), toluene, 4 Å MS, rt, 90 h |  (95) dr 3:1 er 87.0:13.0 | 734 |
| $C_{9-10}$  |  | **383** (*x* mol %), 4-xylene, –15° |  | 720 |

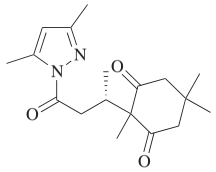
| $R^1$ | $R^2$ | $R^3$ | *x* | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|
| Ph | Me | Me | 10 | 30 | (74) | 85:15 | 85.0:15.0 |
| Ph | Me | allyl | 10 | 30 | (95) | 90:10 | 80.5:19.5 |
| Ph | Me | *c*-$C_6H_{11}$ | 10 | 30 | (63) | 95:5 | 87.0:13.0 |
| Ph | Me | Ph | 10 | 18 | (93) | 99:1 | 97.0:3.0 |
| Ph | Me | 4-$BrC_6H_4$ | 10 | 18 | (95) | 99:1 | 95.0:5.0 |
| Ph | Me | 4-$ClC_6H_4$ | 10 | 18 | (93) | 99:1 | 96.0:4.0 |
| Ph | Me | 3-$FC_6H_4$ | 10 | 18 | (96) | 98:2 | 99.0:1.0 |
| Ph | Me | 4-$FC_6H_4$ | 10 | 18 | (98) | 99:1 | 95.5:4.5 |
| Ph | Me | 3-$HOC_6H_4$ | 10 | 18 | (91) | 80:20 | 98.0:2.0 |
| Ph | Me | 4-$MeOC_6H_4$ | 10 | 18 | (97) | 99:1 | 95.0:5.0 |
| Ph | Me | 4-$O_2NC_6H_4$ | 10 | 18 | (98) | 99:1 | 95.0:5.0 |
| Ph | Me | 4-$MeC_6H_4$ | 10 | 18 | (98) | 97:3 | 95.0:5.0 |
| Ph | Me | Bn | 10 | 30 | (95) | 85:15 | 92.5:7.5 |
| Ph | Et | Me | 10 | 30 | (76) | 75:25 | 86.0:14.0 |
| Ph | Et | Ph | 10 | 18 | (98) | 99:1 | 96.0:4.0 |
| Ph | Et | 4-$BrC_6H_4$ | 10 | 18 | (92) | 93:7 | 93.0:7.0 |
| Ph | Et | Bn | 10 | 30 | (79) | 70:30 | 88.5:11.5 |
| Bn | Me | Ph | 20 | 72 | (71) | 55:45 | 79.0:21.0 |

$C_9$

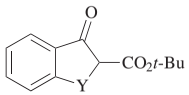


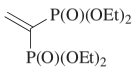


**373** (10 mol %),
$Ni(ClO_4)_2 \cdot 6H_2O$
(10 mol %),
*t*-BuOH/THF (1:1), rt, 48 h

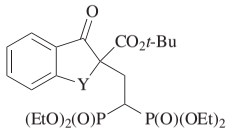


(42) er 95.5:4.5 722



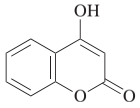


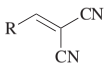
**374** (20 mol %),
0.1 M in toluene, 6 h



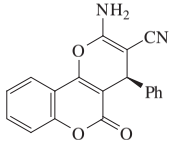
727

| Y | Temp (°) | | er |
|---|---|---|---|
| O | –60 | (83) | 99.0:1.0 |
| S | –40 | (75) | 92.0:8.0 |

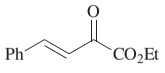




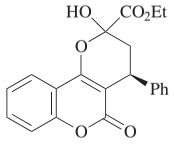
**232a** (5 mol %),
THF, 4 Å MS, 0°, 5 h



(91) er 53.0:47.0 733



**381** (2.5 mol %),
$CHCl_3$, rt, 12 h



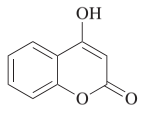
(89) er 92.5:7.5 735

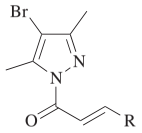
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

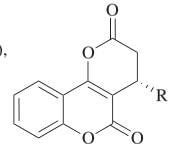
*Please refer to the preceding chart for structures indicated by the **bold** numbers.*

$C_9$





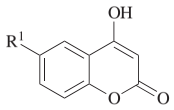
**373** (10 mol %),
$Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %),
TMP (10 mol %),
$Ac_2O$ (2 eq),
0.1 M in THF, rt

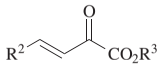


740

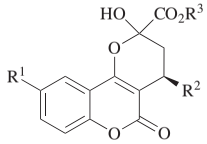
| R | Time (h) | | er |
|---|---|---|---|
| Me | 2.5 | (66) | 96.5:3.5 |
| Ph | 144 | (64) | 98.0:2.0 |
| 4-$BrC_6H_4$ | 96 | (65) | 97.5:2.5 |
| 3,5-$Br_2C_6H_3$ | 24 | (80) | 98.5:1.5 |
| 2-MeO-5-$BrC_6H_3$ | 168 | (53) | 92.0:8.0 |

$C_{9-10}$





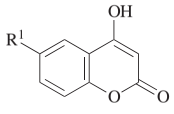
**380** (1 mol %),
$Ni(acac)_2$ (1.5 mol %),
DCE, 4 Å MS, 0°

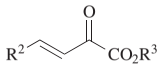


738

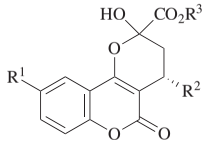
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| H | 2-$C_4H_3S$ | Me | 6 | (98) | 93.5:6.5 |
| H | Ph | Me | 4 | (99) | 94.5:5.5 |
| H | Ph | Et | 9 | (98) | 92.5:7.5 |
| H | 3-$BrC_6H_4$ | Me | 5 | (89) | 93.5:6.5 |
| H | 4-$BrC_6H_4$ | Me | 4 | (99) | 94.5:5.5 |
| H | 3-$ClC_6H_4$ | Me | 10 | (78) | 94.5:5.5 |
| H | 4-$ClC_6H_4$ | Me | 4 | (99) | 93.5:6.5 |
| H | 4-$FC_6H_4$ | Me | 4 | (99) | 95.0:5.0 |
| H | 3-$MeOC_6H_4$ | Me | 4 | (99) | 93.5:6.5 |

| | | | | | |
|---|---|---|---|---|---|
| H | 4-MeOC$_6$H$_4$ | Me | 4 | (99) | 94.0:6.0 |
| H | 3,4-(OCH$_2$O)C$_6$H$_3$ | Me | 5 | (98) | 94.5:5.5 |
| H | 3-MeC$_6$H$_4$ | Me | 4 | (99) | 94.5:5.5 |
| H | 4-MeC$_6$H$_4$ | Me | 4 | (99) | 94.5:5.5 |
| H | PhCH=CH | Me | 10 | (96) | 94.5:5.5 |
| H | 2-Np | Me | 4 | (97) | 94.5:5.5 |
| H | 4-PhC$_6$H$_4$ | Me | 4 | (98) | 93.5:6.5 |
| Me | Ph | Me | 4 | (98) | 93.5:6.5 |





**382** (10 mol %),
$C_6H_5CF_3$, 24 h



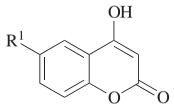
| $R^1$ | $R^2$ | $R^3$ | Temp (°) | | er |
|---|---|---|---|---|---|
| H | Et | Et | –20 | (90) | 96.5:3.5 |
| H | 2-C$_4$H$_3$S | Et | –25 | (93) | 96.0:4.0 |
| H | Ph | Me | –25 | (96) | 97.0:3.0 |
| H | Ph | Et | –25 | (96) | 98.0:2.0 |
| H | 4-ClC$_6$H$_4$ | Et | –25 | (98) | 98.0:2.0 |
| H | 4-FC$_6$H$_4$ | Et | –25 | (98) | 97.5:2.5 |
| H | 4-MeOC$_6$H$_4$ | Et | –25 | (96) | 97.5:2.5 |
| H | 3-MeSC$_6$H$_4$ | Et | –20 | (98) | 98.0:2.0 |
| H | 4-MeSC$_6$H$_4$ | Et | –25 | (97) | 98.0:2.0 |
| H | 2-(CH$_2$=CHCH$_2$)OC$_6$H$_4$ | Et | –20 | (91) | 95.0:5.0 |
| H | 4-(CH$_2$=CHCH$_2$)OC$_6$H$_4$ | Et | –25 | (97) | 97.5:2.5 |
| H | 4-BnOC$_6$H$_4$ | Et | –20 | (95) | 97.5:2.5 |
| H | 2-MeC$_6$H$_4$ | Et | –20 | (95) | 96.0:4.0 |
| H | 4-*i*-PrC$_6$H$_4$ | Et | –25 | (96) | 98.0:2.0 |
| H | 1-Np | Et | –20 | (95) | 97.5:2.5 |
| Cl | Ph | Et | –25 | (97) | 98.0:2.0 |
| Me | Ph | Et | –25 | (96) | 97.0:3.0 |

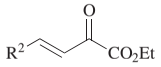
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

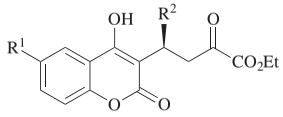
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_{9–10}$



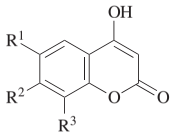

**386** (2.5 mol %), DCE, rt

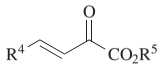



739

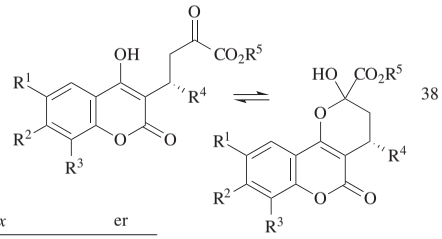
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| H | Me | 10 | (76) | 93.0:7.0 |
| H | *n*-Pr | 10 | (71) | 94.5:5.5 |
| H | 2-$C_4H_3O$ | 10 | (86) | 96.0:4.0 |
| H | 2-$C_4H_3S$ | 10 | (87) | 95.5:4.5 |
| H | Ph | 12 | (93) | 98.0:2.0 |
| H | 3-$BrC_6H_4$ | 10 | (81) | 96.0:4.0 |
| H | 4-$BrC_6H_4$ | 1 | (94) | 97.5:2.5 |
| H | 4-$ClC_6H_4$ | 1 | (92) | >99.5:0.5 |
| H | 2,4-$Cl_2C_6H_3$ | 10 | (86) | 96.0:4.0 |
| H | 4-$MeOC_6H_4$ | 12 | (65) | 96.0:4.0 |
| H | 4-$O_2NC_6H_4$ | 10 | (73) | 95.5:4.5 |
| H | 4-$MeC_6H_4$ | 12 | (88) | 96.5:3.5 |
| H | 4-$CF_3C_6H_4$ | 1 | (95) | >99.5:0.5 |
| H | 2-Np | 10 | (89) | 96.0:4.0 |
| Cl | Ph | 12 | (82) | 97.5:2.5 |
| Cl | 4-$BrC_6H_4$ | 12 | (80) | 97.0:3.0 |
| Me | Ph | 12 | (87) | 99.0:1.0 |
| Me | 4-$CF_3C_6H_4$ | 12 | (82) | 98.5:1.5 |

$C_9$





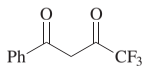
**143** (*x* mol %),
$Cu(OTf)_2$ (1–10 mol %),
$Et_2O$, reflux

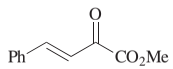


38

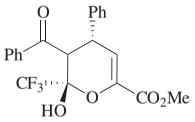
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | *x* | | er |
|---|---|---|---|---|---|---|---|
| H | H | H | Me | Et | 10 | (98) | 95.0:5.0 |
| H | H | H | 2-$C_4H_3O$ | Et | 10 | (95) | 90.5:9.5 |
| H | H | H | Ph | Me | 3 | (98) | 93.0:7.0 |
| H | H | H | 4-$ClC_6H_4$ | Me | 1 | (98) | 86.5:13.5 |
| H | H | H | 4-$MeOC_6H_4$ | Me | 10 | (98) | 82.0:18.0 |
| H | H | H | 4-$MeC_6H_4$ | Me | 10 | (95) | 89.0:11.0 |
| H | F | H | Me | Et | 10 | (45) | 96.0:4.0 |
| H | F | H | Ph | Me | 10 | (45) | 95.5:4.5 |
| H | MeO | H | Ph | Me | 10 | (47) | 95.5:4.5 |
| Cl | H | H | Ph | Me | 10 | (83) | 92.0:8.0 |
| Cl | H | Cl | Ph | Me | 10 | (98) | 89.0:11.0 |

$C_{10}$





**69b** (10 mol %),
$CH_2Cl_2$, rt, 45 h



(57) dr >30:1
er 90.5:9.5

726

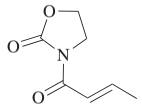
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

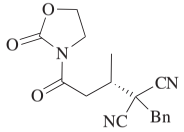
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_{10}$



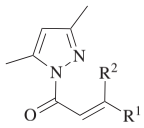


**373** (10 mol %), $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), additive, solvent, rt

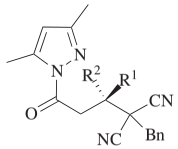


722

| Additive | Solvent | Time (h) | | er |
|---|---|---|---|---|
| — | MeOH/THF (1:1) | 9 | (100) | 88.0:12.0 |
| AcOH | EtOH/THF (1:1) | 24 | (83) | 91.5:8.5 |
| — | *i*-PrOH/THF (1:1) | 24 | (100) | 88.5:11.5 |

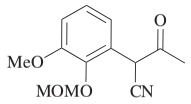


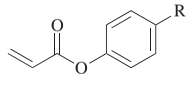
**373** (10 mol %), $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), *t*-BuOH/THF (1:1), rt



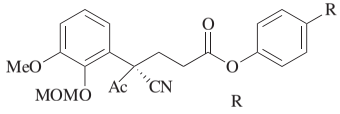
722

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Me | H | 8 | (90) | 98.5:1.5 |
| $EtO_2C$ | H | 1.5 | (91) | 99.5:0.5 |
| $EtO_2C$ | Me | 48 | (55) | 86.0:14.0 |
| *i*-Pr | H | 36 | (33) | 95.5:4.5 |
| Ph | H | 36 | (82) | 96.0:4.0 |



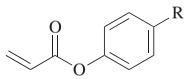


**389** (20 mol %), 4-xylene, rt, 2 d

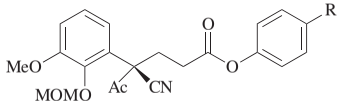


189

| R | | er |
|---|---|---|
| Br | (97) | 90.5:9.5 |
| I | (96) | 90.5:9.5 |

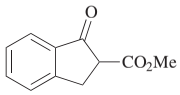


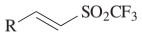
*ent*-**164b** (20 mol %),
4-xylene, rt, 2 d



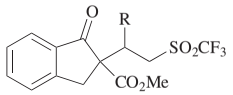
189

| R | | er |
|---|---|---|
| Br | (90) | 89.5:10.5 |
| I | (98) | 90.0:10.0 |



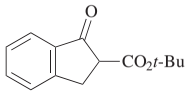


Catalyst (20 mol %),
$CH_2Cl_2$, –20°



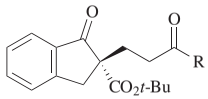
729

| R | Catalyst | Time (h) | | dr | er |
|---|---|---|---|---|---|
| *i*-Bu | **240** | 72 | (100) | 24:1 | 99.0:1.0 |
| *i*-Bu | **267** | 72 | (95) | 8:1 | 97.5:2.5 |
| *n*-$C_5H_{11}$ | **240** | 96 | (90) | 32:1 | 99.0:1.0 |
| *n*-$C_5H_{11}$ | **267** | 96 | (93) | 9:1 | 98.5:1.5 |





**342** (*x* mol %),
*i*-$Pr_2NEt$ (30 mol %),
$CH_2Cl_2$



694

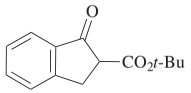
| R | *x* | Temp | Time (d) | | er |
|---|---|---|---|---|---|
| MeO | 10 | –40° | 7 | (55) | 97.0:3.0 |
| EtO | 5 | rt | 7 | (40) | 91.5:8.5 |
| (1-Np)S | 5 | –40° | 3 | (87) | 85.5:14.5 |

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

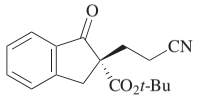
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_{10}$

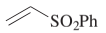




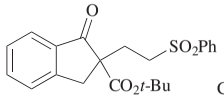
**342** (10 mol %), *i*-$Pr_2NEt$ (30 mol %), $CH_2Cl_2$, rt, 6 d



(98) er 75.5:24.5 663

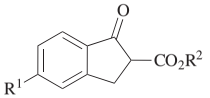


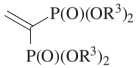
Catalyst (20 mol %), toluene, 48 h



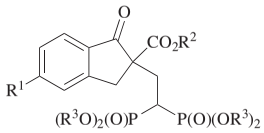
729

| Catalyst | | er |
|---|---|---|
| **240** | (96) | 98.0:2.0 |
| **267** | (100) | 98.5:1.5 |



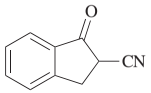
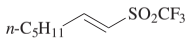
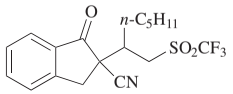


**374** (20 mol %), 0.1 M in toluene, –60°



727

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| H | Me | Et | 0.8 | (76) | 96.5:3.5 |
| H | *i*-Pr | Et | 0.6 | (60) | 96.5:3.5 |
| H | *t*-Bu | Et | 0.6 | (75) | 98.5:1.5 |
| H | Bn | Et | 0.8 | (80) | 92.0:8.0 |
| Cl | *t*-Bu | Et | 0.2 | (90) | 98.5:1.5 |
| MeO | *t*-Bu | Et | 0.6 | (97) | 99.0:1.0 |
| MeO | *t*-Bu | Bn | 6 | (84) | 96.0:4.0 |

| | | | | |
|---|---|---|---|---|
|  |  | Catalyst (20 mol %), $CH_2Cl_2$, –50°, 24 h |  | 729 |

| Catalyst | | dr | er |
|---|---|---|---|
| **240** | (95) | 49:1 | 99.5:0.5 |
| **267** | (94) | 49:1 | 97.0:3.0 |

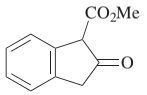
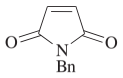
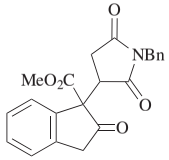
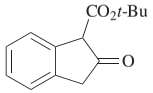
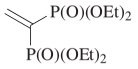
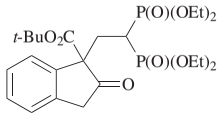
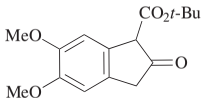
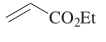
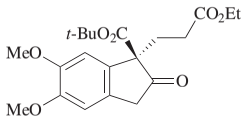
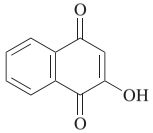
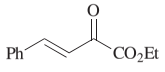
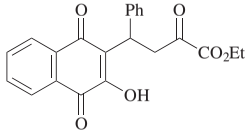
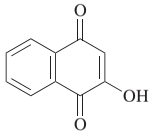
| | | | | |
|---|---|---|---|---|
|  |  | **379** (10 mol %), $Et_3N$, 1.5 M in toluene, rt, 6 d |  | (87) dr 90:10 er 90.5:9.5 | 731 |
|  |  | **374** (20 mol %), 0.1 M in toluene, –40°, 24 h |  | (60) er 92.0:8.0 | 727 |
|  |  | **391** (10 mol %), $CHCl_3$, rt |  | (72) er 95.0:5.0 | 742 |
|  |  | **143** (11 mol %), $Cu(OTf)_2$ (10 mol %), $Et_2O$, reflux |  | (92) er 75.0:25.0 | 38 |

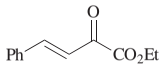
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

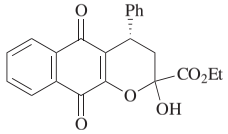
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_{10}$

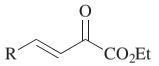




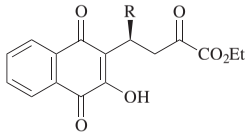
**381** (2.5 mol %), $CHCl_3$, rt, 24 h

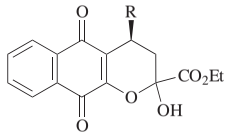


(83) er 95.0:5.0 735



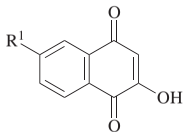
**388** (*x* mol %), 1,4-dioxane, rt, 12 h

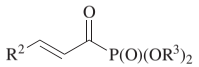




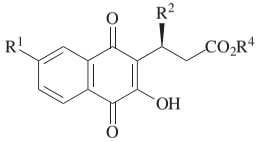
743

| R | *x* | | er |
|---|---|---|---|
| Me | 5 | (78) | 93.5:6.5 |
| 2-$C_4H_3O$ | 5 | (81) | 96.5:3.5 |
| 2-$C_4H_3S$ | 5 | (83) | 98.0:2.0 |
| Ph | 5 | (83) | 98.0:2.0 |
| 3-$BrC_6H_4$ | 2.5 | (85) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 2.5 | (81) | 97.0:3.0 |
| 2-$ClC_6H_4$ | 2.5 | (86) | 95.4:4.5 |
| 4-$ClC_6H_4$ | 2.5 | (87) | 97.5:2.5 |
| 2,4-$Cl_2C_6H_3$ | 2.5 | (86) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 5 | (82) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 2.5 | (83) | 99.0:1.0 |
| 4-$MeC_6H_4$ | 5 | (88) | 95.5:4.5 |
| 4-$CF_3C_6H_4$ | 2.5 | (73) | 96.5:3.5 |
| 2-Np | 5 | (86) | 96.5:3.5 |





1. **389** (5 mol %),
   toluene/$CHCl_3$ (1:1), –25°
2. $R^4OH$, DBU



744

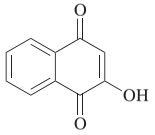
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Time (h) | | er |
|---|---|---|---|---|---|---|
| H | Me | Me | Me | 35 | (99) | 99.0:1.0 |
| H | Me | Me | Et | 35 | (82) | 98.5:1.5 |
| H | Me | Et | Me | 7 | (95) | 99.0:1.0 |
| H | Et | Me | Me | 2 | (81) | 98.0:2.0 |
| H | Et | Et | Me | 48 | (85) | 99.0:1.0 |
| H | *n*-Pr | Me | Me | 1 | (96) | 98.5:1.5 |
| H | *i*-Pr | Me | Me | 24 | (90) | 99.0:1.0 |
| H | *n*-Bu | Me | Me | 144 | (50) | 97.0:3.0 |
| H | *i*-Bu | Me | Me | 1 | (88) | 98.5:1.5 |
| H | *s*-Bu | Me | Me | 144 | (58) | 99.5:0.5 |
| H | Ph | Me | Me | 108 | (99) | >99.5:0.5 |
| MeO | Me | Me | Me | 96 | (95) | 99.5:0.5 |
| MeO | *n*-Pr | Me | Me | 120 | (62) | 98.0:2.0 |
| MeO | *i*-Pr | Me | Me | 96 | (59) | 99.5:0.5 |
| MeO | *n*-Bu | Me | Me | 144 | (65) | 97.0:3.0 |
| MeO | *i*-Bu | Me | Me | 96 | (92) | 99.5:0.5 |

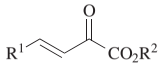
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

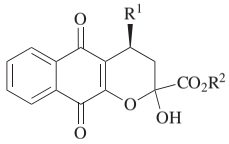
*Please refer to the preceding chart for structures indicated by the* ***bold*** *numbers.*

$C_{10}$





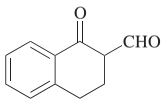
**393** (10 mol %), DCE, –20°

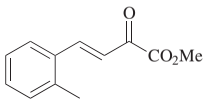


745

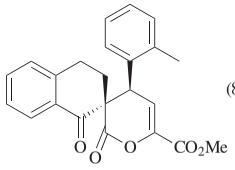
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Et | Et | 36 | (94) | 99.0:1.0 |
| 2-$C_4H_3S$ | Et | 24 | (96) | 97.5:2.5 |
| Ph | Me | 24 | (97) | 98.0:2.0 |
| Ph | Et | 24 | (97) | 98.0:2.0 |
| 2-$BrC_6H_4$ | Et | 36 | (95) | 97.0:3.0 |
| 2-$ClC_6H_4$ | Et | 36 | (95) | 97.5:2.5 |
| 3-$ClC_6H_4$ | Et | 24 | (98) | 98.5:1.5 |
| 4-$ClC_6H_4$ | Et | 24 | (99) | 98.5:1.5 |
| 4-$FC_6H_4$ | Et | 24 | (99) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Et | 36 | (98) | 95.0:5.0 |
| 4-$MeSC_6H_4$ | Et | 36 | (98) | 96.5:3.5 |
| 4-$CH_2$=$CHCH_2OC_6H_4$ | Et | 36 | (97) | 95.0:5.0 |
| 3-$PhOC_6H_4$ | Et | 36 | (96) | 98.0:2.0 |
| 4-$BnOC_6H_4$ | Et | 36 | (97) | 95.0:5.0 |
| 4-*i*-$PrC_6H_4$ | Et | 36 | (97) | 97.0:3.0 |
| 1-Np | Et | 36 | (95) | 95.5:4.5 |

$C_{11}$





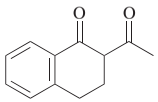
1. **384** (10 mol %), toluene/*t*-BuOH (10:1), –20°, 48 h
2. PCC, $CH_2Cl_2$, reflux

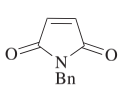


(81) er 97.5:2.5

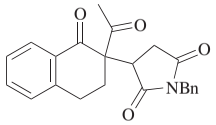
732

$C_{12}$





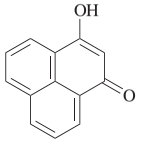
**379** (10 mol %), $Et_3N$, 1.5 M in toluene, rt, 11 d

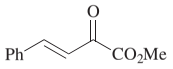


(58) dr 90:10
er 84.0:16.0

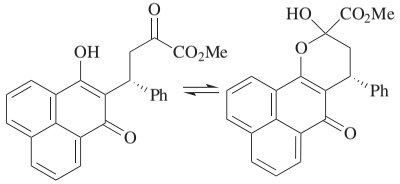
731

$C_{13}$



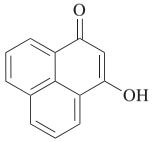


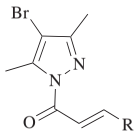
Catalyst (11 mol %), $Cu(OTf)_2$ (10 mol %), solvent, rt



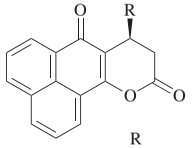
38

| Catalyst | Solvent | | er |
|---|---|---|---|
| **140** | $Et_2O$ | (56) | 88.0:12.0 |
| **143** | THF | (95) | 74.5:25.5 |





**373** (10 mol %), $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), TMP (10 mol %), $Ac_2O$ (2 eq), 0.1 M in THF, rt, 96 h

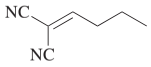
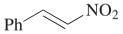
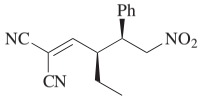
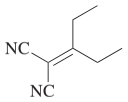
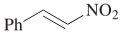
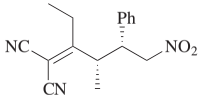
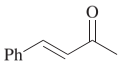
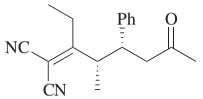
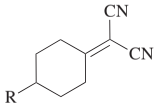
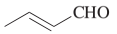
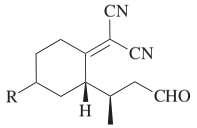
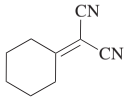
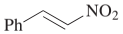
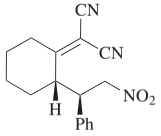


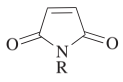
740

| R | | er |
|---|---|---|
| Me | (81) | 95.5:4.5 |
| 2-MeO-5-Br$C_6H_3$ | (31) | 94.5:5.5 |

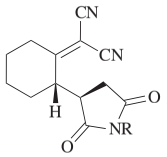
[a] The given values are for the equilibrated diastereoisomeric hemiaminals.

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_7$  |  | **390** (10 mol %), $CH_2Cl_2$, 0°, 72 h |  (22) er 90.5:9.5 | 746 |
| $C_8$  |  | *ent*-**390** (5 mol %), $CH_2Cl_2$, 0°, 72 h |  (31) er 81.5:18.5 | 746 |
| |  | **225c** (20 mol %), TFA (40 mol %), DIPEA (15 mol %), THF, –20°, 96 h |  (51) er 97.5:2.5 | 747 |
| $C_{9-10}$  |  | **145a** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (20 mol %), THF, –50°, 96 h |  dr > 99.5 : 0.5 | 748 |
| | | | R (57) er<br>H 91.0:9.0<br>Me (49) 84.0:16.0 | |
| $C_9$  |  | **384** (5 mol %), $CH_2Cl_2$, –40°, 72 h |  (95) er 83.0:17.0 | 749 |



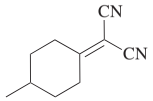
Catalyst (10 mol %),
toluene, –20°, 48 h

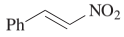


750

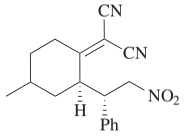
| R | Catalyst | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| Ph | **395a** | (78) | 100:0 | 90.0:10.0 | — |
| Ph | **395b** | (74) | 100:0 | 91.0:9.0 | — |
| Bn | **395a** | (57) | 72:28 | 97.0:3.0 | 85.0:15.0 |
| Bn | **395b** | (56) | 75:25 | 97.5:2.5 | 87.0:13.0 |

$C_{10}$





**390** (10 mol %),
$CH_2Cl_2$, 0°, 72 h

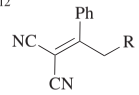


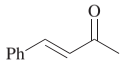
Single diastereomer

(24) er 78.5:21.5

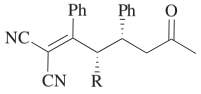
746

$C_{11–12}$





**225c** (20 mol %),
TFA (40 mol %),
DIPEA (15 mol %),
THF, –20°, 96 h

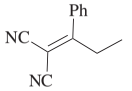


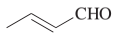
Single diastereomer

| R | | er |
|---|---|---|
| H | (21) | 95.5:4.5 |
| Me | (35) | 95.0:5.0 |

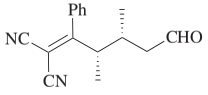
747

$C_{12}$





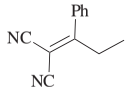
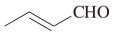
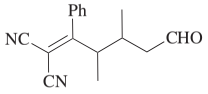
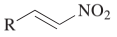
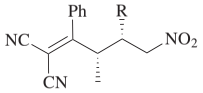
**145a** (20 mol %),
4-$O_2NC_6H_4CO_2H$ (20 mol %),
THF, –50°, 96 h



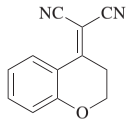
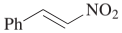
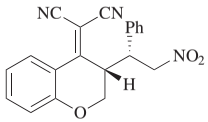
(42) dr 20:1
er (major) 94.0:6.0
er (minor) 74.0:26.0

748

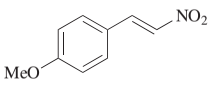
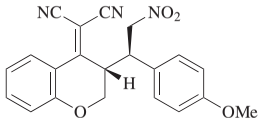
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

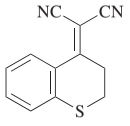
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{12}$  |  | **396** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), brine, 0°, 36 h |  (51) dr 5.3:1 er (major) 87.5:12.5 er (minor) 65.0:35.0 | 751 |
| |  | **384** (5 mol %), $CH_2Cl_2$, –40°, 72 h |  Single diastereomer | 749 |

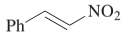
| R | | er |
|---|---|---|
| Ph | (91) | 88.0:12.0 |
| 4-$MeOC_6H_4$ | (89) | 90.5:9.5 |

| | | | | |
|---|---|---|---|---|
|  |  | *ent*-**390** (5 mol %), $CH_2Cl_2$ |  Single diastereomer | 746 |

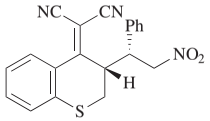
| Temp (°) | Time (h) | | er |
|---|---|---|---|
| –40 | 72 | (26) | 96.0:4.0 |
| –10 | 48 | (89) | 92.5:7.5 |

| | | | | |
|---|---|---|---|---|
| |  | **384** (5 mol %), $CH_2Cl_2$, –40°, 72 h |  (93) er 85.0:15.0 Single diastereomer | 749 |

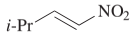




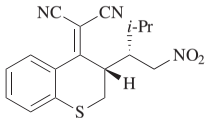
**384** (5 mol %), $CH_2Cl_2$, –40°, 72 h



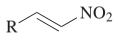
(95) er 93.0:7.0 749



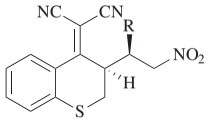
*ent*-**390** (10 mol %), $CH_2Cl_2$, 0°, 72 h



(21) er 84.5:15.5 746

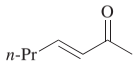


**390** (5 mol %), $CH_2Cl_2$

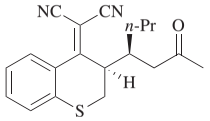


746

| R | Temp (°) | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | –40 | 72 | (64) | 95.0:5.0 |
| Ph | –40 | 72 | (66) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 0 | 24 | (65) | 93.0:7.0 |
| 4-$MeOC_6H_4$ | –40 | 72 | (54) | 97.5:2.5 |
| 4-$Me_2NC_6H_4$ | –40 | 72 | (52) | 97.0:3.0 |



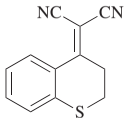
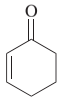
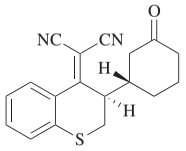
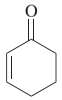
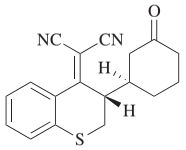
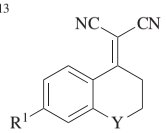
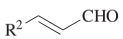
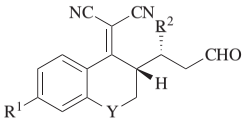
**152a** (20 mol %), TFA (40 mol %), DIPEA (0–15 mol %), THF, –20°, 96 h



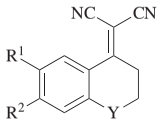
(78) er 93.5:6.5 747

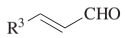
Single diastereomer

TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_{12}$  |  | **152a** (20 mol %), TFA (40 mol %), DIPEA (0–15 mol %), THF, –20°, 96 h |  Single diastereomer | (98) er >99.5:0.5 | 747 |
| |  | **225c** (20 mol %), TFA (40 mol %), THF, 0°, 96 h |  Single diastereomer | (80) er >99.5:0.5 | 747 |
| $C_{12-13}$  |  | **145a** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (20 mol %), THF, –50°, 96 h |  Single diastereomer | | 748 |

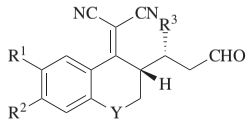
| Y | $R^1$ | $R^2$ | | er |
|---|---|---|---|---|
| O | H | Me | (83) | 97.5:2.5 |
| O | H | *n*-Pr | (78) | 97.5:2.5 |
| O | H | *i*-Pr | (69) | 99.0:1.0 |
| O | H | *n*-Bu | (80) | 97.0:3.0 |
| O | H | 2-$C_4H_3O$ | (71) | 97.5:2.5 |
| O | H | Ph | (83) | 96.0:4.0 |
| O | H | 4-$ClC_6H_4$ | (60) | 95.0:5.0 |
| O | H | 4-$MeOC_6H_4$ | (63) | 96.0:4.0 |
| S | H | Me | (91) | 96.0:4.0 |
| S | H | *n*-Pr | (75) | 96.5:3.5 |




| | | | | |
|---|---|---|---|---|
| S | H | *i*-Pr | (55) | 97.0:3.0 |
| S | H | *n*-Bu | (71) | 96.0:4.0 |
| S | H | Ph | (90) | 93.0:7.0 |
| $CH_2$ | H | Me | (61) | 97.5:2.5 |
| $CH_2$ | H | *n*-Pr | (58) | 97.0:3.0 |
| $CH_2$ | H | *n*-Bu | (51) | 96.5:3.5 |
| $CH_2$ | H | Ph | (80) | 94.5:5.5 |
| $CH_2$ | MeO | Me | (48) | 97.5:2.5 |

**396** (20 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %),
brine, 0°, 36 h



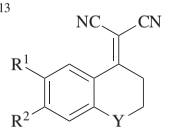

| Y | $R^1$ | $R^2$ | $R^3$ | | er | er[a] |
|---|---|---|---|---|---|---|
| O | H | H | Me | (79) | 96.0:4.0 | 99.0:1.0 |
| O | H | H | Et | (85) | 94.0:6.0 | — |
| O | H | H | *n*-Pr | (84) | 93.5:6.5 | — |
| O | H | H | Ph | (81) | 93.5:6.5 | — |
| O | H | H | 4-$BrC_6H_4$ | (74) | 92.5:7.5 | 98.0:2.0 |
| O | H | H | 4-$ClC_6H_4$ | (76) | 94.0:6.0 | 99.0:1.0 |
| S | H | H | Me | (90) | 95.5:4.5 | 99.0:1.0 |
| S | H | H | Et | (58) | 95.0:5.0 | 99.5:0.5 |
| S | H | H | *n*-Pr | (86) | 92.0:8.0 | 98.0:2.0 |
| $CH_2$ | H | H | Me | (82) | 95.0:5.0 | — |
| $CH_2$ | H | H | Et | (81) | 92.0:8.0 | — |
| $CH_2$ | H | H | *n*-Pr | (80) | 92.5:7.5 | — |
| $CH_2$ | H | H | Ph | (83) | 92.5:7.5 | — |
| $CH_2$ | H | MeO | Me | (54) | 94.0:6.0 | — |
| $CH_2$ | H | MeO | Et | (64) | 92.0:8.0 | — |
| $CH_2$ | MeO | H | Me | (46) | 93.5:6.5 | — |

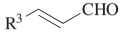
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

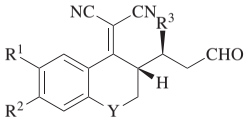
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{12–13}$



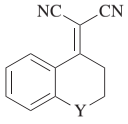



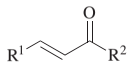

**397** (20 mol %),
4-$O_2NC_6H_4CO_2H$ (20 mol %),
THF, rt, 20 h



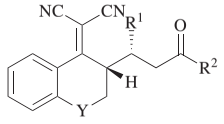

752

| Y | $R^1$ | $R^2$ | $R^3$ | | er | er[a] |
|---|---|---|---|---|---|---|
| O | H | H | Me | (81) | 95.5:4.5 | — |
| O | H | H | Et | (75) | 94.0:6.0 | — |
| O | H | H | Ph | (80) | 78.5:21.5 | — |
| S | H | H | Me | (86) | 95.0:5.0 | >99.5:0.5 |
| S | H | H | Et | (83) | 94.0:6.0 | >99.5:0.5 |
| S | H | H | *n*-Pr | (74) | 90.5:9.5 | — |
| $CH_2$ | H | H | Me | (78) | 93.5:6.5 | 98.5:1.5 |
| $CH_2$ | H | H | *n*-Pr | (60) | 90.0:10.0 | — |
| $CH_2$ | H | MeO | Me | (41) | 93.5:6.5 | 98.0:2.0 |
| $CH_2$ | MeO | H | Me | (56) | 93.0:7.0 | 98.5:1.5 |
| $CH_2$ | MeO | H | Et | (40) | 90.5:9.5 | — |




**225c** (20 mol %),
TFA (40 mol %),
additive (15 mol %),
THF, 96 h



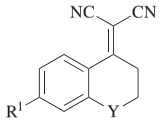

| Y | $R^1$ | $R^2$ | Additive | Temp (°) | | er |
|---|---|---|---|---|---|---|
| O | Ph | Me | DIPEA | –20 | (69) | 94.5:5.5 |
| S | *n*-Pr | Me | none | 0 | (76) | 99.0:1.0 |
| S | 2-$C_4H_3O$ | Me | none | 0 | (82) | 98.5:1.5 |
| S | Ph | Me | none | 0 | (88) | 96.5:3.5 |
| S | Ph | Et | none | 0 | (78) | 97.5:2.5 |
| S | Ph | *n*-Pr | none | 0 | (81) | 99.0:1.0 |
| S | 4-$ClC_6H_4$ | Me | none | 0 | (85) | 95.0:5.0 |
| S | 4-$MeOC_6H_4$ | Me | none | 0 | (83) | 95.5:4.5 |
| $CH_2$ | Ph | Me | DIPEA | –20 | (60) | 95.5:4.5 |

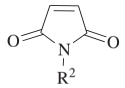
TABLE 3. 1,3-DICARBONYL AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

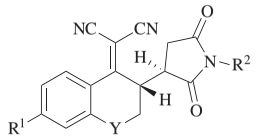
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{12–13}$



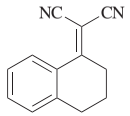

Catalyst (10 mol %),
toluene, –20°, 48 h

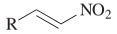



750

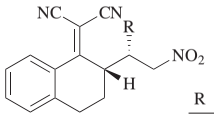
| Y | $R^1$ | $R^2$ | Catalyst | | er |
|---|---|---|---|---|---|
| O | H | Ph | **395a** | (80) | 94.0:6.0 |
| O | H | Ph | **395b** | (86) | 96.0:4.0 |
| O | H | Bn | **395a** | (81) | >99.5:0.5 |
| O | H | Bn | **395b** | (85) | >99.5:0.5 |
| S | H | Ph | **395a** | (90) | 92.5:7.5 |
| S | H | Ph | **395b** | (88) | 91.0:9.0 |
| S | H | Bn | **395a** | (89) | 96.0:4.0 |
| S | H | Bn | **395b** | (88) | 97.5:2.5 |
| $CH_2$ | H | Ph | **395a** | (81) | 92.5:7.5 |
| $CH_2$ | H | Ph | **395b** | (82) | 98.0:2.0 |
| $CH_2$ | MeO | Ph | **395a** | (35) | 90.5:9.5 |
| $CH_2$ | MeO | Ph | **395b** | (36) | 91.0:9.0 |

$C_{13}$



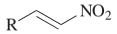


**384** (5 mol %),
$CH_2Cl_2$, –40°, 72 h

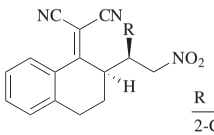


749

| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (85) | 95.5:4.5 |
| 2-$C_4H_3S$ | (93) | 97.0:3.0 |
| Ph | (87) | 95.0:5.0 |
| 4-$BrC_6H_4$ | (90) | 95.5:4.5 |
| 4-$ClC_6H_4$ | (91) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | (93) | 97.0:3.0 |
| 4-$Me_2NC_6H_4$ | (91) | 96.5:3.5 |
| 4-$MeC_6H_4$ | (90) | 95.0:5.0 |



**390** (5 mol %),
$CH_2Cl_2$, 0°, 48 h



746

| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (35) | 94.0:6.0 |
| Ph | (64) | 93.0:7.0 |
| 4-$BrC_6H_4$ | (45) | 94.5:5.5 |
| 4-$ClC_6H_4$ | (47) | 94.0:6.0 |
| 4-$MeOC_6H_4$ | (49) | 94.5:5.5 |
| 4-$Me_2NC_6H_4$ | (65) | 95.5:4.5 |
| 4-$MeC_6H_4$ | (70) | 94.0:6.0 |

[a] The given er value is for the recrystallized product.

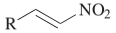
TABLE 4. NITROALKANES AS DONORS
A. NITROALKENES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

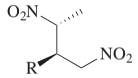
*Please refer to the chart preceding the tables for the structures indicated by the **bold** numbers.*

$C_2$





**132** (10 mol %), $CH_2Cl_2$, –30°, 16–48 h

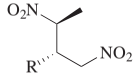


753

| R | | *syn*/*anti* | er |
|---|---|---|---|
| *i*-Pr | (60) | 55:45 | 90.0:10.0 |
| 2-$C_4H_3O$ | (85) | 80:20 | 96.0:4.0 |
| Ph | (87) | 98:2 | 98.5:1.5 |
| 2-$ClC_6H_4$ | (87) | 93:7 | 97.5:2.5 |
| 3-$ClC_6H_4$ | (83) | 88:12 | 98.0:2.0 |
| 2,4-$Cl_2C_6H_3$ | (92) | 84:16 | 99.5:0.5 |
| 4-$FC_6H_4$ | (90) | 85:15 | 97.5:2.5 |
| 3-$MeOC_6H_4$ | (89) | 93:7 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | (91) | 91:9 | 97.0:3.0 |
| 2-$MeC_6H_4$ | (92) | 91:9 | 99.0:1.0 |
| 4-$MeC_6H_4$ | (89) | 92:8 | 98.5:1.5 |
| PhCH=CH | (88) | 82:18 | 94.5:5.5 |
| 1-Np | (91) | 91:9 | 98.5:1.5 |



**392** (2 mol %), $CH_2Cl_2$, –20°

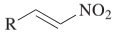


754

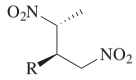
| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Pr | 96 | (16) | 67:33 | 90.0:10.0 |
| 2-$C_4H_3O$ | 60 | (64) | 89:11 | 98.0:2.0 |
| 2-$C_4H_3S$ | 60 | (63) | 79:21 | 97.5:2.5 |
| Ph | 48 | (94) | 95:5 | 98.5:1.5 |
| 4-$BrC_6H_4$ | 48 | (91) | 94:6 | 98.0:2.0 |

| | | | | |
|---|---|---|---|---|
| 2-$ClC_6H_4$ | 48 | (83) | 88:12 | 97.5:2.5 |
| 4-$ClC_6H_4$ | 48 | (95) | 92:8 | 98.0:2.0 |
| 4-$FC_6H_4$ | 48 | (98) | 94:6 | 98.0:2.0 |
| 2-$MeOC_6H_4$ | 60 | (88) | 94:6 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 60 | (90) | 94:6 | 98.5:1.5 |
| 3,4-$(MeO)_2C_6H_3$ | 60 | (71) | 88:12 | 98.0:2.0 |
| 4-$MeC_6H_4$ | 60 | (91) | 91:9 | 98.0:2.0 |
| PhCH=CH | 72 | (46) | 81:19 | 93.5:6.5 |
| 4-$MeOC_6H_4CH$=CH | 72 | (53) | 76:24 | 95.0:5.0 |
| 1-Np | 60 | (79) | 92:8 | 97.5:2.5 |





Catalyst (10 mol %), $Et_2Zn$ (25 mol %),
$Ti(O\textit{i}\text{-}Pr)_4$ (80 mol %),
toluene/hexane (3:2), 3 d





| R | Catalyst | Temp | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | **398a** | 30° | (67) | 6.7:1 | 94.0:6.0 |
| Ph | **398a** | 30° | (87) | 5.8:1 | 95.0:5.0 |
| Ph | **398b** | rt | (54) | 11.7:1 | 97.5:2.5 |
| 2-$ClC_6H_4$ | **398a** | 30° | (83) | 3.8:1 | 95.5:4.5 |
| 4-$ClC_6H_4$ | **398a** | 30° | (68) | 5.2:1 | — |
| 2-$FC_6H_4$ | **398a** | 30° | (87) | 6.2:1 | 95.0:5.0 |
| 4-$FC_6H_4$ | **398a** | 30° | (80) | 3.9:1 | 95.5:4.5 |
| 4-$FC_6H_4$ | **398b** | rt | (79) | 9.3:1 | 96.0:4.0 |
| 2-$MeOC_6H_4$ | **398a** | 30° | (90) | 5.8:1 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | **398a** | 30° | (83) | 6.5:1 | 94.5:5.5 |
| 3,4-$(MeO)_2C_6H_3$ | **398a** | 30° | (67) | 9.6:1 | 93.0:7.0 |
| 4-$MeC_6H_4$ | **398a** | 30° | (83) | 6.1:1 | 95.5:4.5 |
| $BnCH_2$ | **398a** | 30° | (80) | 3.4:1 | 86.0:14.0 |
| 2-Np | **398a** | 30° | (83) | 3.8:1 | 94.0:6.0 |
| 2-Np | **398b** | rt | (66) | 7.4:1 | 94.0:6.0 |

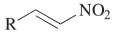
TABLE 4. NITROALKANES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

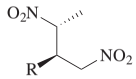
*Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.*

$C_2$



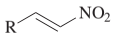


**399a** (12 mol %), $La(OTf)_3$ (10 mol %), imidazole (10 mol %), solvent, rt, 2.5 d



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| R | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Pr | $CHCl_3$ | (22) | 78:22 | 91.5:8.5 |
| 2-$C_4H_3O$ | $CH_2Cl_2$ | (80) | 81:19 | 93.0:7.0 |
| Ph | $CH_2Cl_2$ | (80) | 93:7 | 98.0:2.0 |
| 4-$BrC_6H_4$ | $CH_2Cl_2$ | (88) | 89:11 | 98.0:2.0 |
| 2-$ClC_6H_4$ | $CH_2Cl_2$ | (77) | 85:15 | 98.0:2.0 |
| 3-$ClC_6H_4$ | $CH_2Cl_2$ | (87) | 96:4 | 98.5:1.5 |
| 2,4-$Cl_2C_6H_3$ | $CH_2Cl_2$ | (79) | 83:17 | 97.5:2.5 |
| 2-$MeOC_6H_4$ | $CHCl_3$ | (78) | 71:29 | 95.0:5.0 |
| 2-$MeOC_6H_4$ | $CH_2Cl_2$ | (73) | 73:27 | 94.0:6.0 |
| 3-$MeOC_6H_4$ | $CH_2Cl_2$ | (90) | 84:16 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | $CH_2Cl_2$ | (89) | 86:14 | 96.5:3.5 |
| 2-$O_2NC_6H_4$ | $CH_2Cl_2$ | (70) | 76:24 | 98.0:2.0 |
| 4-$MeC_6H_4$ | $CH_2Cl_2$ | (88) | 88:12 | 98.0:2.0 |
| PhCH=CH | $CH_2Cl_2$ | (79) | 81:19 | 92.5:7.5 |
| 2-Np | $CH_2Cl_2$ | (71) | 92:8 | 96.0:4.0 |



**401** (2 mol %), toluene, 30°

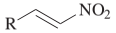


757

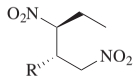
| R | Time (d) | | *syn*/*anti* | er |
|---|---|---|---|---|
| *i*-Pr | 5 | (20) | 52:48 | 89.5:10.5 |
| 2-$C_4H_3O$ | 3 | (80) | 60:40 | 90.0:10.0 |
| 2-$C_4H_3S$ | 3 | (82) | 60:40 | 97.0:3.0 |
| Ph | 2 | (85) | 67:33 | 90.5:9.5 |
| 4-$BrC_6H_4$ | 2 | (87) | 60:40 | 90.5:9.5 |
| 2-$ClC_6H_4$ | 2 | (83) | 55:45 | 90.0:10.0 |
| 3-$ClC_6H_4$ | 2 | (87) | 62:38 | 88.5:11.5 |
| 4-$ClC_6H_4$ | 2 | (82) | 60:40 | 91.0:9.0 |
| 2-$FC_6H_4$ | 2 | (85) | 72:28 | 87.0:13.0 |
| 3-$FC_6H_4$ | 2 | (80) | 57:43 | 91.5:8.5 |
| 4-$FC_6H_4$ | 2 | (84) | 60:40 | 90.0:10.0 |
| 4-$MeOC_6H_4$ | 5 | (73) | 58:42 | 92.0:8.0 |
| 4-$MeC_6H_4$ | 5 | (76) | 54:46 | 91.0:9.0 |
| PhCH=CH | 2 | (80) | 60:40 | 82.5:17.5 |

$C_3$





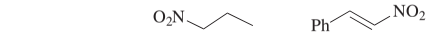
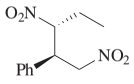
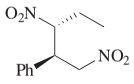
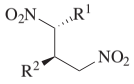
**392** (2 mol %), $CH_2Cl_2$, –20°



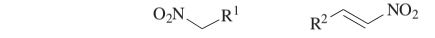
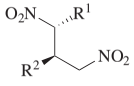
754

| R | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|
| Ph | 60 | (79) | 88:12 | 96.0:4.0 |
| 2-$ClC_6H_4$ | 60 | (72) | 81:19 | 98.0:2.0 |
| 4-$ClC_6H_4$ | 60 | (88) | 89:11 | 98.0:2.0 |
| 2-$MeOC_6H_4$ | 72 | (58) | 90:10 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 72 | (64) | 92:8 | 98.5:1.5 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for the structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$  |  | **398a** (10 mol %), $Et_2Zn$ (25 mol %), $Ti(O\textit{i}\text{-}Pr)_4$ (80 mol %), toluene/hexane (3:2), 30°, 3 d |  (88) *syn*/*anti* = 3.4:1, er 94.0:6.0 | 755 |
| |  | **399a** (12 mol %), $La(OTf)_3$ (10 mol %), imidazole (10 mol %), $CH_2Cl_2$, rt, 2.5 d |  (65) dr 92:8, er 97.5:2.5 | 756 |
| $C_{3–8}$  |  | **132** (10 mol %), $CH_2Cl_2$, –30°, 16–28 h |  | 753 |

| $R^1$ | $R^2$ | | *syn*/*anti* | er |
|---|---|---|---|---|
| Et | Ph | (92) | 95:5 | 98.0:2.0 |
| Et | 2-$ClC_6H_4$ | (88) | 96:4 | 96.5:3.5 |
| Et | 4-$MeOC_6H_4$ | (90) | 95:5 | 97.0:3.0 |
| Et | 2-$MeC_6H_4$ | (89) | 97:3 | 99.5:0.5 |
| Bn | Ph | (89) | 96:4 | 97.5:2.5 |

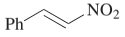
| $C_{3–4}$  |  | **402** (2 mol %), benzene, rt |  | 190 |
|---|---|---|---|---|

| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Et | Ph | 40 | (80) | 84:16 | 97.5:2.5 |
| Et | 2-$BrC_6H_4$ | 40 | (78) | 74:26 | 96.0:4.0 |
| Et | 3-$BrC_6H_4$ | 40 | (69) | 90:10 | 97.0:3.0 |
| Et | 4-$BrC_6H_4$ | 17 | (75) | 87:13 | 96.5:3.5 |
| Et | 2-$ClC_6H_4$ | 40 | (84) | 74:26 | 96.0:4.0 |
| Et | 4-$ClC_6H_4$ | 17 | (75) | 83:17 | 96.0:4.0 |

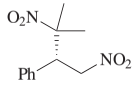
| | | | | | |
|---|---|---|---|---|---|
| Et | 2-$MeOC_6H_4$ | 40 | (55) | 80:20 | 97.0:3.0 |
| Et | 2-$MeOC_6H_4$ | 60 | (94) | 80:20 | 97.0:3.0 |
| Et | 4-$MeOC_6H_4$ | 40 | (60) | 85:15 | 97.0:3.0 |
| Et | 4-$MeC_6H_4$ | 40 | (72) | 81:19 | 97.0:3.0 |
| *n*-Pr | Ph | 40 | (78) | 90:10 | 95.5:4.5 |

$C_3$

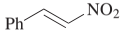




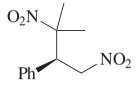
**132** (10 mol %), $CH_2Cl_2$, –30°, 16–28 h



(88) er 82.0:18.0 753

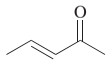
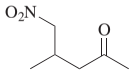
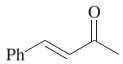
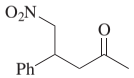
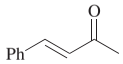
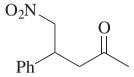
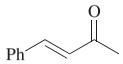
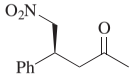
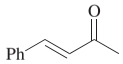
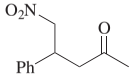
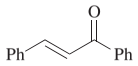
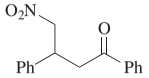


**401** (2 mol %), toluene, 30°, 4 d

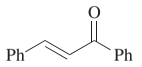


(60) er 91.5:8.5 757

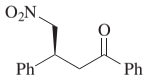
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_1$ | | | | |
| $CH_3NO_2$ |  | **296a** (5 mol %), $CHCl_3$, rt, 17 h |  (47) er 71.0:29.0 | 758 |
| |  | **279** (20 mol %), neat, rt, 240 h |  (90) er 96.0:4.0 | 173 |
| |  | **282** (20 mol %), neat, rt, 150 h |  (48) er 86.5:13.5 | 173 |
| |  | **315b** (20 mol %), 4-$O_2NC_6H_4OH$ (20 mol %) $CH_2Cl_2$, rt, 24 h |  (86) er 95.5:4.5 | 759 |
| |  | **400** (10 mol %), **411** (25 mol %), THF, rt, 6 d |  92% conv. | 760 |
| |  | Catalyst (*x* mol %), toluene, rt |  | 593 |

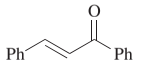
| Catalyst | *x* | Time (h) | | er |
|---|---|---|---|---|
| **160a** | 20 | 90 | (42) | 66.0:34.0 |
| **160b** | 20 | 168 | (35) | 67.5:32.5 |
| **160c** | 10 | 168 | (60) | 56.5:43.5 |



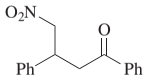
**404** (250 mg), chalcone (0.5 mol), LAH (0.268 mol), rt, 7 h



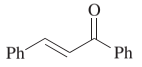
(90) er 75.5:24.5 761



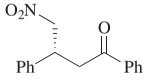
**409** (10 mol %), toluene, rt, 120 h



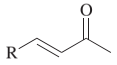
(63) er 96.5:3.5 762



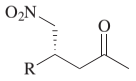
**410** (50 mg), 4-TsOH, toluene, rt, 24 h



(53) er 89.5:10.5 763



**407** (*x* mol %), EtOAc, rt



764

| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| *n*-Pr | 20 | 60 | (93) | 92.0:8.0 |
| *n*-Bu | 20 | 60 | (84) | 92.0:8.0 |
| 2-$C_4H_3S$ | 10 | 96 | (68) | 89.0:11.0 |
| Ph | 20 | 48 | (90) | 92.5:7.5 |
| 4-$ClC_6H_4$ | 10 | 72 | (73) | 93.0:7.0 |
| 2-$MeOC_6H_4$ | 10 | 96 | (70) | 92.5:7.5 |
| 4-$MeOC_6H_4$ | 10 | 72 | (65) | 90.0:10.0 |
| 4-$O_2NC_6H_4$ | 10 | 72 | (60) | 86.5:13.5 |
| 2-$MeC_6H_4$ | 10 | 72 | (91) | 92.0:8.0 |
| 4-$MeC_6H_4$ | 10 | 72 | (82) | 91.0:9.0 |

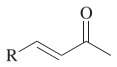
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

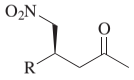
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_1$

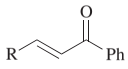
$CH_3NO_2$



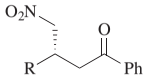
**413** (2 mol %), $Sc(OTf)_3$ (2 mol %), DMAP (2 mol %), neat, 30°



| R | | er | Refs. |
|---|---|---|---|
| *n*-Pr | (71) | 93.5:6.5 | 105 |
| Ph | (97) | 98.5:1.5 | |
| 4-$BrC_6H_4$ | (96) | 97.0:3.0 | |
| 4-$FC_6H_4$ | (99) | 98.0:2.0 | |
| 2-$MeOC_6H_4$ | (82) | 99.0:1.0 | |
| 3-$MeOC_6H_4$ | (99) | 98.5:1.5 | |
| 4-$MeOC_6H_4$ | (95) | 98.5:1.5 | |
| 4-$O_2NC_6H_4$ | (82) | 98.0:2.0 | |
| 3-$MeC_6H_4$ | (89) | 98.5:1.5 | |
| 2-Np | (99) | 98.5:1.5 | |

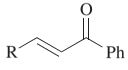


**125** (25 mol %), NAP/MgO, THF, –20°

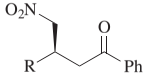


765

| R | Time (h) | | er |
|---|---|---|---|
| Ph | 12 | (95) | 98.0:2.0 |
| 4-$ClC_6H_4$ | 15 | (90) | 97.5:2.5 |
| 2-Np | 18 | (70) | 85.0:15.0 |

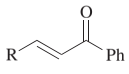


**202a** (60 mol %), La(O*i*-Pr)$_3$ (20 mol %), KHMDS (60 mol %), *t*-BuOH (*x* eq), toluene, 109 h

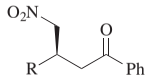


111

| R | *x* | Temp (°) | | er |
|---|---|---|---|---|
| Ph | 1.2 | –20 | (59) | 98.5:1.5 |
| Ph | 1.2 | 0 | (85) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 2.0 | –20 | (71) | 97.5:2.5 |

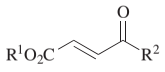


**405a** (20 mol %), *t*-BuOK, toluene, rt

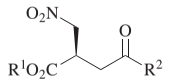


766

| R | Time (h) | | er |
|---|---|---|---|
| Ph | 16 | (90) | 67.5:32.5 |
| 4-$ClC_6H_4$ | 20 | (85) | 71.0:29.0 |
| 2-Np | 24 | (57) | 65.5:34.5 |



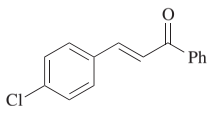
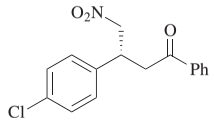
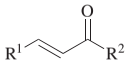
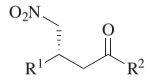
**268** (5 mol %), xylene, rt



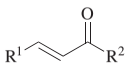
651

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | Ph | (89) | 98.0:2.0 |
| Et | *t*-Bu | (47) | 90.0:10.0 |
| Et | 2-$C_4H_3O$ | (92) | 98.5:1.5 |
| Et | 2-$C_4H_3S$ | (86) | 99.0:1.0 |
| Et | Ph | (95) | 98.0:2.0 |
| Et | 3-$BrC_6H_4$ | (90) | 98.5:1.5 |
| Et | 4-$BrC_6H_4$ | (91) | 98.5:1.5 |
| Et | 4-$FC_6H_4$ | (93) | 98.0:2.0 |
| Et | 3-$MeOC_6H_4$ | (91) | 97.0:3.0 |
| Et | 4-$MeOC_6H_4$ | (84) | 99.0:1.0 |
| Et | 2-$O_2NC_6H_4$ | (65) | 95.5:4.5 |
| Et | 3-$O_2NC_6H_4$ | (95) | 99.0:1.0 |
| Et | 4-$O_2NC_6H_4$ | (94) | 98.5:1.5 |
| Et | 4-$MeC_6H_4$ | (84) | 99.0:1.0 |
| *i*-Pr | Ph | (97) | 98.0:2.0 |
| Bn | Ph | (98) | 98.0:2.0 |
| Bn | 4-$BrC_6H_4$ | (85) | 98.5:1.5 |

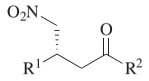
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_1$ | | | | |
| $CH_3NO_2$ |  | **403** (10 mol %), CsF (10 eq), toluene, –40°, 36 h |  (89) er 85.0:15.0 | 208 |
| |  | **232a** (2 mol %), DCE, 80°, 60 h |  | 767 |

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Ph | (94) | 97.5:2.5 |
| Ph | 4-$BrC_6H_4$ | (98) | 98.0:2.0 |
| Ph | 4-$ClC_6H_4$ | (98) | 97.5:2.5 |
| Ph | 4-$FC_6H_4$ | (98) | 98.0:2.0 |
| Ph | 3-$MeOC_6H_4$ | (66) | 97.5:2.5 |
| Ph | 4-$MeOC_6H_4$ | (78) | 98.0:2.0 |
| 2-$BrC_6H_4$ | Ph | (93) | 98.0:2.0 |
| 4-$BrC_6H_4$ | Ph | (96) | 97.5:2.5 |
| 4-$ClC_6H_4$ | Ph | (99) | 97.5:2.5 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | (99) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | Ph | (81) | 97.5:2.5 |
| Ph | 4-$MeC_6H_4$ | (78) | 98.0:2.0 |
| 4-$MeC_6H_4$ | Ph | (91) | 97.5:2.5 |
| 4-$MeC_6H_4$ | 4-$MeC_6H_4$ | (86) | 98.0:2.0 |

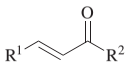


**238a** (10 mol %), neat

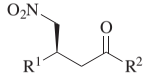


589

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Ph | rt | 94 | (82) | 92.0:8.0 |
| Me | Ph | 50 | 88 | (90) | 89.0:11.0 |
| Ph | Me | 50 | 168 | (31) | 59.0:41.0 |
| Ph | *i*-Pr | 50 | 168 | (<5) | — |
| 2-$C_4H_3O$ | Ph | 50 | 144 | (35) | 90.0:10.0 |
| Ph | Ph | 50 | 70 | (90) | 92.0:8.0 |
| Ph | 4-$ClC_6H_4$ | 50 | 72 | (100) | 94.0:6.0 |
| 4-$ClC_6H_4$ | Ph | 50 | 72 | (100) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | Ph | 50 | 168 | (59) | 92.0:8.0 |
| 4-$O_2NC_6H_4$ | Ph | 50 | 48 | (73) | 90.0:10.0 |
| 1-Np | Ph | 50 | 144 | (32) | 89.0:11.0 |
| 2-Np | Ph | 50 | 144 | (12) | 90.0:10.0 |

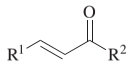
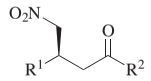


**323** (10 mol %), toluene, rt

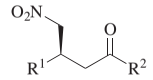


| $R^1$ | $R^2$ | Time (h) | | er | |
|---|---|---|---|---|---|
| Ph | Ph | 110 | (94) | 98.0:2.0 | 180 |
| Ph | 4-$MeOC_6H_4$ | 122 | (80) | 98.0:2.0 | 180, 768 |
| 4-$ClC_6H_4$ | Ph | 122 | (94) | 97.5:2.5 | 180, 768 |
| 4-$FC_6H_4$ | Ph | 122 | (94) | 99.0:1.0 | 180, 768 |
| 2-$MeC_6H_4$ | Ph | 122 | (93) | 94.5:5.5 | 180, 768 |

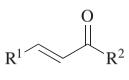
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_1$ | | | | |
| $CH_3NO_2$ |  | **406** (20 mol %), Boc-L-PheOH (20 mol %), $CHCl_3$, rt |  | 769 |

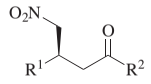
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | Me | 60 | (87) | 96.0:4.0 |
| Ph | Ph | 96 | (65) | 99.0:1.0 |

| | | **408** (2 mol %), DCE, 80°, 60 h |  | 767 |
|---|---|---|---|---|

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Ph | (94) | 97.5:2.5 |
| Ph | 4-$BrC_6H_4$ | (95) | 97.5:2.5 |
| Ph | 4-$ClC_6H_4$ | (98) | 97.5:2.5 |
| Ph | 4-$FC_6H_4$ | (96) | 98.0:2.0 |
| Ph | 3-$MeOC_6H_4$ | (64) | 97.0:3.0 |
| Ph | 4-$MeOC_6H_4$ | (84) | 97.5:2.5 |
| 2-$BrC_6H_4$ | Ph | (98) | 96.5:3.5 |
| 4-$BrC_6H_4$ | Ph | (98) | 97.5:2.5 |
| 4-$ClC_6H_4$ | Ph | (99) | 97.0:3.0 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | (99) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | Ph | (70) | 97.5:2.5 |
| Ph | 4-$MeC_6H_4$ | (94) | 98.0:2.0 |
| 4-$MeC_6H_4$ | Ph | (92) | 97.0:3.0 |
| 4-$MeC_6H_4$ | 4-$MeC_6H_4$ | (87) | 97.5:2.5 |



**413** (2 mol %),
$Sc(OTf)_3$ (2 mol %),
DMAP (2 mol %), neat, 30°



| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 2-$C_4H_3S$ | Ph | (86) | 99.5:0.5 |
| Ph | 2-$C_4H_3S$ | (87) | >99.5:0.5 |
| Ph | Ph | (99) | 99.5:0.5 |
| Ph | 4-$ClC_6H_4$ | (99) | >99.5:0.5 |
| Ph | 4-$FC_6H_4$ | (99) | >99.5:0.5 |
| 4-$BrC_6H_4$ | Ph | (92) | 99.5:0.5 |
| 2-$ClC_6H_4$ | Ph | (98) | 99.5:0.5 |
| 3-$ClC_6H_4$ | Ph | (97) | 99.5:0.5 |
| 4-$ClC_6H_4$ | Ph | (99) | 99.5:0.5 |
| 4-$FC_6H_4$ | Ph | (99) | 99.5:0.5 |
| 2-$MeOC_6H_4$ | Ph | (95) | 99.5:0.5 |
| 3-$MeOC_6H_4$ | Ph | (98) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | Ph | (94) | 99.0:1.0 |
| 3,4-$(OCH_2O)C_6H_3$ | Ph | (99) | 99.5:0.5 |
| Ph | 3-$MeC_6H_4$ | (99) | 99.5:0.5 |
| Ph | 4-$MeC_6H_4$ | (99) | 99.5:0.5 |
| 3-$MeC_6H_4$ | Ph | (99) | 99.5:0.5 |
| 4-$MeC_6H_4$ | Ph | (99) | 99.5:0.5 |
| PhCH=CH | Ph | (95) | 99.5:0.5 |
| Ph | 2-Np | (88) | 99.5:0.5 |
| 2-Np | Ph | (81) | 99.5:0.5 |

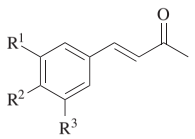
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

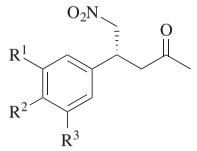
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_1$

$CH_3NO_2$

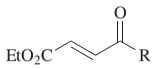


**282** (20 mol %), rt, 168 h

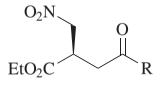


770

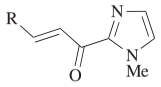
| $R^1$ | $R^2$ | $R^3$ | | er |
|---|---|---|---|---|
| MeO | H | H | (68) | 87.0:13.0 |
| MeO | HO | H | (55) | 83.5:16.5 |
| MeO | MeO | H | (49) | 91.0:9.0 |
| MeO | MeO | MeO | (72) | 90.0:10.0 |
| MeO | BnO | H | (55) | 85.5:14.5 |
| $-OCH_2CH_2O-$ | | H | (52) | 100.0:0.0 |



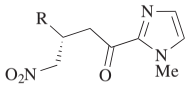
**413** (2.2 mol %), $Sc(OTf)_2$ (2 mol %), DMAP (2.0 mol %), neat, rt, 12 h



| R | | er | Refs. |
|---|---|---|---|
| 2-$C_4H_3S$ | (88) | 99.5:0.5 | 648 |
| Ph | (85) | 99.5:0.5 | |
| 4-$BrC_6H_4$ | (78) | 99.0:1.0 | |
| 2-$ClC_6H_4$ | (93) | 97.5:2.5 | |
| 3-$ClC_6H_4$ | (85) | 98.0:2.0 | |
| 4-$ClC_6H_4$ | (83) | 99.5:0.5 | |
| 3,4-$Cl_2C_6H_3$ | (83) | >99.5:0.5 | |
| 4-$FC_6H_4$ | (83) | 99.5:0.5 | |
| 4-$MeOC_6H_4$ | (85) | 99.5:0.5 | |
| 4-$MeC_6H_4$ | (87) | 99.5:0.5 | |
| 2-Np | (83) | 99.5:0.5 | |

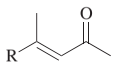


1.3 mg/mL **285**,
0.3 mM [Cu(**284**)$(NO_3)_2$],
pH 6.5 MOPS buffer solution,
5°, 3 d

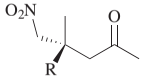


608

| R | Conv. (%) | er |
|---|---|---|
| Me | 95 | 81.0:19.0 |
| 2-$C_4H_3O$ | 100 | 93.5:6.5 |
| Ph | 65 | 92.5:7.5 |
| 2-$BrC_6H_4$ | 70 | 97.0:3.0 |
| 4-$ClC_6H_4$ | 72 | 92.5:7.5 |
| 4-$MeOC_6H_4$ | 89 | 91.0:9.0 |

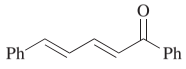


**80b** (2 mol %),
$PhCO_2H$ (5 mol %),
toluene, 2 kbar, rt, 20 h

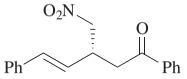


| R | | er |
|---|---|---|
| $EtO_2C$ | (74) | 98.5:1.5 |
| 2-$C_4H_3S$ | (52) | 99.0:1.0 |
| *c*-$C_6H_{11}$ | (65) | 90.0:10.0 |

771

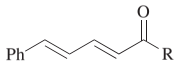


**232a** (10 mol %),
DCE, 80°, 96 h

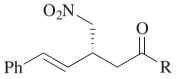


(53) er 97.0:3.0

767



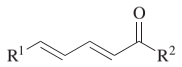
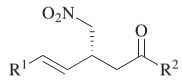
**323** (30 mol %), $N_2$, rt, 7 d



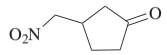
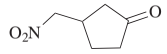
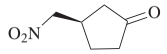
642

| R | | er |
|---|---|---|
| 4-$BrC_6H_4$ | (77) | 92.0:8.0 |
| 4-$FC_6H_4$ | (81) | 95.5:4.5 |
| 4-$NCC_6H_4$ | (86) | 97.0:3.0 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_1$ | | | | |
| $CH_3NO_2$ |  | **323** (30 mol %), rt, 7 d |  | 772 |

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Ph | (97) | 98.0:2.0 |
| Ph | 4-$ClC_6H_4$ | (92) | 97.0:3.0 |
| Ph | 2-$HOC_6H_4$ | (33) | 95.0:5.0 |
| Ph | 4-$MeOC_6H_4$ | (81) | 96.5:3.5 |
| Ph | 2-$H_2NC_6H_4$ | (19) | 93.5:6.5 |
| 4-$MeOC_6H_4$ | Ph | (91) | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | Ph | (66) | 94.0:6.0 |
| Ph | 4-$MeC_6H_4$ | (83) | 95.0:5.0 |

| | | | |
|---|---|---|---|
|  | **279** (20 mol %), neat, rt |  | (75) er 80.5:19.5 | 173 |
|  | **400** (10 mol %), **411** (25 mol %), THF, rt, 168 h |  | (15) | 760 |
|  | **407** (10 mol %), EtOAc, rt, 120 h |  | (70) er 90.0:10.0 | 764 |
|  | **80b** (2 mol %), $PhCO_2H$ (5 mol %), toluene, 2 kbar, rt, 20 h |  | (74) er 94.0:6.0 | 771 |

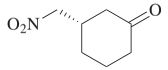
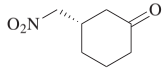
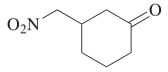
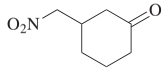
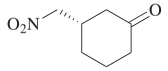
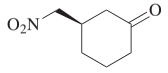
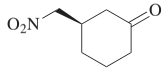
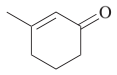
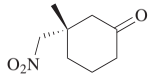
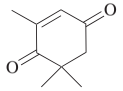
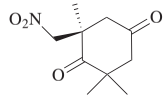
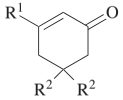
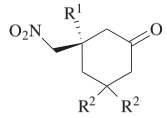
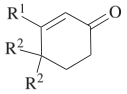
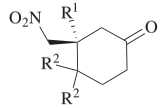
| | | | | |
|---|---|---|---|---|
|  | **223a** (5 mol %), DCE, 80°, 72 h |  | (37) er 86.5:13.5 | 767 |
|  | **238a** (10 mol %), neat, 50°, 168 h |  | (61) er 90.0:10.0 | 589 |
|  | **279** (20 mol %), neat, rt |  | (70) er 88.5:11.5 | 173 |
|  | **296a** (5 mol %), $CHCl_3$, rt, 51 h |  | (55) er 72.5:27.5 | 758 |
|  | **400** (10 mol %), **411** (25 mol %), THF, rt, 149 h |  | (18) er 90.0:10.0 | 760 |
|  | Catalyst (2 mol %), **411** (1 eq), $CHCl_3$, rt, 5 d |  | Catalyst (75) er<br>**412** (75) 78.5:21.5<br>**415** (75) 77.5:22.5 | 773 |
|  | 4**11** (1 eq), **414** (2 mol %), $CHCl_3$, rt, 5 d |  | (95) er 79.0:21.0 | 774 |
|  | **400** (10 mol %), **411** (25 mol %), THF, rt, 14 d |  | (57) er 86.0:14.0 | 760 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_1$ | | | | |
| $CH_3NO_2$ |  | **80b** (2 mol %), $PhCO_2H$ (5 mol %), toluene, 2 kbar, rt, 20 h |  (82) er 93.5:6.5 | 771 |
| |  | **80b** (2 mol %), $PhCO_2H$ (5 mol %), toluene, 2 kbar, rt, 20 h |  | 771 |
| |  | **407** (*x* mol %), EtOAc, rt |  | 764 |

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | H | (87) | 99.0:1.0 |
| Me | Me | (74) | 99.5:0.5 |
| *i*-Pr | H | (75) | 99.0:1.0 |
| *i*-Bu | H | (81) | 98.5:1.5 |
| 2-$C_4H_3S$ | H | (75) | 98.5:1.5 |
| Ph | H | (73) | 99.0:1.0 |
| 4-$BrC_6H_4$ | H | (74) | 98.0:2.0 |
| Bn | H | (82) | 98.5:1.5 |

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| H | H | 5 | 36 | (70) | 98.0:2.0 |
| Me | H | 10 | 120 | (82) | 97.0:3.0 |
| H | Me | 10 | 120 | (85) | 93.5:6.5 |
| *n*-Pr | H | 20 | 120 | (70) | 97.0:3.0 |
| *n*-Bu | H | 20 | 120 | (72) | 96.5:3.5 |
| *n*-$C_5H_{11}$ | H | 20 | 120 | (79) | 96.5:3.5 |

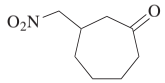
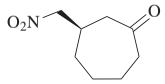
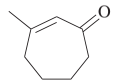
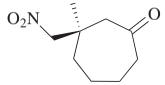
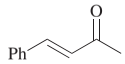
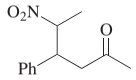
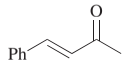
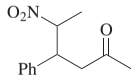
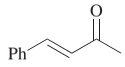
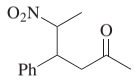
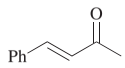
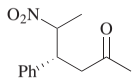
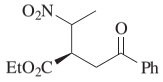
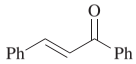
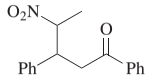
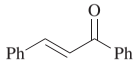
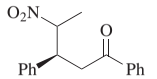
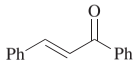
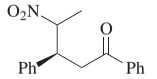
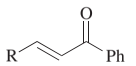
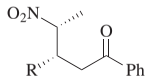
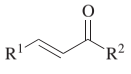
| | | | | |
|---|---|---|---|---|
| $C_2$ |  | **296a** (5 mol %), $CHCl_3$, rt, 43 h |  | (47) er 70.5:29.5 758 |
| |  | **407** (120 mol %), EtOAc, rt, 120 h |  | (25) er 96.0:4.0 764 |
| |  | **80b** (2 mol %), $PhCO_2H$ (5 mol %), toluene, 2 kbar, rt, 20 h |  | (82) er 99.5:0.5 771 |
| |  | **279** (20 mol %), neat, rt, 100 h |  | (83) dr 1:0.9<br>er 94.5:5.5<br>er 94.5:5.5 173 |
| |  | **282** (20 mol %), neat, rt, 130 h |  | (75) dr 1:0.9<br>er 85.5:14.5<br>er 86.5:13.5 173 |
| |  | **400** (10 mol %), **411** (25 mol %), THF, rt, 6 d |  | 95% conv., dr 53:47<br>er (major) 76.0:24.0<br>er (minor) 76.0:24.0 760 |
| |  | **407** (10 mol %), EtOAc, rt, 48 h |  | (98) dr 1:1<br>er 92.0:8.0<br>er 92.0:8.0 764 |

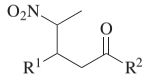
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_2$  |  | **268** (5 mol %), xylene, rt |  (89) dr 65:35<br>er (major) 98.5:1.5<br>er (minor) 98.0:2.0 | 651 |
| |  | **232a** (2 mol %),<br>DCE, 80°, 60 h |  (51) dr 53:47<br>er (major) 98.0:2.0<br>er (minor) 97.0:3.0 | 767 |
| |  | **323** (10 mol %),<br>toluene, rt, 41 h |  (94) dr 59:41<br>er (major) 97.0:3.0<br>er (minor) 97.0:3.0 | 768 |
| |  | **413** (2 mol %),<br>$Sc(OTf)_3$ (2 mol %),<br>DMAP (2 mol %), neat, 30° |  (100) dr 56:44<br>er (major) 99.0:1.0<br>er (minor) >99.5:0.5 | 105 |
| |  | **238a** (10 mol %),<br>neat, 50°, 120 h |  | 589 |

| R | | dr | er (3*R*,4*R*) | er (3*R*,4*S*) |
|---|---|---|---|---|
| Ph | (88) | 47:53 | 92.0:8.0 | 92.0:8.0 |
| 4-$ClC_6H_4$ | (94) | 50:50 | 93.0:7.0 | 96.0:4.0 |

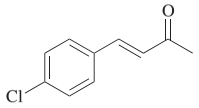


**410** (50 mg), 4-TsOH, toluene, rt, 24 h

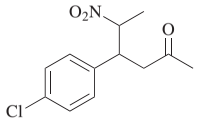


763

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Ph | Ph | (42) | 84.5:15.5 |
| Ph | 4-$FC_6H_4$ | (42) | 95.5:4.5 |
| 4-$FC_6H_4$ | 4-$FC_6H_4$ | (54) | 98.5:1.5 |



**406** (20 mol %), Boc-L-PheOH (20 mol %), $CHCl_3$, rt, 24 h

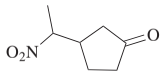


(85) *syn*/*anti* = 54:46
er (*syn*) 96.5:3.5
er (*anti*) 97.0:3.0

769



**400** (10 mol %), **411** (25 mol %), THF, rt, 57 h

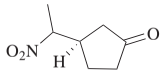


(62) dr 52:48
er (major) 84.0:16.0
er (minor) 84.0:16.0

760



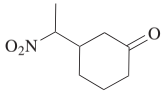
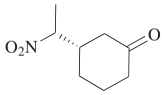
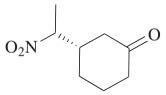
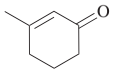
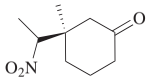
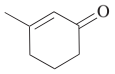
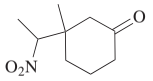
Catalyst (2 mol %), **411** (100 mol %) $CHCl_3$, rt, 5 d



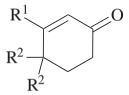
773

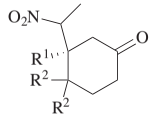
| Catalyst | | dr | er | er |
|---|---|---|---|---|
| **412** | (65) | 1:1 | 80.5:19.5 | 77.0:23.0 |
| **415** | (71) | 1:1 | 73.5:26.5 | 74.0:26.0 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_2$  |  | **400** (10 mol %), **411** (25 mol %), THF, rt, 70 h |  (85) dr 53:47 er (major) 88.0:12.0 er (minor) 87.0:13.0 | 760 |
| |  | Catalyst (2 mol %), **411** (100 mol %), $CHCl_3$, rt, 5 d |  (100) dr 1:1 | 773 |
| |  | **411** (1 eq), **414** (2 mol %), $CHCl_3$, rt, 5 d |  (83) dr 1:1 er 78.0:22.0 er 82.5:17.5 | 774 |
| |  | **80b** (2 mol %), $PhCO_2H$ (5 mol %), toluene, 2 kbar, rt, 20 h |  (91) dr 1:1 er 99.5:0.5 er 99.5:0.5 | 771 |
| |  | **400** (10 mol %), **411** (25 mol %), THF, rt, 14 d |  (54) dr 63:37 er (major) 88.0:12.0 er (minor) 80.0:20.0 | 760 |

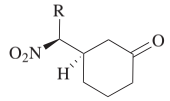
| Catalyst | er | er |
|---|---|---|
| **412** | 83.0:17.0 | 83.5:16.5 |
| **415** | 79.0:21.0 | 79.5:20.5 |



**407** (*x* mol %), EtOAc, rt  764

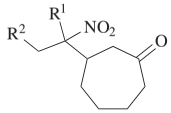
| $R^1$ | $R^2$ | *x* | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|---|
| H | H | 2 | 48 | (84) | 3:2 | 98.0:2.0 | 99.0:1.0 |
| H | Me | 10 | 48 | (92) | 3:2 | 95.5:4.5 | 99.0:1.0 |
| Me | H | 10 | 120 | (92) | 7:3 | 97.5:2.5 | 95.0:5.0 |

$C_{2-5}$  

**421** (2 mol %), toluene, 2 h  775

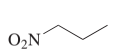
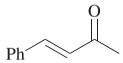
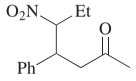
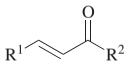
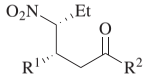
| R | Temp (°) | | *anti*/*syn* | er |
|---|---|---|---|---|
| Me | –78 to –40 | (74) | 97:3 | 98.0:2.0 |
| $MeOCH_2$ | –78 to –20 | (75) | 92:8 | 98.5:1.5 |
| *i*-Pr | –78 to –20 | (90) | 99:1 | 94.0:6.0 |
| $MeO_2C(CH_2)_2$ | –78 to –20 | (75) | 94:6 | 96.0:4.0 |
| $CH_2{=}CH(CH_2)_2$ | –78 to –40 | (81) | 99:1 | 97.0:3.0 |

$C_{2-4}$  

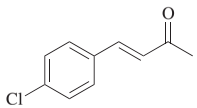
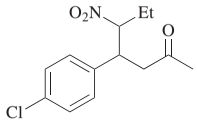
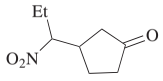
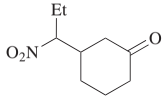
Catalyst (10 mol %), $CHCl_3$, rt  758

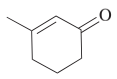
| $R^1$ | $R^2$ | Catalyst | Time (h) | | dr | er[a] |
|---|---|---|---|---|---|---|
| H | HO | **416a** | 48 | (46) | 1:1 | 61.5:38.5 |
| H | TBSO | **416a** | 48 | (50) | 1:1 | 72.5:27.5 |
| H | THPO | **416a** | 48 | (65) | 1:1 | 74.0:26.0 |
| Me | HO | **296a** | 48–72 | (48) | 2:1 | 74.0:26.0 |
| Me | THPO | **296a** | 48–72 | (69) | 1:1 | 81.5:18.5 |
| H | $MeO_2CCH_2$ | **416a** | 52 | (57) | 1:1 | 76.5:23.5 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

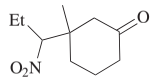
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **400** (10 mol %), **411** (25 mol %), THF, rt, 6 d |  97% conv., dr 60:40, er 76.0:24.0 | 760 |
| |  | **238a** (10 mol %), neat, 50° |  | 589 |

| $R^1$ | $R^2$ | Time (h) | | dr | er (3*R*,4*R*) | er (3*R*,4*S*) |
|---|---|---|---|---|---|---|
| Ph | Ph | 120 | (81) | 60:40 | 91.0:9.0 | 96.0:4.0 |
| Ph | 4-$ClC_6H_4$ | 50 | (100) | 64:36 | 98.0:2.0 | 91.0:9.0 |
| 4-$ClC_6H_4$ | Ph | 92 | (93) | 54:46 | 92.0:8.0 | 89.0:11.0 |

| | | | | |
|---|---|---|---|---|
| |  | **406** (20 mol %), Boc-L-PheOH (20 mol %), $CHCl_3$, rt, 36 h |  (81) *syn*/*anti* = 61:39, er 96.0:4.0 | 769 |
| |  | **400** (10 mol %), **411** (25 mol %), THF, rt, 80 h |  (72) dr 51:49, er (major) 87.0:13.0, er (minor) 87.0:13.0 | 760 |
| |  | **400** (10 mol %), **411** (25 mol %), THF, rt, 70 h |  (80) dr 51:49, er (major) 89.0:11.0, er (minor) 90.0:10.0 | 760 |

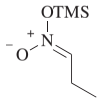


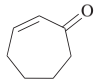
**400** (10 mol %),
**411** (25 mol %),
THF, rt, 14 d



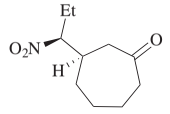
(29) dr 72:28
er (major) 91.0:9.0
er (minor) 71.0:29.0

760





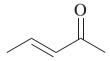
**421** (2 mol %), toluene,
–78 to –40°, 2 h



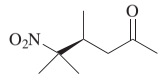
(70) *anti*/*syn* = 95.5
er 95.0:5.0

775





**296a** (10 mol %), $CHCl_3$, rt

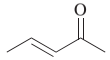


(74) er 84.0:16.0

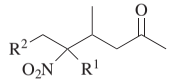
600

$C_{3–4}$





**296a** (10 mol %),
$CHCl_3$, rt

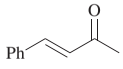


758

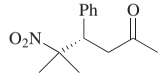
| $R^1$ | $R^2$ | Time (h) | | dr | er[a] |
|---|---|---|---|---|---|
| Me | THPO | 46 | (68) | — | 70.5:29.5 |
| H | $MeO_2CCH_2$ | 24 | (45) | 1:1.4 | 72.5:27.5 |

$C_3$





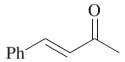
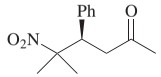
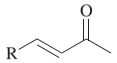
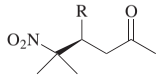
**400** (10 mol %),
**411** (25 mol %),
THF, rt, 6 d



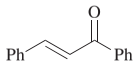
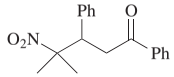
98% conv.
er 68.0:32.0

760

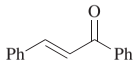
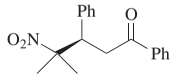
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

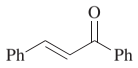
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$ | | | | |
|  |  | **407** (10 mol %), EtOAc, rt, 48 h |  (96) er 91.0:9.0 | 764 |
| |  | Catalyst ($x$ mol %), $CHCl_3$, rt |  | 758 |

| R | Catalyst | $x$ | Time (h) | | er |
|---|---|---|---|---|---|
| Me | **296a** | 5 | 17 | (74) | 84.0:16.0 |
| Me | **296b** | 10 | 15 | (80) | 83.0:17.0 |
| Me | **416a** | 10 | 14 | (76) | 69.0:31.0 |
| Me | **416b** | 10 | 17 | (53) | 84.5:15.5 |
| Me | **416c** | 10 | 17 | (61) | 81.5:18.5 |
| $n$-$C_5H_{11}$ | **296a** | 10 | 39 | (91) | 80.0:20.0 |

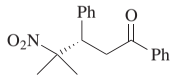
| | | | | |
|---|---|---|---|---|
|  | Catalyst (20 mol %), toluene, rt |  | | 593 |

| Catalyst | Time (h) | | er |
|---|---|---|---|
| **160a** | 96 | (23) | 80.5:19.5 |
| **160b** | 120 | (20) | 77.0:23.0 |

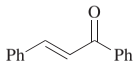
| | | | | |
|---|---|---|---|---|
|  | **323** (10 mol %), toluene, rt, 41 h |  | (91) er 96.0:4.0 | 768 |



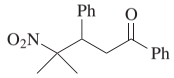
**417** (7 mol %),
*t*-BuONa (35 mol %)
toluene



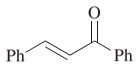
| Temp | Time (h) | | er | |
|---|---|---|---|---|
| 20° | 24 | (82) | 95.0:5.0 | 776 |
| rt | 9 | (82) | 95.0:5.0 | 777 |



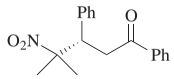
Catalyst (7 mol %),
*t*-BuONa (35 mol %)
toluene, rt



| Catalyst | Time (h) | | er | |
|---|---|---|---|---|
| **418** | 9 | (78) | 92.0:8.0 | 778 |
| **419a** | 48 | (53) | 80.5:19.5 | 779 |
| **419b** | 48 | (31) | 81.5:18.5 | 779 |
| **419c** | 48 | (42) | 80.5:19.5 | 779 |
| **419d** | 48 | (38) | 80.0:20.0 | 779 |
| **419e** | 48 | (39) | 91.0:9.0 | 779 |
| **419f** | 48 | (40) | 89.5:10.5 | 779 |
| **420c** | 48 | (45) | 94.0:6.0 | 780 |



Catalyst (3 mol %),
NaOMe (3 mol %),
toluene, rt, 120 h



| Catalyst | | er | |
|---|---|---|---|
| **422a** | (12) | 96.0:4.0 | 781 |
| **422b** | (12) | 96.0:4.0 | |
| **422c** | (20) | 90.0:10.0 | |

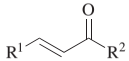
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

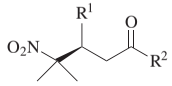
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



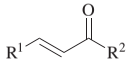


**125** (25 mol %), NAP/MgO, THF, –20°

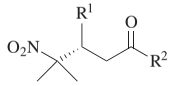


765

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | Ph | 16 | (95) | 91.0:9.0 |
| Ph | 4-$ClC_6H_4$ | 24 | (90) | 84.0:16.0 |
| 4-$O_2NC_6H_4$ | Ph | 20 | (90) | 90.0:10.0 |
| Ph | 4-$MeC_6H_4$ | 24 | (84) | 83.0:17.0 |
| 4-$MeC_6H_4$ | Ph | 30 | (74) | 81.5:18.5 |

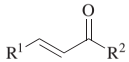


**279** (20 mol %), neat, rt

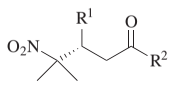


173

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Me | 200 | (87) | 91.5:8.5 |
| Ph | Me | 78 | (97) | 93.5:6.5 |
| 4-$ClC_6H_4$ | Me | 72 | (83) | 93.5:6.5 |
| 4-$HOC_6H_4$ | Me | 70 | (83) | 94.5:5.5 |
| 4-$O_2NC_6H_4$ | Me | 100 | (96) | 82.0:18.0 |
| Ph | Et | 170 | (94) | 94.5:5.5 |

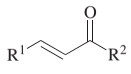


**282** (20 mol %), neat, rt

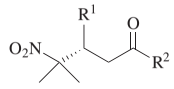


173

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Me | 200 | (64) | 85.0:15.0 |
| Ph | Me | 240 | (95) | 89.5:10.5 |
| 4-$ClC_6H_4$ | Me | 130 | (82) | 87.5:12.5 |
| 4-$HOC_6H_4$ | Me | 180 | (81) | 87.5:12.5 |
| 4-$O_2NC_6H_4$ | Me | 130 | (90) | 82.5:17.5 |
| Ph | Et | 300 | (64) | 91.5:8.5 |

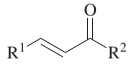


**315b** (20 mol %),
4-$O_2NC_6H_4OH$ (20 mol %)
$CH_2Cl_2$, rt

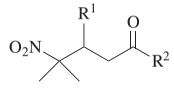


759

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| *n*-Bu | Me | 24 | (65) | 95.5:4.5 |
| 2-$C_4H_3O$ | Me | 24 | (90) | 94.0:6.0 |
| Ph | Me | 24 | (90) | 94.0:6.0 |
| 2-$ClC_6H_4$ | Me | 24 | (84) | 93.0:7.0 |
| 3-$ClC_6H_4$ | Me | 24 | (88) | 93.5:6.5 |
| 4-$ClC_6H_4$ | Me | 24 | (99) | 95.0:5.0 |
| 4-$FC_6H_4$ | Me | 24 | (86) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | Me | 24 | (98) | 95.5:4.5 |
| 4-$O_2NC_6H_4$ | Me | 24 | (86) | 95.5:4.5 |
| Ph | Et | 24 | (85) | 95.0:5.0 |
| Ph | Ph | 96 | (62) | 97.0:3.0 |



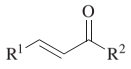
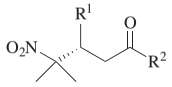
**405a** (20 mol %),
*t*-BuOK, toluene, rt



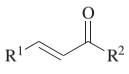
766

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | 2-$C_4H_3O$ | 14 | (63) | 80.5:19.5 |
| Ph | 2-$C_4H_3S$ | 14 | (62) | 78.5:21.5 |
| Ph | Ph | 16 | (94) | 65.5:34.5 |
| Ph | 3-$BrC_6H_4$ | 15 | (62) | 85.5:14.5 |
| Ph | 4-$BrC_6H_4$ | 15 | (92) | 79.5:20.5 |
| 3-Cl-4-$FC_6H_3$ | Ph | 15 | (87) | 76.5:23.5 |
| Ph | 4-$CF_3C_6H_4$ | 15 | (61) | 69.5:30.5 |
| 4-$CF_3C_6H_4$ | Ph | 15 | (63) | 80.0:20.0 |
| 1-Np | 3-$BrC_6H_4$ | 20 | (64) | 78.5:21.5 |
| 1-Np | 4-$BrC_6H_4$ | 20 | (68) | 78.5:21.5 |
| 2-Np | 3-$BrC_6H_4$ | 20 | (75) | 84.5:15.5 |
| 2-Np | 4-$BrC_6H_4$ | 20 | (82) | 75.5:24.5 |

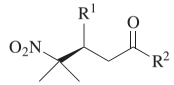
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_3$  |  | **406** (20 mol %), Boc-L-PheOH (20 mol %), $CHCl_3$, rt |  | 769 |

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Me | 55 | (93) | 97.0:3.0 |
| Ph | Me | 48 | (96) | 97.0:3.0 |
| 4-$ClC_6H_4$ | Me | 48 | (96) | 98.0:2.0 |
| 2,4-$Cl_2C_6H_3$ | Me | 60 | (86) | 97.5:2.5 |
| 4-$FC_6H_4$ | Me | 48 | (92) | 98.0:2.0 |
| 3-$MeOC_6H_4$ | Me | 48 | (94) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | Me | 48 | (90) | 96.0:4.0 |
| 4-$MeSC_6H_4$ | Me | 48 | (93) | 97.0:3.0 |
| 2-$O_2NC_6H_4$ | Me | 60 | (88) | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | Me | 48 | (92) | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | Me | 48 | (93) | 96.0:4.0 |
| 3,4-$(OCH_2O)C_6H_3$ | Me | 60 | (90) | 96.0:4.0 |
| 4-$MeC_6H_4$ | Me | 48 | (95) | 96.5:3.5 |
| $BnCH_2$ | Me | 80 | (68) | 97.5:2.5 |
| PhCH=CH | Me | 80 | (75) | 95.5:4.5 |
| Ph | 2-$C_5H_4N$ | 96 | (61) | 95.0:5.0 |
| Ph | Ph | 96 | (76) | 97.5:2.5 |

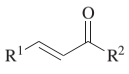


**420a** (6.9 mol %),
*t*-BuONa (2.88 eq),
toluene, rt

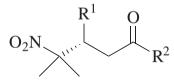


782

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | Ph | 42 | (53) | 80.5:19.5 |
| Ph | 4-$ClC_6H_4$ | 24 | (49) | 71.0:29.0 |
| Ph | 4-$MeOC_6H_4$ | 86 | (23) | 70.5:29.5 |
| 2-$ClC_6H_4$ | 4-$FC_6H_4$ | 72 | (66) | 66.0:34.0 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | 70 | (51) | 60.0:40.0 |
| 4-$MeOC_6H_4$ | 4-$O_2NC_6H_4$ | 20 | (56) | 68.0:32.0 |
| Ph | 4-$MeC_6H_4$ | 72 | (49) | 68.5:31.5 |



**420b** (6.9 mol %),
*t*-BuONa (2.88 eq),
toluene, rt



783

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | Ph | 48 | (48) | 76.5:23.5 |
| 2-$C_4H_3S$ | Ph | 49 | (36) | 75.5:24.5 |
| 2-$C_5H_4N$ | Ph | 20 | (72) | 78.5:21.5 |
| Ph | Ph | 52 | (37) | 96.0:4.0 |
| Ph | 4-$ClC_6H_4$ | 40 | (42) | 74.0:26.0 |
| Ph | 4-$MeOC_6H_4$ | 160 | (27) | 74.5:25.5 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | 67 | (54) | 70.0:30.0 |
| 3,4-$(OCH_2O)C_6H_3$ | Ph | 72 | (54) | 73.5:26.5 |
| 4-$O_2NC_6H_4$ | Ph | 51 | (28) | 60.5:39.5 |
| Ph | 4-$MeC_6H_4$ | 70 | (42) | 72.0:28.0 |
| 4-$MeC_6H_4$ | Ph | 58 | (38) | 65.0:35.0 |
| 1-Np | Ph | 167 | (28) | 60.0:40.0 |

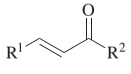
TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

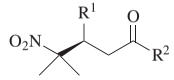
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_3$



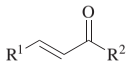


**420c** (6.9 mol %), *t*-BuONa (2.88 eq), toluene, rt

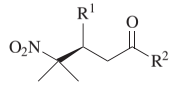


782

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | Ph | 40 | (45) | 93.5:6.5 |
| Ph | 4-$ClC_6H_4$ | 22 | (50) | 73.0:27.0 |
| 2-$ClC_6H_4$ | 4-$FC_6H_4$ | 58 | (84) | 64.0:36.0 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | 52 | (54) | 57.0:43.0 |
| 4-$MeOC_6H_4$ | 4-$O_2NC_6H_4$ | 26 | (45) | 58.0:42.0 |
| Ph | 4-$MeC_6H_4$ | 70 | (44) | 70.0:30.0 |
| 4-$MeC_6H_4$ | Ph | 72 | (58) | 69.5:30.5 |



**420e** (6.9 mol %), *t*-BuONa (2.88 eq), toluene, rt



782

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | Ph | 32 | (43) | 97.0:3.0 |
| Ph | 4-$ClC_6H_4$ | 16 | (75) | 78.0:22.0 |
| Ph | 4-$MeOC_6H_4$ | 72 | (38) | 86.0:14.0 |
| 2-$ClC_6H_4$ | 4-$FC_6H_4$ | 42 | (70) | 71.5:28.5 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | 46 | (51) | 69.5:30.5 |
| 4-$MeOC_6H_4$ | Ph | 48 | (52) | 83.5:16.5 |
| 3,4-$(MeO)_2C_6H_3$ | 4-$O_2NC_6H_4$ | 62 | (26) | 71.0:29.0 |
| 4-$O_2NC_6H_4$ | Ph | 48 | (67) | 89.0:11.0 |
| 4-$Me_2NC_6H_4$ | Ph | 70 | (50) | 64.5:35.5 |
| Ph | 4-$MeC_6H_4$ | 48 | (45) | 82.0:18.0 |
| 4-$MeC_6H_4$ | Ph | 70 | (72) | 74.0:26.0 |

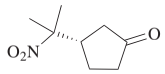
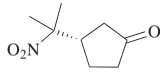
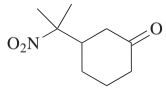
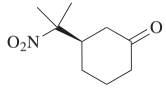
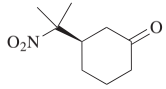
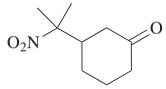
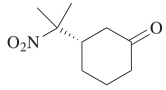
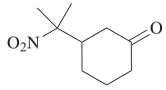
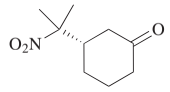
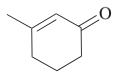
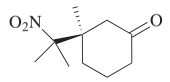
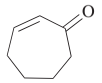
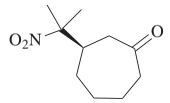
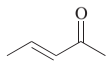
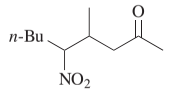
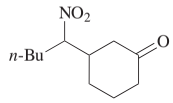
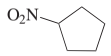
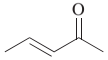
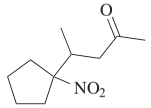
| | | | | |
|---|---|---|---|---|
|  | **400** (10 mol %), **411** (25 mol %), THF, rt, 80 h |  | (68) er 86.0:14.0 | 760 |
|  | Catalyst (2 mol %), **411** (100 mol %) $CHCl_3$, rt, 5 d |  | Catalyst (40) er<br>**412** (40) 88.0:12.0<br>**415** (50) 82.0:18.0 | 773 |
|  | **70** (30 mol %), **424** (30 mol %), DMF, rt, 5 d |  | (86) er 87.5:12.5 | 784 |
|  | **296a** (10 mol %), $CHCl_3$, rt |  | (81) er 79.5:20.5 | 600 |
|  | Catalyst (*x* mol %), $CHCl_3$, rt, 24 h |  | Catalyst *x* (81) er<br>**296a** 5 (81) 79.5:20.5<br>**416a** 10 (94) 80.0:20.0 | 758 |
|  | **315b** (20 mol %), 4-$O_2NC_6H_4OH$ (20 mol %) $CH_2Cl_2$, rt, 24 h |  | (84) er 80.0:20.0 | 759 |
|  | **400** (10 mol %), **411** (25 mol %), THF, rt, 70 h |  | (78) er 88.0:12.0 | 760 |
|  | **407** (5–20 mol %), EtOAc, rt, 96 h |  | (80) er 98.5:1.5 | 764 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_3$ | | | | |
|  |  | Catalyst (2 mol %),<br>**411** (100 mol %)<br>$CHCl_3$, rt, 5 d |  <br>Catalyst er<br>**412** (46) 88.5:11.5<br>**415** (80) 90.5:9.5 | 773 |
| |  | **80b** (2 mol %),<br>$PhCO_2H$ (5 mol %),<br>toluene, 2 kbar, rt, 20 h |  <br>(90) er 98.5:1.5 | 771 |
| |  | Catalyst (10 mol %),<br>$CHCl_3$, rt |  <br>Catalyst Time (h) er<br>**296a** 43 (79) 86.5:13.5<br>**296b** 15 (70) 86.0:14.0<br>**416a** 43 (70) 89.5:10.5<br>**416b** 24 (73) 88.0:12.0<br>**416c** 48 (41) 91.0:9.0 | 758 |
| $C_5$ | | | | |
|  |  | **296a** (5 mol %),<br>$CHCl_3$, rt, 21 h |  <br>(64) dr 1:1<br>er 70.0:30.0<br>er 77.5:22.5 | 600, 758 |
| |  | **296a** (5 mol %),<br>$CHCl_3$, rt, 19 h |  <br>(84) dr 1.4:1<br>er 73.5:26.5<br>er 76.5:23.5 | 600, 758 |

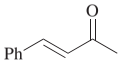



Catalyst (10 mol %), $CHCl_3$, rt

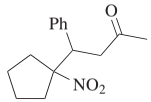


758

| Catalyst | Time (h) | | er |
|---|---|---|---|
| **296a** | 24 | (64) | 79.5:20.5 |
| **416c** | 21 | (66) | 81.5:18.5 |



Catalyst (20 mol %), neat, rt

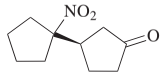


| Catalyst | Time (h) | | er |
|---|---|---|---|
| **279** | 120 | (90) | 90.0:10.0 |
| **282** | 100 | (93) | 88.5:11.5 |

173



Catalyst (2 mol %),
**411** (1 eq)
$CHCl_3$, rt, 5 d

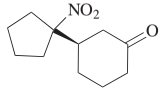


| Catalyst | | er |
|---|---|---|
| **412** | (64) | 88.5:11.5 |
| **415** | (41) | 80.0:20.0 |

773



Catalyst (2 mol %),
**411** (1 eq)
$CHCl_3$, rt, 5 d

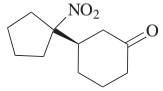


| Catalyst | | er |
|---|---|---|
| **412** | (100) | 94.0:6.0 |
| **415** | (57) | 91.0:9.0 |

773



**414** (2 mol %),
**411** (1 eq),
$CHCl_3$, rt, 5 d

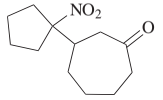


(71) er 92.0:8.0

774



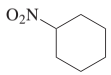
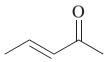
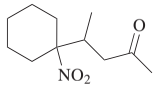
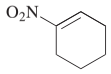
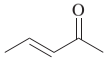
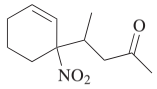
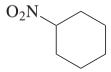
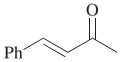
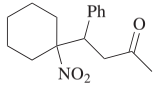
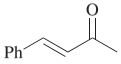
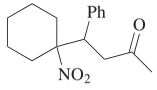
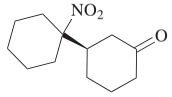
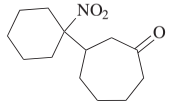
**296a** (10 mol %),
$CHCl_3$, rt, 24 h



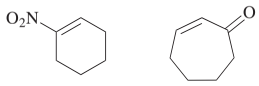
(74) er 83.5:16.5

758

TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

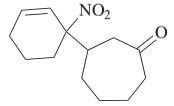
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_6$  |  | **296a** (10 mol %), $CHCl_3$, rt, 62 h |  (57) er 76.0:24.0 | 758 |
|  |  | **296a** (10 mol %), $CHCl_3$, rt, 48 h |  (49) dr 1:1 er 71.5:28.5[a] | 758 |
|  |  | **279** (20 mol %), neat, rt, 300 h |  (82) er 92.5:7.5 | 173 |
| |  | **282** (20 mol %), neat, rt, 275 h |  (60) er 85.5:14.5 | 173 |
| |  | **414** (2 mol %), **411** (1 eq), $CHCl_3$, rt, 5 d |  (24) er 89.0:11.0 | 774 |
| |  | Catalyst (10 mol %), $CHCl_3$, rt |  | 758 |

| Catalyst | Time (h) | | er |
|---|---|---|---|
| **296a** | 20 | (84) | 92.0:8.0 |
| **416a** | 24 | (74) | 93.0:7.0 |





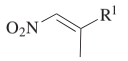
**416a** (10 mol %),
$CHCl_3$, rt, 24 h

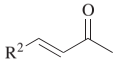


(60) dr 2:1
er 71.5:28.5[a]

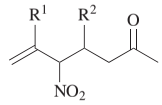
758

$C_{7-9}$



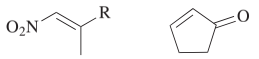


**440** (10 mol %),
DMAP (10 mol %),
D-mandelic acid (10 mol %),
$Et_2O$, rt, 36 h



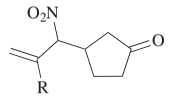
785

| $R^1$ | $R^2$ | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | Ph | (90) | 2.6:1 | 97.0:3.0 | 97.0:3.0 |
| 4-$BrC_6H_4$ | Ph | (85) | 24:1 | 98.0:2.0[b] | — |
| 3-$ClC_6H_4$ | Ph | (84) | 1.5:1 | 92.5:7.5 | 94.5:5.5 |
| 4-$ClC_6H_4$ | Ph | (93) | 24:1 | 98.5:1.5 | — |
| 4-$ClC_6H_4$ | 3,4-$(OCH_2O)C_6H_3$ | (93) | 33:1 | 97.5:2.5 | 94.5:5.5 |
| 4-$ClC_6H_4$ | 2-Np | (90) | 25:1 | 95.0:5.0 | — |
| 4-$ClC_6H_4$ | 4-$PhC_6H_4$ | (91) | 5:1 | 98.0:2.0 | — |





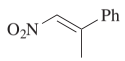
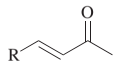
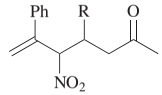
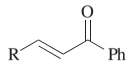
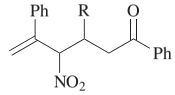
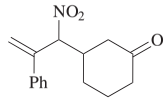
**440** (10 mol %),
DMAP (10 mol %),
D-mandelic acid (10 mol %),
$Et_2O$, rt, 24 h



785

| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| 2-$C_4H_3O$ | (90) | 1.2:1 | 99.5:0.5 | 99.5:0.5 |
| Ph | (95) | 1.1:1 | 99.5:0.5 | 99.5:0.5 |
| 4-$BrC_6H_4$ | (89) | 1.1:1 | 99.0:1.0 | 98.5:1.5 |
| 3-$ClC_6H_4$ | (70) | 1.2:1 | 99.5:0.5 | 99.5:0.5 |
| 4-$ClC_6H_4$ | (94) | 1.2:1 | 99.0:1.0 | 98.5:1.5 |
| 3,4-$Cl_2C_6H_3$ | (87) | 1.5:1 | 99.5:0.5 | 98.5:1.5 |
| 2-$FC_6H_4$ | (96) | 1.1:1 | 98.5:1.5 | 99.5:0.5 |
| 4-$FC_6H_4$ | (93) | 1.1:1 | 98.0:2.0 | 96.5:3.5 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_9$ | | | | |
|  |  | **440** (10 mol %), DMAP (10 mol %), D-mandelic acid (10 mol %), $Et_2O$, rt, 48 h |  | 785 |
| | | R (90) 1.3:1 96.5:3.5 94.5:5.5<br>2-$C_4H_3O$ (70) 3.0:1 93.5:6.5 94.5:5.5<br>2-$C_4H_3S$ (88) 1.7:1 96.5:3.5 97.0:3.0<br>Ph (78) 1.5:1 96.0:4.0 96.5:3.5<br>3-$ClC_6H_4$ (93) 2.3:1 96.5:3.5 94.5:5.5<br>4-$FC_6H_4$ (91) 1.3:1 98.0:2.0 95.0:5.0<br>3-$MeOC_6H_4$ (87) 3.0:1 95.0:5.0 94.5:5.5<br>4-$MeOC_6H_4$ (92) 2.7:1 95.5:4.5 95.5:4.5<br>3-$MeC_6H_4$ (75) 1.6:1 96.0:4.0 95.0:5.0<br>3-$CF_3C_6H_4$ (75) 1.3:1 94.5:5.5 95.5:4.5<br>2-Np | | |
| |  | **440** (20 mol %), DMAP (10 mol %), D-mandelic acid (10 mol %), $Et_2O$, rt, 72 h |  | 785 |
| | | R (61) *syn*/*anti* 1.1:1 er (*syn*) 90.0:10.0 er (*anti*) 90.5:9.5<br>Ph (60) 1.5:1 90.0:10.0 91.5:8.5<br>3-$MeC_6H_4$ | | |
| |  | **440** (10 mol %), DMAP (10 mol %), D-mandelic acid (10 mol %), $Et_2O$, rt, 48 h |  (60) dr 1.1:1<br>er (major) 93.5:6.5<br>er (minor) 93.5:6.5 | 785 |

[a] These values were determined after several transformations.

[b] The absolute configuration was confirmed as (4*S*,5*S*)-6-(4-bromophenyl)-5-nitro-4-phenylhept-6-en-2-one.

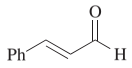
TABLE 4. NITROALKANES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

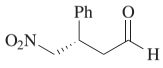
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_1$

$CH_3NO_2$



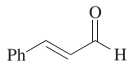
**366** (20 mol %), 96% aq MeOH, rt



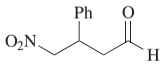
Catalyst Recycling

| Run | Conv. (%) | er |
|---|---|---|
| 1 | >99 | 97.5:2.5 |
| 2 | >99 | 97.5:2.5 |
| 3 | >99 | 97.0:3.0 |
| 4 | >99 | 97.5:2.5 |
| 5 | >99 | 97.5:2.5 |
| 6 | >99 | 97.0:3.0 |
| 7 | >99 | 97.5:2.5 |
| 8 | >99 | 97.0:3.0 |
| 9 | >99 | 97.5:2.5 |
| 10 | >99 | 97.5:2.5 |

786

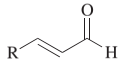


**425** (20 mol %), rt, 72 h

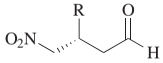


(36) er 73.5:26.5

787



**145b** (10 mol %), MeOH, rt



| R | Time (h) | | er |
|---|---|---|---|
| *n*-Bu | 96 | (77) | 95.5:4.5 |
| *i*-Bu | 120 | (68) | 95.5:4.5 |
| $BnCH_2$ | 96 | (76) | 96.0:4.0 |

153

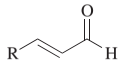
TABLE 4. NITROALKANES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

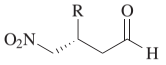
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_1$

$CH_3NO_2$

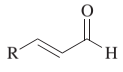


**145b** (*x* mol %), $PhCO_2H$ (20 mol %), MeOH

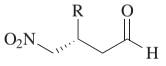


153

| R | *x* | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| *n*-Bu | 10 | rt | 42 | (53) | 95.0:5.0 |
| 2-$C_4H_3O$ | 10 | rt | 24 | (82) | 96.5:3.5 |
| Ph | 10 | rt | 16 | (90) | 97.5:2.5 |
| 4-$BrC_6H_4$ | 10 | rt | 17 | (87) | 97.5:2.5 |
| 4-$ClC_6H_4$ | 2 | rt | 40 | (80) | 96.0:4.0 |
| 4-$ClC_6H_4$ | 10 | rt | 17 | (83) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 10 | rt | 16 | (88) | 97.5:2.5 |
| 4-$O_2NC_6H_4$ | 10 | 4° | 48 | (76) | 97.5:2.5 |
| 3,4-$(OCH_2O)C_6H_3$ | 10 | rt | 17 | (80) | 96.5:3.5 |
| 2-Np | 10 | rt | 16 | (94) | 96.5:3.5 |



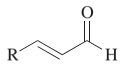
**145b** (*x* mol %), LiOAc (10 mol %), MeOH/$CH_2Cl_2$ (9:1), rt



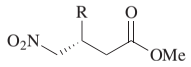
788

| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| Me | 2 | 96 | (67) | 90.5:9.5 |
| Et | 5 | 96 | (74) | 94.0:6.0 |
| *n*-Pr | 5 | 96 | (76) | 95.0:5.0 |
| *n*-Bu | 5 | 72 | (65) | 96.0:4.0 |
| 2-$C_4H_3O$ | 10 | 40 | (74) | 96.0:4.0 |
| (*Z*)-EtCH=$CH(CH_2)_2$ | 5 | 72 | (68) | 96.5:3.5 |
| Ph | 2 | 40 | (80) | 97.5:2.5 |
| 4-$BrC_6H_4$ | 5 | 48 | (65) | 96.0:4.0 |

| | | | | |
|---|---|---|---|---|
| 2-$ClC_6H_4$ | 2 | 84 | (61) | 97.5:2.5 |
| 3-$ClC_6H_4$ | 2 | 33 | (72) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 10 | 60 | (61) | 95.0:5.0 |
| 4-$FC_6H_4$ | 2 | 96 | (66) | 98.0:2.0 |
| 2-$MeOC_6H_4$ | 2 | 48 | (63) | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 10 | 60 | (67) | 96.0:4.0 |
| 2-$O_2NC_6H_4$ | 5 | 100 | (60) | 97.0:3.0 |
| *n*-$C_7H_{15}$ | 5 | 72 | (73) | 96.0:4.0 |
| 4-$MeC_6H_4$ | 5 | 96 | (67) | 96.5:3.5 |




1. **145b** (10 mol %), $PhCO_2H$ (20 mol %), MeOH, rt, 16 h
2. NBS (*x* eq), 4°, 16 h



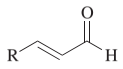
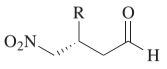

| R | *x* | | er |
|---|---|---|---|
| *n*-$C_6H_{13}$ | 1.5 | (54) | 97.0:3.0 |
| Ph | 1.5 | (58) | 97.0:3.0 |
| 4-$BrC_6H_4$ | 3 | (62) | 97.0:3.0 |
| 3-$ClC_6H_4$ | 1.5 | (70) | 97.0:3.0 |
| 4-$ClC_6H_4$ | 3 | (67) | 97.0:3.0 |
| 4-$FC_6H_4$ | 1.5 | (63) | 97.0:3.0 |
| 2,4,5-$F_3C_6H_2$ | 1.5 | (56) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 1.5 | (62) | 97.0:3.0 |
| 2-$MeC_6H_4$ | 1.5 | (59) | 97.0:3.0 |
| 4-$MeC_6H_4$ | 3 | (54) | 98.0:2.0 |
| 4-$NCC_6H_4$ | 1.5 | (59) | 98.0:2.0 |
| 3-$CF_3C_6H_4$ | 3 | (69) | 96.5:3.5 |
| 4-$CF_3C_6H_4$ | 1.5 | (66) | 97.0:3.0 |
| 4-*t*-$BuC_6H_4$ | 3 | (78) | 98.0:2.0 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

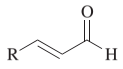
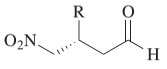
$C_1$

$CH_3NO_2$  **166** (10 mol %), $PhCO_2H$ (10 mol %), MeOH, rt, 22 h  790

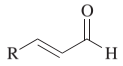
Catalyst Recycling (R = Ph)

| Run | Time (d) | | er | Time (h) | | er |
|---|---|---|---|---|---|---|
| 1 | 1 | (94) | 96.5:3.5 | 22 | (94) | 96.5:3.5 |
| 2 | 2 | (90) | 95.5:4.5 | 22 | (62) | 96.0:4.0 |
| 3 | 3 | (83) | 95.5:4.5 | 22 | (70) | 96.0:4.0 |
| 4 | 4 | (87) | 95.5:4.5 | 22 | (67) | 95.5:4.5 |
| 5 | | | | 22 | (50) | 95.5:4.5 |

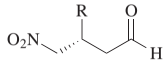
| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (95) | 95.0:5.0 |
| Ph | (94) | 97.0:3.0 |
| 2-$MeOC_6H_4$ | (80) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | (90) | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | (48) | 96.0:4.0 |
| 4-$Me_2NC_6H_4$ | (87) | 94.5:5.5 |

 **166** (10–20 mol %), $PhCO_2H$ (20 mol %), $CH_2Cl_2$  421

| R | MW | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 3 W | 30 | 7 | (31) | 97.0:3.0 |
| 2-$C_4H_3O$ | 7 W | 45 | 6 | (52) | 97.5:2.5 |
| Ph | none | rt | 56 | (86) | 98.0:2.0 |
| Ph | 7 W | 45 | 6 | (61) | 98.0:2.0 |
| 4-$ClC_6H_4$ | 7 W | 45 | 6 | (85) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 7 W | 45 | 6 | (80) | 95.5:4.5 |
| 4-$O_2NC_6H_4$ | 7 W | 45 | 6 | (88) | 95.0:5.0 |

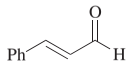


**168a** (7 mol %),
$PhCO_2H$ (42 mol %)
$H_2O$/*i*-PrOH (3:1), 4°

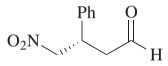


791

| R | Time (h) | | er |
|---|---|---|---|
| Me | 20 | (62) | 92.0:8.0 |
| 2-$C_4H_3O$ | 53 | (73) | 93.5:6.5 |
| Ph | 46 | (82) | 96.5:3.5 |
| 4-$BrC_6H_4$ | 55 | (65) | 96.5:3.5 |
| 2-$ClC_6H_4$ | 55 | (66) | 97.0:3.0 |
| 4-$FC_6H_4$ | 55 | (68) | 95.5:4.5 |
| 2-$MeOC_6H_4$ | 48 | (70) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | 64 | (70) | 97.0:3.0 |
| 2-$O_2NC_6H_4$ | 48 | (48) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 68 | (74) | 94.5:5.5 |



**168a** (10 mol %),
$PhCO_2H$ (42 mol %)
$H_2O$/*i*-PrOH (3:1), 4°



791

Catalyst Recycling

| Run | Time (h) | | er | Time (h) | | er |
|---|---|---|---|---|---|---|
| 1 | 37 | (84) | 96.5:3.5 | 40 | (86) | 96.5:3.5 |
| 2 | 48 | (76) | 96.0:4.0 | 40 | (75) | 96.5:3.5 |
| 3 | 53 | (70) | 96.0:4.0 | 40 | (67) | 96.0:4.0 |
| 4 | 84 | (73) | 94.5:5.5 | 40 | (58) | 95.5:4.5 |
| 5 | 120 | (64) | 92.0:8.0 | 40 | (45) | 94.5:5.5 |

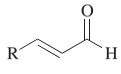
TABLE 4. NITROALKANES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

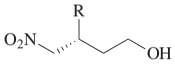
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_1$

$CH_3NO_2$

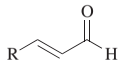


1. **172** (5 mol %),
   $PhCO_2H$ (5 mol %), solvent
2. $NaBH_4$, EtOH, –5°

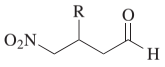


167

| R | Solvent | Temp | Time (h) | | er |
|---|---|---|---|---|---|
| Me | $H_2O$ | rt | 18 | (60) | 93.5:6.5 |
| Me | $H_2O$ | 0° | 18 | (42) | 95.5:4.5 |
| Ph | $H_2O$ | rt | 18 | (70) | 98.0:2.0 |
| Ph | EtOH/$H_2O$ (1:1) | rt | 18 | (65) | 98.0:2.0 |
| 4-$ClC_6H_4$ | $H_2O$ | rt | 18 | (69) | 97.5:2.5 |
| 3-$MeOC_6H_4$ | $H_2O$ | rt | 18 | (57) | 97.5:2.5 |
| 4-$MeOC_6H_4$ | $H_2O$ | rt | 18 | (71) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | EtOH/$H_2O$ (1:1) | rt | 18 | (68) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | $H_2O$ | rt | 6 | (60) | 99.0:1.0 |
| 3-*c*$C_5H_9$O-4-$MeOC_6H_3$ | $H_2O$ | rt | 18 | (62) | 99.0:1.0 |
| 4-$MeC_6H_4$ | $H_2O$ | rt | 18 | (66) | 98.5:1.5 |



Catalyst (10 mol %), MeOH, rt

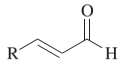


792

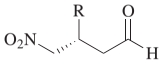
Catalyst **366/426** Recycling (R = Ph)

| Run | Time (h) | Conv. (%) | er (config) |
|---|---|---|---|
| 1 | 24 | >99/>99 | 97.0:3.0 (*S*)/97.0:3.0 (*R*) |
| 2 | 24 | >99/>99 | 97.0:3.0 (*S*)/96.5:3.5 (*R*) |
| 3 | 24 | >99/>99 | 97.0:3.0 (*S*)/96.5:3.5 (*R*) |
| 4 | 48 | >99/>99 | 97.0:3.0 (*S*)/96.5:3.5 (*R*) |
| 5 | 72 | >99/>99 | 97.0:3.0 (*S*)/96.5:3.5 (*R*) |

| R | Catalyst | Time (h) | | er | Config. |
|---|---|---|---|---|---|
| Me | **366** | 96 | (55) | 92.5:7.5 | (*S*) |
| Ph | **366** | 24 | (84) | 97.0:3.0 | (*S*) |
| Ph | **426** | 24 | (86) | 97.0:3.0 | (*R*) |
| 4-$BrC_6H_4$ | **366** | 24 | (95) | 95.5:4.5 | (*S*) |
| 4-$ClC_6H_4$ | **366** | 24 | (86) | 97.0:3.0 | (*S*) |
| 4-$ClC_6H_4$ | **426** | 24 | (91) | 95.0:5.0 | (*R*) |
| 4-$FC_6H_4$ | **366** | 24 | (80) | 96.5:3.5 | (*S*) |
| 4-$MeOC_6H_4$ | **366** | 48 | (87) | 96.5:3.5 | (*S*) |
| 4-$O_2NC_6H_4$ | **366** | 24 | (64) | 96.5:3.5 | (*S*) |
| 3-$C_5H_9O$-4-$MeOC_6H_3$ | **366** | 24 | (80) | 95.0:5.0 | (*S*) |
| 3-$C_5H_9O$-4-$MeOC_6H_3$ | **426** | 24 | (83) | 94.5:5.5 | (*R*) |
| ferrocenyl | **366** | 48 | (51) | 99.5:0.5 | (*S*) |



**371** (10 mol %), MeOH, rt



705

| R | Time (h) | | er |
|---|---|---|---|
| Ph | 24 | (83) | 97.5:2.5 |
| 4-$ClC_6H_4$ | 24 | (90) | 95.5:4.5 |
| 4-$MeOC_6H_4$ | 48 | (72) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | 24 | (68) | 99.0:1.0 |
| 3-$C_5H_9O$-4-$MeOC_6H_3$ | 24 | (76) | 95.5:4.5 |

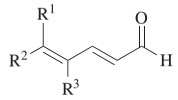
TABLE 4. NITROALKANES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

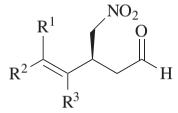
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_1$

$CH_3NO_2$

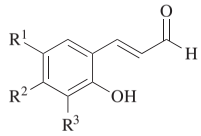


**422** (10 mol %), MeOH, rt

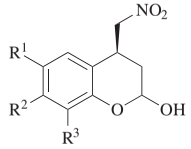


793

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| H | H | H | 106 | (54) | 93.5:6.5 |
| Me | H | H | 66 | (66) | 97.5:2.5 |
| $EtO_2C$ | H | H | 76 | (66) | 97.0:3.0 |
| Me | Me | H | 117 | (77) | 95.0:5.0 |
| 2-$C_4H_3O$ | H | H | 96 | (70) | 93.0:7.0 |
| Ph | H | H | 56 | (73) | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | H | H | 116 | (71) | 97.0:3.0 |
| Ph | Me | H | 120 | (71) | 95.0:5.0 |
| Ph | H | Me | 114 | (78) | 97.5:2.5 |
| $BnCH_2$ | H | H | 116 | (81) | 97.0:3.0 |



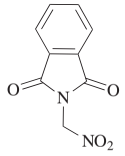
**145b** (10 mol %), AcOH (10 mol %), *i*-PrOH, 0°

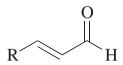


794

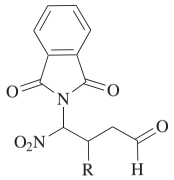
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| H | H | MeO | 44 | (83) | 66:34 | 99.5:0.5 |
| H | MeO | H | 44 | (74) | 63:37 | 99.0:1.0 |
| Br | H | H | 56 | (91) | 64:36 | 99.0:1.0 |
| Br | Br | H | 96 | (73) | 64:36 | 99.0:1.0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Cl | H | H | 48 | (92) | 63:37 | 99.5:0.5 |
| Cl | Cl | H | 72 | (72) | 64:36 | 99.5:0.5 |
| MeO | H | H | 45 | (88) | 63:37 | 98.5:1.5 |
| $O_2N$ | H | H | 120 | (69) | 63:37 | 98.0:2.0 |
| Me | H | H | 38 | (89) | 63:37 | 99.5:0.5 |





**145b** (10 mol %),
DABCO (*x* mol %),
solvent, 4°

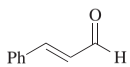


795

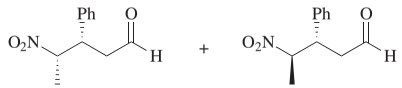
| R | *x* | Solvent | | dr | er |
|---|---|---|---|---|---|
| Me | 5 | $CHCl_3$ | (60) | 1:1 | 95.0:5.0 |
| Et | 5 | $CHCl_3$ | (88) | 1:1 | 95.0:5.0 |
| *n*-Pr | 5 | $CHCl_3$ | (80) | 5:4 | 96.5:3.5 |
| *n*-Bu | 5 | $CHCl_3$ | (88) | 1:1 | 96.5:3.5 |
| 2-$C_4H_3O$ | 0 | EtOH | (80) | 5:4 | 94.0:6.0 |
| *n*-$C_5H_{11}$ | 5 | $CHCl_3$ | (88) | 1:1 | 96.0:4.0 |
| *n*-$C_6H_{13}$ | 5 | $CHCl_3$ | (73) | 5:4 | 97.5:2.5 |
| (*Z*)-EtCH=CH$(CH_2)_2$ | 5 | $CHCl_3$ | (78) | 1:1 | 97.0:3.0 |
| Ph | 0 | EtOH | (80) | 10:3 | 95.0:5.0 |
| 2-$MeOC_6H_4$ | 0 | EtOH | (84) | 5:1 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 0 | EtOH | (80) | 5:1 | 98.0:2.0 |
| 3,4-$(OCH_2O)C_6H_3$ | 0 | EtOH | (65) | 3:1 | 95.0:5.0 |
| 3-AcO-4-$MeOC_6H_3$ | 0 | EtOH | (78) | 5:1 | 98.0:2.0 |
| *n*-$C_7H_{15}$ | 5 | $CHCl_3$ | (70) | 1:1 | 96.0:4.0 |
| *n*-$C_8H_{17}$ | 5 | $CHCl_3$ | (70) | 5:4 | 96.5:3.5 |

$C_2$





**145b** (10 mol %),
$PhCO_2H$ (20 mol %),
MeOH, rt



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(95) *syn*/*anti* = 1:1
er (*syn*) 97.5:2.5; er (*anti*) 98.0:2.0

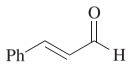
TABLE 4. NITROALKANES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

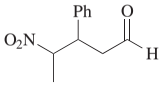
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_2$



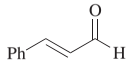


**145b** (2 mol %), LiOAc (10 mol %), $MeOH/CH_2Cl_2$ (9:1), rt

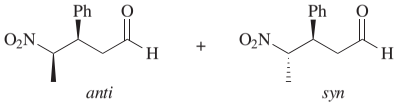


(74) dr 48:52
er 97.5:2.5
er 98.0:2.0

788



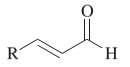
**435** (20 mol %), 50°



*anti* *syn*

39% conv., *anti*/*syn* = 60:40
er (*anti*) 74.0:26.0; er (*syn*) 75.0:25.0

796



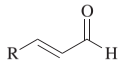
**168a** (7 mol %), $PhCO_2H$ (42 mol %) $H_2O$/*i*-PrOH (3:1), 4°



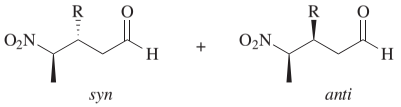
*syn* *anti*

| R | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| Ph | 50 | (83) | 2:3 | 95.0:5.0 | 96.5:3.5 |
| 2-$MeOC_6H_4$ | 48 | (95) | 1:2 | 95.5:4.5 | 95.5:4.5 |
| 2-$O_2NC_6H_4$ | 50 | (88) | 2:1 | 96.0:4.0 | 95.5:4.5 |

791



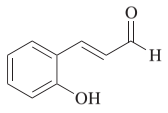
**425** (20 mol %), rt



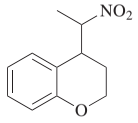
*syn* *anti*

| R | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|
| *n*-Pr | 40 | (74) | 1:1 | 58.0:42.0 | 54.5:45.5 |
| 2-$C_4H_3O$ | 68 | (61) | 1:1.1 | 84.0:16.0 | 83.0:17.0 |
| Ph | 47 | (91) | 1:1 | 91.0:9.0 | 90.0:10.0 |
| 2-$MeOC_6H_4$ | 45 | (91) | 1:2.3 | 84.0:16.0 | 85.5:14.5 |
| 4-$MeOC_6H_4$ | 65 | (60) | 1:1.3 | 88.5:11.5 | 78.0:22.0 |

787

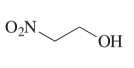


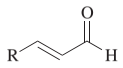
1. **145b** (10 mol %),
   AcOH (10 mol %),
   *i*-PrOH, 0°
2. $Et_3SiH$, $BF_3$•$OEt_2$, $CH_2Cl_2$



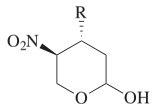
(44) dr 69:31
er (major) 99.0:1.0
er (minor) 97.5:2.5

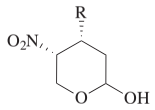
794





1. **145b** (*x* mol %),
   $PhCO_2H$ (*y* mol %),
   MeOH, rt, time
2. $NaHCO_3$, MeOH, rt



**I** +  **II**

797

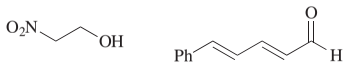
| R | *x* | *y* | Time (h) | | **I/II** | er **I** |
|---|---|---|---|---|---|---|
| *i*-Bu | 20 | 0 | 71 | (72) | 78:22 | 96.0:4.0 |
| 2-$C_4H_3O$ | 10 | 20 | 26 | (80) | 80:20 | 95.5:4.5 |
| 2-$C_4H_3S$ | 10 | 20 | 21 | (82) | 90:10 | 97.0:3.0 |
| *c*-$C_6H_{11}$ | 20 | 0 | 79 | (55) | 76:24 | 98.0:2.0 |
| Ph | 2 | 4 | 46 | (87) | 84:16 | 98.0:2.0 |
| Ph | 10 | 20 | 20 | (86) | 89:11 | 97.5:2.5 |
| 4-$BrC_6H_4$ | 10 | 20 | 15 | (85) | 86:14 | 96.5:3.5 |
| 2-$MeOC_6H_4$ | 10 | 20 | 21 | (94) | 85:15 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 10 | 20 | 26 | (95) | 84:16 | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | 1 | 20 | 15 | (80) | 86:14 | 99.5:0.5 |
| $BnCH_2$ | 10 | 0 | 27 | (76) | 76:24 | 96.0:4.0 |
| 2-Np | 10 | 20 | 28 | (92) | 87:13 | 97.0:3.0 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

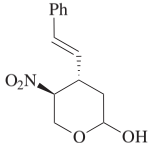
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_2$



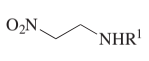


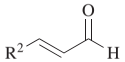
**423** (10 mol %), MeOH, rt, 69 h



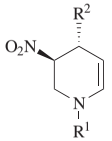
(74) er 92.0:8.0

793



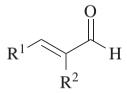


1. **145b** (*x* mol %), $PhCO_2H$ (*y* mol %), $CH_2Cl_2$, 0°
2. TFA

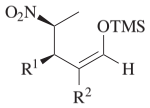


798

| $R^1$ | $R^2$ | *x* | *y* | | dr | er |
|---|---|---|---|---|---|---|
| Ac | Et | 20 | 0 | (64) | 89:11 | 96.0:4.0 |
| Ac | *i*-Pr | 20 | 0 | (43) | 96:4 | 99.0:1.0 |
| Ac | $CH=C(CH_2)_2$ | 20 | 0 | (50) | 88:12 | 96.5:3.5 |
| Ac | $2\text{-}C_4H_3O$ | 10 | 10 | (83) | 96:4 | 99.5:0.5 |
| Ac | Ph | 10 | 10 | (77) | 89:11 | 98.0:2.0 |
| Ac | $2\text{-}BrC_6H_4$ | 10 | 10 | (71) | >99:1 | 98.0:2.0 |
| Ac | $4\text{-}BrC_6H_4$ | 10 | 10 | (78) | 87:13 | 97.5:2.5 |
| Ac | $4\text{-}FC_6H_4$ | 10 | 10 | (75) | 87:13 | 97.0:3.0 |
| Ac | $2\text{-}MeOC_6H_4$ | 10 | 10 | (80) | 91:9 | 98.0:2.0 |
| Ac | $2\text{-}O_2NC_6H_4$ | 10 | 10 | (72) | 93:7 | 97.0:3.0 |
| Ac | $4\text{-}O_2NC_6H_4$ | 10 | 10 | (64) | 89:11 | 99.5:0.5 |
| Boc | Et | 20 | 0 | (43) | 87:13 | 97.0:3.0 |
| Boc | Ph | 10 | 10 | (79) | 88:12 | 97.5:2.5 |

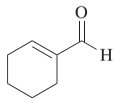



**421** (2 mol %), toluene

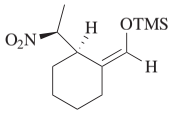


217

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|---|---|
| *n*-Pr | H | –78 | 1 | (92) | 81:19 | 96.5:3.5 |
| Ph | H | –78 | 1 | (90) | 83:17 | 98.5:1.5 |
| Ph | Me | –78 to –40 | 2 | (90) | 95:5 | 97.5:2.5 |



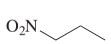
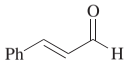
**421** (2 mol %), toluene, –78 to –40°, 2 h



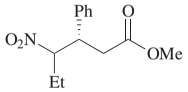
(99) *anti*/*syn* = 81:19, er 95.0:5.0

217

$C_3$

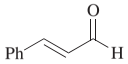



1. **145b** (20 mol %), $PhCO_2H$ (40 mol %), MeOH, rt, 16 h
2. NBS (1.5 eq), 4°

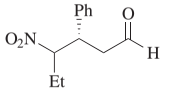


(94) dr 55:45
er (major) 92.5:7.5
er (minor) 96.0:4.0

789



**366** (10 mol %), MeOH, rt, 48 h



(94) *syn*/*anti* 1:1.25
er (*syn*) 97.0:3.0
er (*anti*) 99.0:1.0

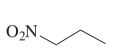
792

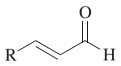
TABLE 4. NITROALKANES AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

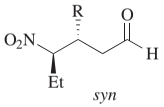
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



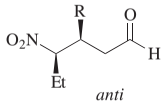


**425** (20 mol %), solvent, rt



*syn*

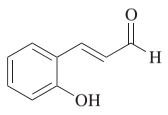
+



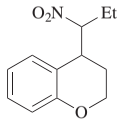
*anti*

787

| R | Solvent | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|
| 2-$C_4H_3O$ | neat | 48 | (49) | 1:1 | 88.5:11.5 | 83.5:16.5 |
| Ph | neat | 68 | (75) | 1:1 | 87.0:13.0 | 81.5:18.5 |
| 2-$MeOC_6H_4$ | neat | 49 | (81) | 1:2.6 | 95.0:5.0 | 89.5:10.5 |
| 4-$MeOC_6H_4$ | neat | 62 | (43) | 1:1.3 | 84.0:16.0 | 76.5:23.5 |
| 2-$O_2NC_6H_4$ | DMF | 48 | (21) | 1.2:1 | — | — |
| 4-$O_2NC_6H_4$ | DMF | 48 | (31) | 1.2:1 | — | — |



1. **145b** (10 mol %),
AcOH (10 mol %)
*i*-PrOH, 0°
2. $Et_3SiH$, $BF_3$•$OEt_2$, $CH_2Cl_2$



(56) dr 64:36
er (major) 99.5:0.5
er (minor) 97.5:2.5

794

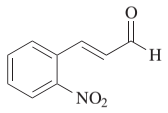
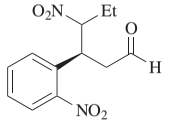
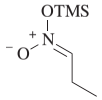
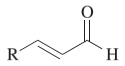
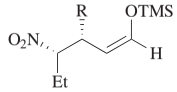
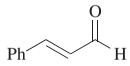
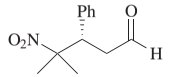
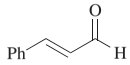
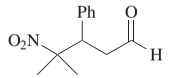
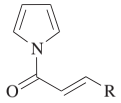
| | | | | | |
|---|---|---|---|---|---|
| |  | **168a** (7 mol %), $PhCO_2H$ (42 mol %) $H_2O$/*i*-PrOH (3:1), 4°, 60 h |  | (73) *syn*/*anti* = 3:2<br>er (*syn*) 97.0:3.0<br>er (*anti*) 97.0:3.0 | 791 |
|  |  | **421** (2 mol %), toluene, –78°, 1 h |  | R (99) 76:24 98.5:1.5 (*n*-Pr)<br>R (87) 90:10 99.0:1.0 (Ph) | 217 |
|  |  | **145b** (10 mol %), $PhCO_2H$ (20 mol %), neat, rt |  | (47) er 91.0:9.0 | 153 |
| |  | **425** (20 mol %), rt, 170 h |  | (65) er 74.0:26.0 | 787 |

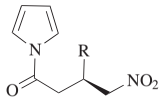
TABLE 4. NITROALKANES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

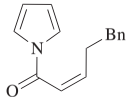
$C_1$

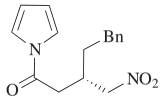
$CH_3NO_2$ 

**323** (*x* mol %), neat, 25–50° 

768

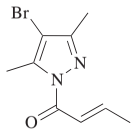
| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 10 | 146 | (81) | 96.5:3.5 |
| 2-$C_4H_3S$ | 10 | 146 | (59) | 96.0:4.0 |
| c-$C_6H_{11}$ | 10 | 78 | (93) | 97.0:3.0 |
| Ph | 10 | 87 | (93) | 96.5:3.5 |
| 4-$ClC_6H_4$ | 20 | 64 | (88) | 94.5:5.5 |
| 4-$MeOC_6H_4$ | 10 | 146 | (90) | 96.5:3.5 |
| $BnCH_2$ | 10 | 23 | (95) | 96.5:3.5 |
| PhCH=CH | 10 | 139 | (54) | 97.0:3.0 |
| $CH_2$=$CH(CH_2)_8$ | 10 | 22 | (87) | 95.0:5.0 |
| 3-($cC_5H_9O$)-4-$MeOC_6H_3$ | 20 | 183 | (78) | 96.5:3.5 |
| 3-($cC_5H_9O$)-4-$MeOC_6H_3$ | 30 | 72 | (25) | 91.0:9.0 |

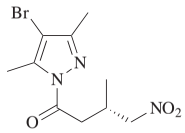


**323** (10 mol %), neat, 25–50°, 3 h 

(81) er 67.0:33.0

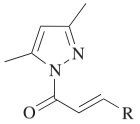
768



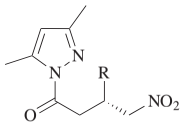
**373** (10 mol %), $Ni(OAc)_2$•$4H_2O$ (10 mol %), *t*-BuOH, rt, 24 h 

(95) er 99.0:1.0

723

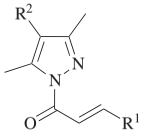


**373** (10 mol %),
$Ni(OAc)_2 \cdot 4H_2O$ (10 mol %),
*t*-BuOH, 4 Å MS, rt

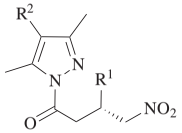


799

| R | Time (h) | | er |
|---|---|---|---|
| Me | 3 | (>99) | >99.5:0.5 |
| $EtO_2C$ | 2 | (90) | 99.0:1.0 |
| *i*-Pr | 72 | (71) | 98.0:2.0 |
| *t*-Bu | 72 | (25) | 99.0:1.0 |
| Ph | 12 | (77) | >99.5:0.5 |



**373** (10 mol %),
$Ni(OAc)_2 \cdot 4H_2O$ (10 mol %),
TMP (10 mol %), THF



100

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Me | H | –20 | 96 | (85) | 97.0:3.0 |
| Me | H | 0 | 48 | (91) | 95.0:5.0 |
| Me | H | rt | 5 | (97) | 92.0:8.0 |
| Me | Br | –20 | 96 | (97) | 97.5:2.5 |
| Me | I | –20 | 96 | (62) | 98.0:2.0 |
| $EtO_2C$ | H | rt | 3 | (91) | 91.5:8.5 |
| Et | H | 0 | 24 | (93) | 97.0:3.0 |
| *n*-Pr | H | –20 | 96 | (96) | 95.5:4.5 |
| *i*-Pr | H | –20 | 168 | (74) | 98.5:1.5 |
| (*E*)-MeCH=CH | H | –20 | 96 | (49) | 88.5:11.5 |
| *t*-Bu | H | 0 | 168 | (39) | 97.5:2.5 |
| 2-$C_4H_3O$ | H | –20 | 96 | (75) | 98.5:1.5 |
| 2-$C_4H_3S$ | H | –20 | 168 | (83) | 98.5:1.5 |
| *c*-$C_6H_{11}$ | H | –20 | 168 | (90) | 95.5:4.5 |
| Ph | H | –20 | 168 | (90) | 96.5:3.5 |
| 3,4-$(OCH_2O)C_6H_3$ | H | –20 | 168 | (77) | 99.0:1.0 |
| 3-(*c*-$C_5H_9O$)4-$MeOC_6H_3$ | H | –20 | 168 | (91) | 99.0:1.0 |

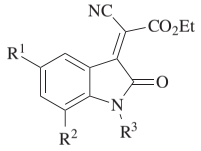
TABLE 4. NITROALKANES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

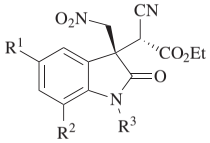
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_1$

$CH_3NO_2$




**427** (10 mol %), neat, –10°

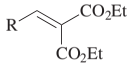



800

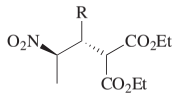
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| H | H | H | 3.5 | (99) | 9:1 | 93.5:6.5 |
| H | Cl | H | 5 | (96) | >20:1 | 92.5:7.5 |
| Br | H | H | 3 | (95) | 12:1 | 99.0:1.0 |
| Cl | H | H | 3 | (94) | >20:1 | 92.5:7.5 |
| I | H | H | 3 | (95) | 11:1 | 94.5:5.5 |
| MeO | H | H | 2 | (93) | >20:1 | 92.5:7.5 |
| $O_2N$ | H | H | 1.5 | (94) | 12:1 | 96.0:4.0 |
| H | H | Me | 4 | (96) | 6:1 | 98.5:1.5 |
| Br | H | Me | 6 | (98) | 8:1 | 96.0:4.0 |
| I | H | Me | 6 | (95) | 10:1 | 95.5:4.5 |
| MeO | H | Me | 4 | (95) | >20:1 | 95.0:5.0 |
| H | H | Ac | 6 | (94) | 6:1 | 98.0:2.0 |
| H | H | $MeO_2CCH_2$ | 4 | (95) | 4:1 | 94.0:6.0 |
| Br | H | $MeO_2CCH_2$ | 6 | (97) | 10:1 | 92.5:7.5 |
| Br | H | Bn | 8 | (97) | 4:1 | 97.5:2.5 |

$C_2$

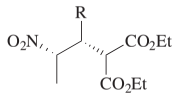




**271** (*x* mol %), rt

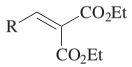


+

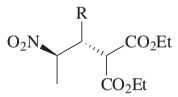


801

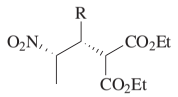
| R | *x* | Time (d) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 10 | 8 | (45) | 61:39 | 90.5:9.5 | 83.5:16.5 |
| 4-$C_5H_4N$ | 10 | 2 | (68) | 71:29 | 95.0:5.0 | 90.0:10.0 |
| Ph | 10 | 7 | (61) | 70:30 | 95.5:4.5 | 92.5:7.5 |
| 4-$BrC_6H_4$ | 10 | 5 | (70) | 62:38 | 95.0:5.0 | 92.0:8.0 |
| 2-$FC_6H_4$ | 10 | 4 | (68) | 67:33 | 96.5:3.5 | 92.0:8.0 |
| 4-$FC_6H_4$ | 10 | 6 | (60) | 64:36 | 96.5:3.5 | 91.5:8.5 |
| 4-$MeOC_6H_4$ | 10 | 7 | (36) | 69:31 | 97.0:3.0 | 93.0:7.0 |
| 4-$O_2NC_6H_4$ | 20 | 3 | (28) | 81:19 | 95.5:4.5 | 83.5:16.5 |
| 2-$C_8H_6N$ | 10 | 4 | (67) | 63:37 | 90.5:9.5 | 90.5:9.5 |



**428** (*x* mol %)



+



801

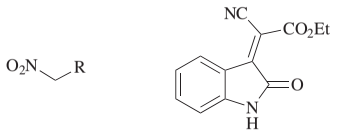
| R | *x* | Temp (°) | Time (d) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|---|
| *n*-Bu | 20 | 0 | 4 | (81) | 70:30 | 85.5:14.5 | 59.0:41.0 |
| *i*-Bu | 20 | 0 | 6 | (73) | 72:28 | 84.5:15.5 | 52.5:47.5 |
| 2-$C_4H_3O$ | 10 | 0 | 7 | (37) | 78:22 | 92.0:8.0 | 78.5:21.5 |
| 4-$C_5H_4N$ | 5 | 0 | 2 | (60) | 85:15 | 96.5:3.5 | 85.5:14.5 |
| Ph | 10 | 0 | 6 | (40) | 82:18 | 97.5:2.5 | 83.5:16.5 |
| 4-$BrC_6H_4$ | 10 | 0 | 4 | (55) | 82:18 | 96.5:3.5 | 81.0:19.0 |
| 2-$FC_6H_4$ | 10 | 0 | 5 | (54) | 81:19 | 97.0:3.0 | 84.5:15.5 |
| 4-$FC_6H_4$ | 10 | 0 | 6 | (51) | 80:20 | 97.0:3.0 | 85.0:15.0 |
| 4-$MeOC_6H_4$ | 10 | 0 | 7 | (46) | 64:36 | 95.5:4.5 | 91.0:9.0 |
| 4-$O_2NC_6H_4$ | 20 | 0 | 3 | (67) | 80:20 | 96.5:3.5 | 85.5:14.5 |
| 4-$FC_6H_4CH{=}CH$ | 20 | –20 | 9 | (41) | 74:26 | 86.0:14.0 | 52.5:47.5 |
| 4-$O_2NC_6H_4CH{=}CH$ | 20 | 0 | 4 | (79) | 68:32 | 81.5:18.5 | 53.5:46.5 |
| 2-$C_8H_6N$ | 10 | 0 | 5 | (52) | 77:23 | 94.0:6.0 | 89.0:11.0 |

TABLE 4. NITROALKANES AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

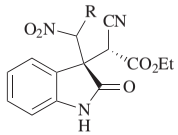
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{2-3}$





**427** (10 mol %), neat, –10°, 3 h

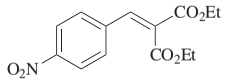


800

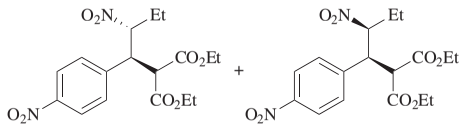
| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| Me | (95) | 7:1 | 94.0:6.0 | 62.5:37.5 |
| Et | (97) | 6:1 | 98.5:1.5 | 99.0:1.0 |

$C_3$





Catalyst (10 mol %)

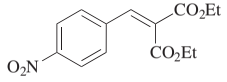


801

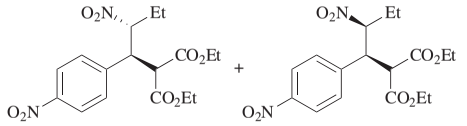
| Catalyst | Temp | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|
| **271** | rt | 3 | (72) | 73:27 | 95.5:4.5 | 79.5:20.5 |
| **428** | 0° | 5 | (71) | 74:26 | 94.5:5.5 | 77.5:22.5 |

$C_{4-8}$





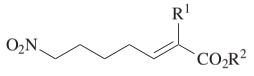
Catalyst (*x* mol %), rt



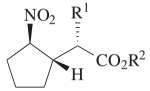
801

| R | Catalyst | *x* | Time (h) | | *syn*/*anti* | er (*syn*) | er (*anti*) |
|---|---|---|---|---|---|---|---|
| $MeO_2C(CH_2)_2$ | **271** | 10 | 2 | (71) | 67:33 | 94.5:5.5 | 85.5:14.5 |
| $MeO_2C(CH_2)_2$ | **428** | 2.5 | 7 | (62) | 63:37 | 93.0:7.0 | 84.0:16.0 |
| Bn | **271** | 10 | 4 | (71) | 70:30 | 94.0:6.0 | 75.0:25.0 |
| Bn | **428** | 2.5 | 2 | (66) | 70:30 | 92.0:8.0 | 76.5:23.5 |

$C_{7-14}$



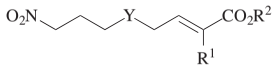
**430** (10 mol %),
$K_2CO_3$ (0.2 eq),
toluene, rt, 18 h



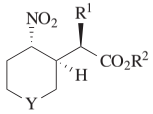
802

| $R^1$ | $R^2$ | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| H | Et | (>99) | 3:2 | 75.0:25.0 | 65.0:35.0 |
| H | *t*-Bu | (61) | 7:3 | 59.0:41.0 | — |
| H | Bn | (89) | 1:1 | 65.0:35.0 | 64.0:36.0 |
| F | Et | (83) | 3:2:2:0 | 62.0:38.0 | 69.0:31.0 |
| CbzHN | Me | (90) | 6:3:1:0 | 55.0:45.0 | — |
| *n*-$C_6H_{13}$ | Et | (27) | 5:2:<1:0 | 55.0:45.0 | — |
| Ph | Et | (73) | 5:3:2:0 | 69.0:31.0 | — |
| Bn | Et | (40) | 2:1:<1:0 | 74.0:26.0 | 67.0:33.0 |
| Bn | Bn | (44) | 4:1:<1:0 | 68.0:32.0 | — |

$C_{7-15}$



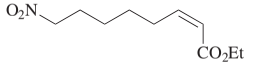
**429** (10 mol %),
0.5 M in MeCN, rt



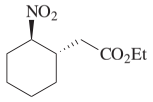
185, 803

| Y | $R^1$ | $R^2$ | Time (d) | | dr | er |
|---|---|---|---|---|---|---|
| O | H | Et | 7 | (69) | >19:1 | 96.0:4.0 |
| $CH_2$ | H | Me | 7 | (57) | 4:1 | 98.0:2.0 |
| $CH_2$ | H | Et | 7 | (87) | >19:1 | 98.0:2.0 |
| $CH_2$ | H | Bn | 7 | (66) | 4:1 | 99.0:1.0 |
| $CH_2$ | BocHN | Me | 7 | (11) | 3:1:<1 | >99.5:0.5 |
| $CH_2$ | CbzHN | Me | 7 | (65) | 2:1:<1 | 97.5:2.5 |
| $CH_2$ | Me | Et | 7 | (50) | >19:6:1 | 97.0:3.0 |
| $Me_2C$ | H | Et | 2 | (76) | >19:1 | 98.0:2.0 |
| $CH_2$ | Bn | Et | 7 | (52) | >19:4:1 | >99.5:0.5 |

$C_8$



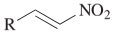
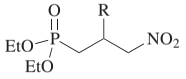
**429** (10 mol %),
0.5 M in MeCN, rt, 7 d



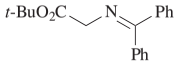
(20) dr 7:3
er 69.0:31.0

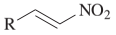
185, 803

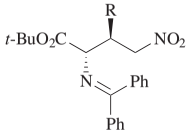
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS
A. NITROALKENES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_1$  |  | **431** (50 mol %), LDA (3 eq), THF, –78° to rt, 18 h |  | 804 |

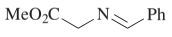
| R | | er |
|---|---|---|
| Ph | (41) | 84.0:16.0 |
| 4-$ClC_6H_4$ | (61) | 99.5:0.5 |
| 4-$MeOC_6H_4$ | (43) | 91.0:9.0 |

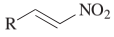
$C_2$ 



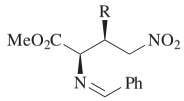
Catalyst (10 mol %), $CuClO_4$ (10 mol %), $Et_3N$ (10 mol %), THF, –10°  805, 806

| R | Catalyst | | *anti*/*syn* | er (*anti*) |
|---|---|---|---|---|
| 2-$C_4H_3O$ | **432b** | (>99) | 94:6 | 97.5:2.5 |
| Ph | **432a** | (72) | 95:5 | 98.5:1.5 |
| Ph | **432b** | (>99) | 94:6 | 98.5:1.5 |
| 2-$BrC_6H_4$ | **432a** | (72) | 90:10 | 96.5:3.5 |
| 2-$BrC_6H_4$ | **432b** | (>99) | 90:10 | 88.0:12.0 |
| 3-$BrC_6H_4$ | **432b** | (>99) | 92:8 | 99.0:1.0 |
| 4-$BrC_6H_4$ | **432b** | (>99) | 95:5 | 98.5:1.5 |
| 2-$ClC_6H_4$ | **432a** | (85) | 91:9 | 96.5:3.5 |
| 2-$ClC_6H_4$ | **432b** | (>99) | 90:10 | 94.5:5.5 |
| 4-$ClC_6H_4$ | **432b** | (>99) | 98:2 | 99.0:1.0 |
| 4-$FC_6H_4$ | **432b** | (>99) | 98:2 | 98.5:1.5 |
| 3-$MeOC_6H_4$ | **432b** | (>99) | 96:4 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | **432b** | (>99) | 98:2 | 99.0:1.0 |
| 4-$MeC_6H_4$ | **432b** | (>99) | 95:5 | 98.5:1.5 |
| 2-$CF_3C_6H_4$ | **432a** | (73) | 85:15 | 93.0:7.0 |
| 2-$CF_3C_6H_4$ | **432b** | (>99) | 82:18 | 82.0:18.0 |



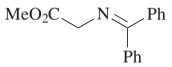


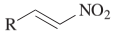
**433** (10 mol %),
CuOAc (10 mol %),
$CH_2Cl_2$, –15°, 18–40 h



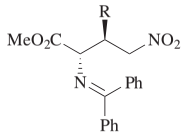
807, 808

| R | | er |
|---|---|---|
| 2-$C_4H_3O$ | (86) | 99.0:1.0 |
| 2-$C_4H_3S$ | (91) | 98.5:1.5 |
| Ph | (88) | 99.0:1.0 |
| 2-$ClC_6H_4$ | (72) | 99.0:1.0 |
| 3-$ClC_6H_4$ | (72) | >99.5:0.5 |
| 4-$ClC_6H_4$ | (72) | 99.0:1.0 |
| 4-$FC_6H_4$ | (75) | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | (65) | 99.0:1.0 |
| 4-$MeC_6H_4$ | (68) | 98.5:1.5 |
| 1-Np | (62) | >99.5:0.5 |





**433** (*x* mol %),
CuOTf (10–20 mol%),
DBU (0–10 mol %),
additive (*y* mol %),
THF, –15°, 30–48 h



807, 808

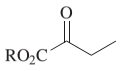
| R | *x* | Additive | *y* | | er |
|---|---|---|---|---|---|
| *i*-Pr | 20 | 2-phenyl-2-propanol | 20 | (49) | 90.0:10.0 |
| 2-$C_4H_3O$ | 10 | — | — | (83) | 93.0:7.0 |
| 2-$C_4H_3S$ | 10 | — | — | (83) | 90.5:9.5 |
| *c*-$C_6H_{11}$ | 20 | 2-phenyl-2-propanol | 20 | (52) | 90.0:10.0 |
| Ph | 10 | *t*-BuOH | 60 | (89) | 99.5:0.5 |
| 2-$ClC_6H_4$ | 10 | 2-phenyl-2-propanol | 20 | (83) | 91.0:9.0 |
| 3-$ClC_6H_4$ | 10 | 2-phenyl-2-propanol | 20 | (85) | 94.0:6.0 |
| 4-$ClC_6H_4$ | 10 | 2-phenyl-2-propanol | 20 | (82) | 92.0:8.0 |
| 4-$FC_6H_4$ | 10 | *t*-BuOH | 60 | (68) | 90.0:10.0 |
| 4-$MeC_6H_4$ | 10 | 2-phenyl-2-propanol | 20 | (84) | 94.0:6.0 |
| 1-Np | 10 | 2-phenyl-2-propanol | 20 | (73) | 90.5:9.5 |
| 2-Np | 20 | 2-phenyl-2-propanol | 20 | (88) | 90.0:10.0 |

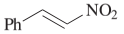
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

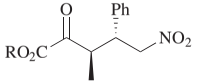
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_4$



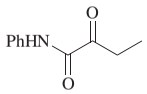


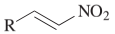
*ent*-**164b** (10 mol %), EtOAc, 18 h



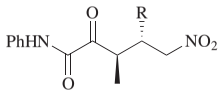
809

| R | Temp | | *anti*/*syn* | er (*anti*) | er (*syn*) |
|---|---|---|---|---|---|
| Et | rt | (91) | 3.5:1 | 90.0:10.0 | 93.5:6.5 |
| *t*-Bu | rt | (95) | 2:1 | 96.5:3.5 | 98.0:2.0 |
| Bn | –35° | (75) | 8:1 | 96.5:3.5 | — |
| Bn | 0° | (85) | 9:1 | 96.0:4.0 | — |
| Bn | rt | (90) | 7:1 | 94.0:6.0 | — |





*ent*-**164b** (10 mol %), EtOAc, rt

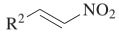


810

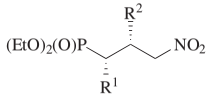
| R | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|
| 2-$C_3H_4S$ | 60 | (67) | 13:1 | 99.0:1.0 |
| Ph | 60 | (83) | >20:1 | >99.5:0.5 |
| 4-$BrC_6H_4$ | 60 | (71) | 14:1 | 96.5:3.5 |
| 4-$FC_6H_4$ | 48 | (76) | 10:1 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | 60 | (73) | >20:1 | 97.0:3.0 |

$C_{4-11}$





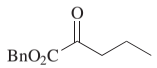
**431** (50 mol %),
LDA (3 eq),
THF, –78° to rt, 18 h

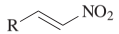


804

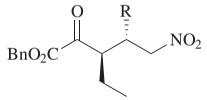
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| *n*-Pr | 4-$ClC_6H_4$ | (47) | 72:28 | 93.0:7.0 |
| Ph | 2-$C_4H_3O$ | (90) | 96:4 | >99.5:0.5 |
| Ph | 3-$C_4H_3O$ | (60) | 62:38 | 99.0:1.0 |
| Ph | Ph | (98) | 68:32 | >99.5:0.5 |
| Ph | 4-$ClC_6H_4$ | (81) | 96:4 | >99.5:0.5 |
| Ph | 4-$MeOC_6H_4$ | (99) | 88:12 | 91.0:9.0 |
| Ph | 3,4-$(OCH_2O)C_6H_3$ | (95) | 100:0 | 97.0:3.0 |
| Ph | 4-$O_2NC_6H_4$ | (65) | 68:32 | >99.5:0.5 |
| Ph | 4-$Me_2NC_6H_4$ | (63) | 52:48 | 93.0:7.0 |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | (69) | 100:0 | >99.5:0.5 |
| 4-$O_2NC_6H_4$ | 4-$ClC_6H_4$ | (45) | 92:8 | 90.0:10.0 |
| 2-Np | 4-$ClC_6H_4$ | (74) | 100:0 | >99.5:0.5 |

$C_5$





*ent*-**164b** (10 mol %),
EtOAc, 0°

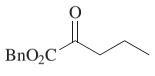
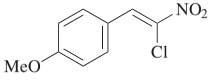
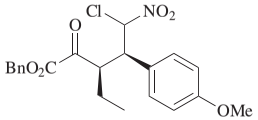
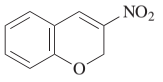
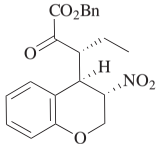
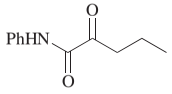
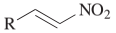
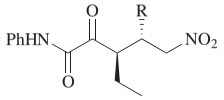


*anti*/*syn* >20:1

809

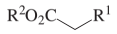
| R | Time (h) | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | 18 | (72) | 97.0:3.0 |
| 2-$C_4H_3S$ | 18 | (88) | 97.5:2.5 |
| 3-$C_8H_6N$ | 72 | (89) | 97.0:3.0 |
| Ph | 18 | (89) | 97.0:3.0 |
| 2-$BrC_6H_4$ | 18 | (98) | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 18 | (84) | 97.0:3.0 |
| 2-$O_2NC_6H_4$ | 18 | (99) | 99.0:1.0 |
| 4-$O_2NC_6H_4$ | 18 | (88) | 97.0:3.0 |
| $BnCH_2$ | 18 | (55) | 97.0:3.0 |

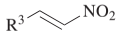
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_5$ | | | | |
|  |  | *ent*-**164b** (10 mol %), EtOAc, 0°, 18 h |  only two diostereoiners | (94) dr 3:1<br>er (major) 98.5:1.5<br>er (minor) 97.0:3.0 | 809 |
| |  | *ent*-**164b** (10 mol %), EtOAc, 0°, 18 h |  | (80) er 98.5:1.5 | 809 |
|  |  | *ent*-**164b** (10 mol %), EtOAc, rt, 60 h |  | *syn*/*anti* >20:1 | 810 |

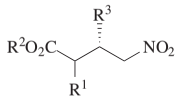
| R | | er |
|---|---|---|
| 2-$C_3H_4S$ | (73) | 97.5:2.5 |
| Ph | (93) | 99.0:1.0 |
| 4-$MeOC_6H_4$ | (75) | 97.5:2.5 |

$C_{5-11}$





*ent*-**235a** (5 mol %),
dioxane, 3 Å MS, rt, 18 h



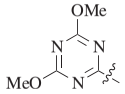
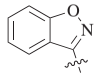
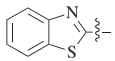
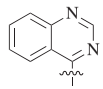
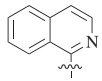
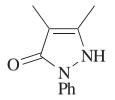
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
|  | *t*-Bu | 4-$MeC_6H_4$ | (50) | 9:1 | 95.0:5.0 |
|  | *t*-Bu | 4-$MeC_6H_4$ | (66) | 7:1 | 97.0:3.0 |
| | Et | 2-$C_4H_3O$ | (98) | 5:1 | 95.5:4.5 |
|  | Et | 4-$MeOC_6H_4$ | (87) | 8.5:1 | 90.0:10.0 |
| | Et | 4-$MeC_6H_4$ | (71) | 12:1 | 94.5:5.5 |
|  | Me | 4-$MeC_6H_4$ | (59) | 1.6:1 | 96.5:3.5 |
| | Me | 4-$MeC_6H_4$ | (94) | 2:1 | 98.0:2.0 |
|  | t-Bu | 4-$MeC_6H_4$ | (91) | 3.5:1 | 97.0:3.0 |
|  | *t*-Bu | 4-$MeC_6H_4$ | (60) | 6:1 | 90.5:9.5 |
|  | *t*-Bu | 4-$MeC_6H_4$ | (78) | 9:1 | 99.5:0.5 |

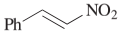
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

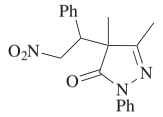
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_5$



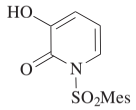


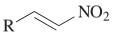
**441** (20 mol %), $CHCl_3/CH_2Cl_2$ (4:1), –60°, 24 h



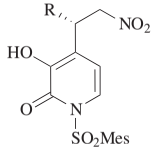
(86) dr 1:1
er 75.0:25.0

812



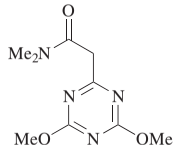


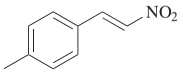
**442** (20 mol %), solvent, 0°



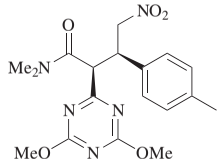
813

| R | Solvent | | er |
|---|---|---|---|
| 2-$O_2NC_6H_4$ | $ClC_6H_5$ | (75) | 96.0:4.0 |
| 3-$O_2NC_6H_4$ | $CH_2Cl_2$ | (75) | 90.0:10.0 |





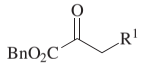
*ent*-**235a** (5 mol %), dioxane, 3 Å MS, rt, 18 h

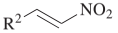


(99) dr 10:1
er 96.5:3.5

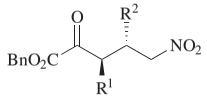
811

$C_{6–10}$





*ent*-**164b** (10 mol %), EtOAc, 0°

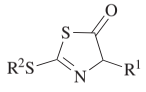


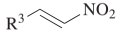
*anti*/*syn* >20:1

809

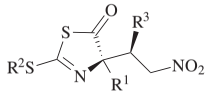
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| *i*-Pr | Ph | 36 | (36) | 95.5:4.5 |
| *i*-Pr | 4-$BrC_6H_4$ | 72 | (41) | 95.0:5.0 |
| allyl | $I(CH_2)_2$ | 96 | (44) | 95.0:5.0 |
| allyl | Ph | 18 | (70) | 90.0:10.0 |
| Bn | Ph | 18 | (87) | 96.5:3.5 |

$C_{6-7}$





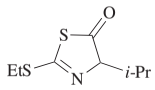
**443** (10 mol %), MTBE, 0°

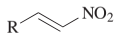


814

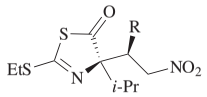
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *i*-Pr | Bn | 4-$NCC_6H_4$ | 12 | (71) | 4:1 | 96.0:4.0 |
| *i*-Bu | Et | 2-$O_2NC_6H_4$ | 8 | (62) | 3:1 | 90.0:10.0 |
| *t*-Bu | Et | 4-$NCC_6H_4$ | 18 | (68) | 9:1 | 92.0:8.0 |

$C_6$





**443** (10 mol %), MTBE, 0°

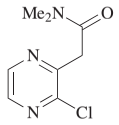
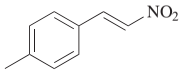
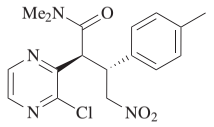
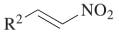
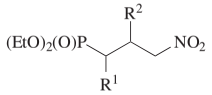


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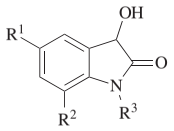
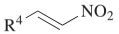
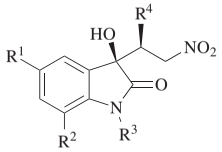
| R | Time (h) | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | 12 | (93) | 4:1 | 94.0:6.0 |
| 2-$C_4H_3S$ | 36 | (80) | 5:1 | 93.5:6.5 |
| Ph | 6 | (81) | 5:1 | 97.0:3.0 |
| 2-$BrC_6H_4$ | 6 | (84) | 7:1 | 97.0:3.0 |
| 3-$BrC_6H_4$ | 8 | (70) | 7:1 | 97.0:3.0 |
| 4-$BrC_6H_4$ | 8 | (87) | 6:1 | 97.0:3.0 |
| 2-$ClC_6H_4$ | 6 | (83) | 9:1 | 98.0:2.0 |
| 3-$ClC_6H_4$ | 6 | (83) | 8:1 | 97.0:3.0 |
| 4-$ClC_6H_4$ | 10 | (82) | 8:1 | 97.0:3.0 |
| 2-$FC_6H_4$ | 8 | (87) | 9:1 | 97.5:2.5 |
| 4-$FC_6H_4$ | 8 | (74) | 8:1 | 96.5:3.5 |
| 3-$MeOC_6H_4$ | 6 | (64) | 9:1 | 98.0:2.0 |

| R | Time (h) | | dr | er |
|---|---|---|---|---|
| 4-$MeOC_6H_4$ | 8 | (75) | 8:1 | 95.5:4.5 |
| 2,5-$(MeO)_2C_6H_3$ | 24 | (71) | 9:1 | 98.0:2.0 |
| 2-$O_2NC_6H_4$ | 6 | (84) | 10:1 | 98.0:2.0 |
| 3-$O_2NC_6H_4$ | 8 | (79) | 6:1 | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | 8 | (73) | 5:1 | 96.0:4.0 |
| 2-$MeC_6H_4$ | 6 | (65) | 7:1 | 95.0:5.0 |
| 4-$MeC_6H_4$ | 6 | (83) | 8:1 | 96.0:4.0 |
| 4-$NCC_6H_4$ | 6 | (71) | 7:1 | 97.0:3.0 |
| 3,4-$Me_2C_6H_3$ | 6 | (83) | 9:1 | 96.0:4.0 |
| PhCH=CH | 12 | (66) | 1:4 | 98.5:1.5 |
| 1-Np | 12 | (64) | 3:1 | 96.0:4.0 |
| 2-Np | 36 | (82) | 6:1 | 91.5:8.5 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_6$  |  | *ent*-**235a** (5 mol %), dioxane, 3 Å MS, rt, 18 h |  (83) dr >19:1 er 91.5:8.5 | 811 |
| $C_{7-11}$  |  | **431** (50 mol %), LDA (3 eq), THF, –78° to rt, 18 h |  | 815 |

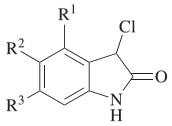
| $R^1$ | $R^2$ | | dr | er | Config. |
|---|---|---|---|---|---|
| Ph | Ph | (98) | 68:32 | 99.0:1.0 | (*R*,*R*) |
| Ph | 4-$ClC_6H_4$ | (81) | 96:4 | 100.0:0.0 | (*R*,*R*) |
| Ph | 4-$MeOC_6H_4$ | (99) | 88:12 | 91.0:9.0 | (*R*,*R*) |
| 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | (69) | 100:0 | 100.0:0.0 | (*R*,*R*) |
| 1-Np | 4-$ClC_6H_4$ | (74) | 100:0 | 100.0:0.0 | (*S*,*R*) or (*R*,*S*) |

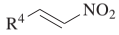
| | | | | | |
|---|---|---|---|---|---|
| $C_{8-10}$  |  | **17** (20 mol %), $CH_2Cl_2$, rt, 16 h |  | | 816 |

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | | dr | er (*syn*) |
|---|---|---|---|---|---|---|
| H | H | H | Ph | (50) | 2:1 | 83.0:17.0 |
| H | H | Me | Ph | (73) | 3:1 | 95.0:5.0 |
| H | H | Bn | 2-$C_4H_3O$ | (94) | 3.6:1 | 98.0:2.0 |
| H | H | Bn | 2-$C_4H_3S$ | (89) | 2.7:1 | 97.5:2.5 |
| H | H | Bn | Ph | (91) | 4:1 | 97.0:3.0 |

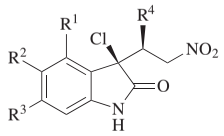
| | | | | | | |
|---|---|---|---|---|---|---|
| H | H | Bn | 2-$BrC_6H_4$ | (60) | 4:1 | 92.5:7.5 |
| H | H | Bn | 4-$ClC_6H_4$ | (80) | 3.2:1 | 92.0:8.0 |
| H | H | Bn | 4-$MeOC_6H_4$ | (98) | 4:1 | 96.5:3.5 |
| H | H | Bn | 4-$MeC_6H_4$ | (96) | 4:1 | 97.0:3.0 |
| H | H | Bn | 4-$CF_3C_6H_4$ | (78) | 3.2:1 | 95.0:5.0 |
| H | Br | Bn | Ph | (75) | 2:1 | 86.5:13.5 |
| Br | H | Bn | Ph | (76) | 2.8:1 | 94.0:6.0 |
| Me | H | Bn | Ph | (78) | 3.3:1 | 97.5:2.5 |
| Me | Me | Bn | Ph | (78) | 2.8:1 | 93.5:6.5 |

$C_{8-9}$





**444** (5 mol %), $CH_2Cl_2$



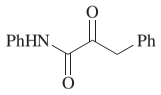
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|---|
| H | H | H | 2-$C_4H_3O$ | 4 | 2 | (95) | 5.6:1 | 94.0:6.0 |
| H | H | H | 2-$C_4H_3S$ | 4 | 3 | (96) | 10:1 | 95.0:5.0 |
| H | H | H | 3-$C_5H_4N$ | 4 | 7 | (91) | 9.1:1 | 95.0:5.0 |
| H | H | H | Ph | 4 | 15 | (95) | 10:1 | 95.5:4.5 |
| H | H | H | 3-$BrC_6H_4$ | 4 | 5 | (96) | 11:1 | 95.0:5.0 |
| H | H | H | 4-$BrC_6H_4$ | 4 | 24 | (96) | 11:1 | 95.0:5.0 |
| H | H | H | 4-$CF_3OC_6H_4$ | 4 | 5 | (90) | 7.7:1 | 93.0:7.0 |
| H | H | H | 4-$O_2NC_6H_4$ | 4 | 23 | (91) | 6.7:1 | 93.5:6.5 |
| H | H | H | 3-$MeC_6H_4$ | 4 | 24 | (91) | 11:1 | 95.5:4.5 |
| H | H | H | 2-Np | 4 | 18 | (95) | 10:1 | 95.0:5.0 |
| H | H | Cl | Ph | 4 | 2–24 | (97) | 5.1:1 | 95.0:5.0 |
| H | H | Cl | 4-$MeOC_6H_4$ | 4 | 2–24 | (99) | 6.3:1 | 95.0:5.0 |
| H | Br | H | 2-$C_4H_3S$ | rt | 2–24 | (97) | 7.1:1 | 93.5:6.5 |
| H | Br | H | Ph | rt | 2–24 | (99) | 9.1:1 | 96.0:4.0 |
| Cl | H | H | Ph | 4 | 2–24 | (99) | 8.3:1 | 88.0:12.0 |
| H | Me | H | 3-$C_5H_4N$ | 4 | 2–24 | (90) | 8.3:1 | 95.5:4.5 |
| H | Me | H | Ph | 4 | 2–24 | (94) | 10:1 | 96.0:4.0 |

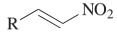
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

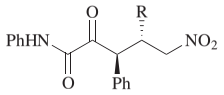
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_9$





*ent*-**164b** (10 mol %), EtOAc, –35°

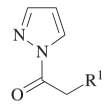


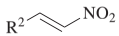
*syn*/*anti* >20:1

810

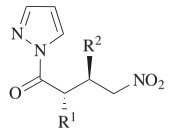
| R | Time (h) | | er |
|---|---|---|---|
| Ph | 16 | (94) | 95.5:4.5 |
| 4-$FC_6H_4$ | 16 | (82) | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 16 | (93) | 92.5:7.5 |
| 4-$O_2NC_6H_4$ | 16 | (93) | 95.0:5.0 |
| $BnCH_2$ | 40 | (92) | 92.5:7.5 |

$C_{9–12}$





**69a** (10 mol %), $CHCl_3$

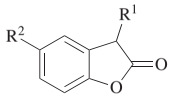


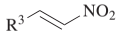
818

| $R^1$ | $R^2$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| 2-$C_4H_3S$ | Ph | –20 | 24 | (94) | >20:1 | 89.0:11.0 |
| Ph | Ph | rt | 72 | (62) | 20:1 | 93.5:6.5 |
| 4-$BrC_6H_4$ | Ph | –20 | 48 | (83) | 20:1 | 97.0:3.0 |
| 4-$ClC_6H_4$ | Ph | –20 | 48 | (81) | 18:1 | 96.0:4.0 |
| 4-$FC_6H_4$ | Ph | –20 | 48 | (78) | >20:1 | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | 3-$C_4H_3O$ | –20 | 18 | (92) | >20:1 | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | 3-$C_4H_3S$ | –20 | 12 | (89) | 10:1 | 96.5:3.5 |
| 4-$O_2NC_6H_4$ | Ph | –20 | 12 | (96) | >20:1 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 3-$BrC_6H_4$ | –-20 | 12 | (89) | >20:1 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 4-$BrC_6H_4$ | –20 | 12 | (90) | 18:1 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 3,4-$Cl_2C_6H_3$ | –20 | 12 | (89) | >20:1 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | 4-$MeOC_6H_4$ | –20 | 12 | (96) | >20:1 | 97.0:3.0 |

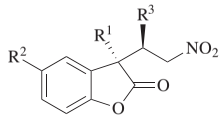
| | | | | | | |
|---|---|---|---|---|---|---|
| 4-$O_2NC_6H_4$ | 4-$O_2NC_6H_4$ | –20 | 12 | (96) | >20:1 | 97.0:3.0 |
| 4-$O_2NC_6H_4$ | *n*-$C_7H_{15}$ | –20 | 24 | (85) | >20:1 | 94.0:6.0 |
| 4-$O_2NC_6H_4$ | 4-$MeC_6H_4$ | –20 | 18 | (91) | >20:1 | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | 2-$CF_3C_6H_4$ | –20 | 12 | (98) | >20:1 | 98.5:1.5 |
| 4-$MeC_6H_4$ | Ph | rt | 72 | (34) | 16:1 | 94.5:5.5 |
| 4-$CF_3C_6H_4$ | Ph | –20 | 24 | (81) | 20:1 | 98.5:1.5 |

$C_{9–16}$





**252b** (10 mol %),
toluene, 4 Å MS, –60°



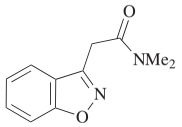
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| Me | H | *i*-Bu | 96 | (88) | 15:1 | 91.0:9.0 |
| Me | H | Ph | 48 | (96) | 4:1 | 83.0:17.0 |
| Me | H | 2-$BrC_6H_4$ | 48 | (98) | 19:1 | 90.0:10.0 |
| Me | H | 2-$ClC_6H_4$ | 48 | (95) | 19:1 | 93.0:7.0 |
| Me | H | 4-$ClC_6H_4$ | 48 | (87) | 2:1 | 76.0:24.0 |
| Me | H | 2,6-$Cl_2C_6H_3$ | 72 | (87) | 11:1 | 95.5:4.5 |
| Me | H | 3,4-$Cl_2C_6H_3$ | 48 | (87) | 3:1 | — |
| Me | H | 6-Cl-2-$FC_6H_3$ | 72 | (85) | 4:1 | 91.0:9.0 |
| Me | H | 4-$FC_6H_4$ | 48 | (90) | 3:1 | 82.0:18.0 |
| Me | H | 4-$MeOC_6H_4$ | 72 | (92) | 3:1 | 82.5:17.5 |
| Me | H | 3-$O_2NC_6H_4$ | 72 | (91) | 1:1 | 87.5:12.5 |
| Me | H | $BnCH_2$ | 96 | (90) | 19:1 | 92.5:7.5 |
| Me | H | 2-Np | 48 | (85) | 2:1 | 88.5:11.5 |
| Me | H | 4-$PhC_6H_4$ | 60 | (90) | 3:1 | 79.0:21.0 |
| Ph | H | Ph | 48 | (95) | 4:1 | 77.5:22.5 |
| Ph | Br | Ph | 24 | (98) | 6:1 | 88.5:11.5 |
| Ph | Cl | Ph | 24 | (87) | 5:1 | 86.5:13.5 |
| 4-$ClC_6H_4$ | H | Ph | 48 | (90) | 4:1 | 76.5:23.5 |
| Bn | H | Ph | 72 | (91) | 1:1 | 92.0:8.0 |
| Ph | Et | Ph | 48 | (91) | 5:1 | 79.0:21.0 |

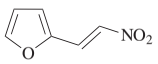
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

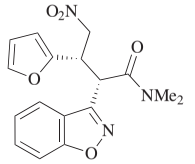
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_9$



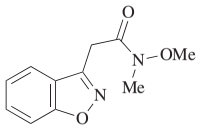


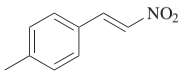
*ent*-**235a** (5 mol %), dioxane, 3 Å MS, rt, 18 h



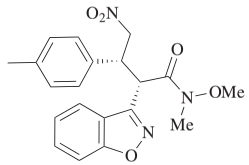
(73) dr 2:1
er (major) 94.0:6.0
er (minor) 83.0:17.0

811



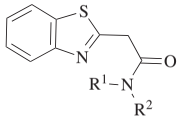


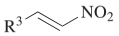
*ent*-**235a** (5 mol %), dioxane, 3 Å MS, rt, 18 h



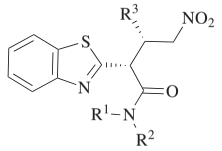
(43) dr 1:1
er 90.5:9.5
er 94.5:5.5

811





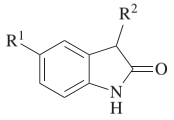
*ent*-**235a** (5 mol %), dioxane, 3 Å MS, rt, 18 h

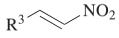


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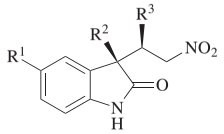
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| Me | Me | 2-$C_4H_3O$ | (95) | >19:1 | >99.5:0.5 |
| Me | Me | 4-$BrC_6H_4$ | (84) | >19:1 | 94.5:5.5 |
| Me | Me | 4-$FC_6H_4$ | (78) | >19:1 | 97.5:2.5 |
| Me | Me | 4-$MeOC_6H_4$ | (74) | >19:1 | 93.0:7.0 |
| Me | Me | 2-$MeC_6H_4$ | (64) | 6:1 | 83.0:17.0 |
| Me | Me | 4-$MeC_6H_4$ | (79) | >19:1 | 97.5:2.5 |
| Me | MeO | 4-$MeC_6H_4$ | (85) | >19:1 | 98.0:2.0 |
| $-(CH_2)_2O(CH_2)_2-$ | | 4-$MeC_6H_4$ | (87) | >19:1 | 97.5:2.5 |

$C_{9–18}$





**436** (*x* mol %),
$Et_2O$, 5 Å MS



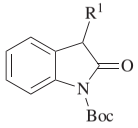
| $R^1$ | $R^2$ | $R^3$ | *x* | Temp (°) | | dr | er |
|---|---|---|---|---|---|---|---|
| Br | Me | 2-$C_4H_3S$ | 20 | rt | (86) | 12:1 | 97.5:2.5 |
| Br | Me | 4-$BrC_6H_4$ | 20 | rt | (77) | 9:1 | 97.5:2.5 |
| H | $Me_2C{=}CHCH_2$ | 4-$BrC_6H_4$ | 20 | rt | (78) | 8:1 | 97.0:3.0 |
| Br | $Me_2CH(CH_2)_2$ | 4-$BrC_6H_4$ | 20 | rt | (89) | 8:1 | 97.5:2.5 |
| H | Ph | *n*-Pr | 10 | 0 | (76) | 6:1 | 99.0:1.0 |
| H | Ph | *i*-Bu | 10 | 0 | (84) | 6:1 | 99.0:1.0 |
| H | Ph | 4-$BrC_6H_4$ | 10 | –20 | (89) | 13:1 | 99.5:0.5 |
| H | Ph | 2,4-$Cl_2C_6H_3$ | 10 | –20 | (96) | 21:1 | 99.0:1.0 |
| H | Ph | 4-$MeOC_6H_4$ | 10 | –20 | (85) | 7:1 | 98.5:1.5 |
| H | Ph | 4-$CF_3C_6H_4$ | 10 | –20 | (92) | 13:1 | 99.0:1.0 |
| H | 4-$ClC_6H_4$ | Ph | 10 | –20 | (84) | 18:1 | 98.5:1.5 |
| Br | Ph | Ph | 10 | –20 | (78) | 7:1 | 98.5:1.5 |
| Cl | Ph | Ph | 10 | –20 | (92) | 8:1 | 98.5:1.5 |
| F | Ph | 2-$C_4H_3O$ | 10 | –20 | (84) | 3:1 | 98.0:2.0 |
| F | Ph | Ph | 10 | –20 | (84) | 10:1 | 98.0:2.0 |
| F | Ph | 4-$CF_3C_6H_4$ | 10 | –20 | (85) | 9:1 | 99.0:1.0 |
| MeO | Ph | Ph | 10 | –20 | (83) | 11:1 | 99.0:1.0 |
| H | 2-$ClC_6H_4CH_2$ | 4-$BrC_6H_4$ | 20 | rt | (95) | 7:1 | 98.0:2.0 |
| H | 4-$ClC_6H_4CH_2$ | 4-$BrC_6H_4$ | 20 | rt | (95) | 8:1 | 95.5:4.5 |
| H | 2-Np | Ph | 10 | –20 | (77) | 11:1 | 99.5:0.5 |

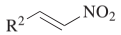
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

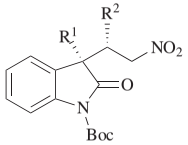
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{9–16}$





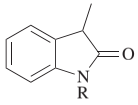
**437** (10 mol %), $CHCl_3$, –20°, 24 h

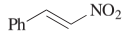


821

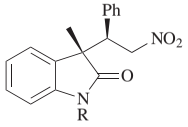
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| Me | Ph | (96) | 10:1 | 99.5:0.5 |
| Et | Ph | (95) | 5:1 | 98.0:2.0 |
| allyl | $(MeO)_2CH$ | (68) | >20:1 | 96.5:3.5 |
| allyl | 2-$C_4H_3O$ | (97) | 6:1 | 99.5:0.5 |
| allyl | Ph | (89) | 6:1 | 97.0:3.0 |
| allyl | 3-$BrC_6H_4$ | (91) | 9:1 | 97.5:2.5 |
| allyl | 4-$BrC_6H_4$ | (92) | 6:1 | 95.5:4.5 |
| allyl | 3,4-$Cl_2C_6H_3$ | (72) | 3:1 | 94.5:5.5 |
| allyl | 4-$HOC_6H_4$ | (92) | 7:1 | 96.0:4.0 |
| allyl | 4-$MeOC_6H_4$ | (91) | 5:1 | 95.0:5.0 |
| allyl | *n*-$C_7H_{15}$ | (95) | >20:1 | 97.0:3.0 |
| 4-$BrC_6H_4CH_2$ | Ph | (92) | 6:1 | 95.5:4.5 |
| PhCH=CH | Ph | (90) | 11:1 | 96.0:4.0 |

$C_9$

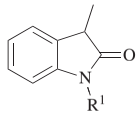


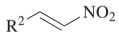


**439** (10 mol %), toluene, 4°, 12 h

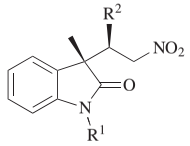


| R | | dr | er | |
|---|---|---|---|---|
| Me | (93) | 3:1 | 77.0:23.0 | 822 |
| Boc | (94) | 9:1 | 87.0:13.0 | |





**439** (10 mol %),
$CH_2Cl_2$, –40°



822

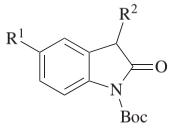
| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Me | Ph | 96 | (65) | 3:1 | 84.0:16.0 |
| Boc | Ph | 72 | (96) | 19:1 | 94.5:5.5 |
| Ph | *i*-Pr | 48 | (96) | 3:1 | 99.0:1.0 |
| Ph | Ph | 48 | (96) | 4:1 | 96.5:3.5 |
| Ph | 2-$BrC_6H_4$ | 48 | (98) | 2:1 | 98.0:2.0 |
| Ph | 2-$ClC_6H_4$ | 48 | (95) | 3:1 | 97.5:2.5 |
| Ph | 4-$ClC_6H_4$ | 48 | (95) | 3:1 | 96.0:4.0 |
| Ph | 4-$MeOC_6H_4$ | 72 | (92) | 4:1 | 97.5:2.5 |
| Ph | 2,4-$(MeO)_2C_6H_3$ | 72 | (93) | 3:1 | 98.0:2.0 |
| Ph | 3-$O_2NC_6H_4$ | 72 | (94) | 3:1 | 90.0:10.0 |
| Ph | 4-$O_2NC_6H_4$ | 72 | (92) | 2:1 | 89.0:11.0 |
| Ph | 3,4-$(OCHO)C_6H_3$ | 60 | (91) | 5:1 | 97.5:2.5 |
| Ph | 4-$MeC_6H_4$ | 48 | (99) | 5:1 | 97.5:2.5 |
| Ph | $BnCH_2$ | 54 | (95) | 3:1 | 99.0:1.0 |
| Ph | 2-Np | 48 | (97) | 4:1 | 97.0:3.0 |
| Ph | 4-$PhC_6H_4$ | 60 | (90) | 4:1 | 97.0:3.0 |

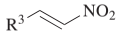
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

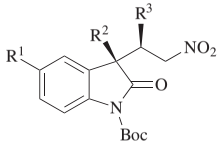
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{9–16}$





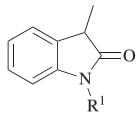
**441** (10 mol %), $CHCl_3/CH_2Cl_2$ (4:1), –60°, 24 h

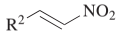


812

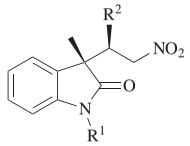
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| H | Me | Ph | (88) | >99:1 | 91.5:8.5 |
| H | Ph | Ph | (96) | >99:1 | 91.0:.9.0 |
| MeO | Ph | 4-$MeC_6H_4$ | (97) | >99:1 | >99.5:0.5 |
| H | Bn | 2-$C_4H_3O$ | (95) | 98:2 | 97.0:3.0 |
| H | Bn | Ph | (95) | >99:1 | 98.5:1.5 |
| H | Bn | 4-$FC_6H_4$ | (91) | >98:2 | 98.5:1.5 |
| H | Bn | 4-$MeC_6H_4$ | (92) | >98:2 | 95.5:4.5 |
| H | 3-$FC_6H_4CH_2$ | Ph | (98) | 98:2 | 96.0:4.0 |
| H | 4-$MeOC_6H_4CH_2$ | Ph | (98) | 99:1 | 96.0:4.0 |
| H | 3,4-$(OCH_2O)C_6H_4CH_2$ | Ph | (97) | 99:1 | 95.5:4.5 |
| Me | Ph | 2-$C_4H_3O$ | (98) | 98:2 | 92.0:8.0 |
| Me | Ph | Ph | (98) | >99:1 | 91.5:8.5 |
| H | 4-$MeC_6H_4CH_2$ | Ph | (98) | 99:1 | 96.0:4.0 |

$C_9$





**448** (2 mol %), $CHCl_3$



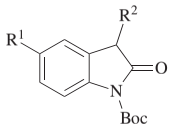
| $R^1$ | $R^2$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| H | Ph | rt | 36 | (73) | 61:39 | 92.5:7.5 |
| H | Ph | 0 | 120 | (45) | 60:40 | 94.5:5.5 |
| $EtO_2C$ | Ph | –20 | 12 | (90) | 96:4 | 95.0:5.0 |
| Boc | Et | 0 | 72 | (33) | 97:3 | 94.0:6.0 |
| Boc | 2-$C_4H_3O$ | –20 | 12 | (83) | 90:10 | 88.0:12.0 |
| Boc | 2-$C_4H_3S$ | –20 | 12 | (86) | 84:16 | 85.0:15.0 |
| Boc | Ph | –20 | 12 | (97) | 98:2 | 93.0:7.0 |
| Boc | 4-$BrC_6H_4$ | -–20 | 12 | (92) | 88:12 | 90.5:9.5 |
| Boc | 2-$ClC_6H_4$ | –20 | 12 | (90) | 74:26 | 92.5:7.5 |
| Boc | 4-$ClC_6H_4$ | –20 | 12 | (94) | 87:13 | 90.0:10.0 |
| Boc | 4-$FC_6H_4$ | –20 | 12 | (94) | 79:21 | 82.0:18.0 |
| Boc | 4-$MeOC_6H_4$ | –20 | 12 | (95) | 97:3 | 93.5:6.5 |
| Boc | 3,4-$(MeO)_2C_6H_3$ | –20 | 12 | (84) | 97:3 | 89.5:10.5 |
| Boc | 4-$MeC_6H_4$ | –20 | 12 | (95) | 98:2 | 94.0:6.0 |
| Boc | $BnCH_2$ | –20 | 12 | (79) | 94:6 | 88.0:12.0 |
| Ph | Ph | rt | 24 | (91) | 73:27 | 77.0:23.0 |

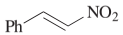
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

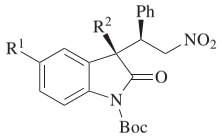
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{9–15}$





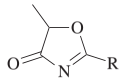
**448** (2 mol %), $CHCl_3$, –20°, 12 h

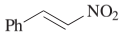


823

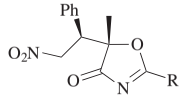
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| F | Me | (96) | 90:10 | 89.5:10.5 |
| MeO | Me | (96) | 88:12 | 92.0:8.0 |
| H | Et | (97) | 79:21 | 93.5:6.5 |
| H | Ph | (96) | 87:13 | 72.0:28.0 |
| H | Bn | (95) | 90:10 | 93.0:7.0 |

$C_{10–14}$





**434b** (5 mol %), $Et_2Zn$ (10 mol %) 0.19 M in THF/MeCN, rt, 16 h

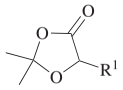


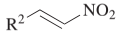
(>95)

824

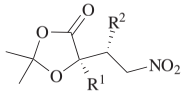
| R | dr | er |
|---|---|---|
| Ph | 15.6:1 | 94.0:6.0 |
| 4-$BrC_6H_4$ | 11.9:1 | 93.0:7.0 |
| 4-$MeOC_6H_4$ | 11.9:1 | 92.0:8.0 |
| 3,5-$(MeO)_2C_6H_3$ | 3.9:1 | 94.0:6.0 |
| 3-$MeC_6H_4$ | 18.2:1 | 95.0:5.0 |
| 4-$MeC_6H_4$ | 12.0:1 | 92.5:7.5 |
| 4-*t*-$BuC_6H_4$ | 9.5:1 | 92.0:8.0 |
| 1-Np | 14.0:1 | 95.0:5.0 |

$C_{11–12}$



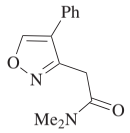
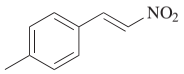
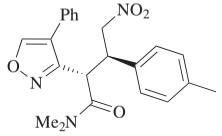
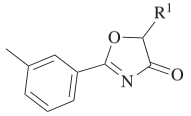
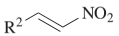
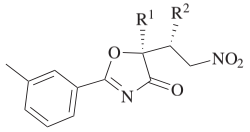


**230a** (10 mol %),
solvent, 0°



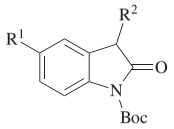
| $R^1$ | $R^2$ | Solvent | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| Ph | 2-$C_4H_3O$ | toluene | 24 | (69) | >96.5:3.5 | 80.0:20.0 |
| Ph | 2-$C_4H_3S$ | toluene | 48 | (88) | >99:1 | 83.0:17.0 |
| Ph | Ph | toluene | 48 | (>98) | >99:1 | 88.0:12.0 |
| Ph | 2-$BrC_6H_4$ | toluene | 336 | (58) | >99:1 | 94.5:5.5 |
| Ph | 2-$BrC_6H_4$ | $CH_2Cl_2$ | 288 | (72) | >99:1 | 89.5:10.5 |
| Ph | 3-$BrC_6H_4$ | toluene | 30 | (71) | >99:1 | 84.0:16.0 |
| Ph | 4-$BrC_6H_4$ | toluene | 72 | (59) | >99:1 | 86.5:13.5 |
| Ph | 4-$BrC_6H_4$ | $CH_2Cl_2$ | 48 | (85) | >98.5:1.5 | 84.0:16.0 |
| Ph | 2-$ClC_6H_4$ | toluene | 264 | (52) | >98.5:1.5 | 91.0:9.0 |
| Ph | 2-$MeOC_6H_4$ | toluene | 72 | (65) | >98.5:1.5 | 87.0:13.0 |
| Ph | 3-$MeOC_6H_4$ | toluene | 24 | (50) | >98.5:1.5 | 85.5:14.5 |
| Ph | 3-$MeOC_6H_4$ | $CH_2Cl_2$ | 48 | (70) | >99:1 | 84.0:16.0 |
| Ph | 4-$MeOC_6H_4$ | toluene | 72 | (81) | >98.5:1.5 | 86.5:13.5 |
| Ph | 3-$MeC_6H_4$ | toluene | 40 | (70) | >98.5:1.5 | 84.5:15.5 |
| Ph | 4-$MeC_6H_4$ | toluene | 40 | (67) | >98.5:1.5 | 85.0:15.0 |
| Ph | 2-Np | toluene | 72 | (62) | >98.5:1.5 | 87.5:12.5 |
| 4-$BrC_6H_4$ | Ph | toluene | 24 | (92) | >99:1 | 80.0:20.0 |
| 4-$MeOC_6H_4$ | Ph | toluene | 48 | (77) | >99:1 | 85.0:15.0 |
| 4-$CF_3C_6H_4$ | Ph | toluene | 2 | (71) | >99:1 | 80.0:20.0 |

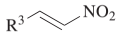
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{11}$  |  | *ent*-**235a** (5 mol %), dioxane, 3 Å MS, rt, 18 h |  (49) dr 1:1 er (major) 99.5:0.5 er (minor) 99.5:0.5 | 811 |
| $C_{11-17}$  |  | **434b** (5 mol %), $Et_2Zn$ (10 mol %), 0.08 M in THF/MeCN, rt, 16 h |  | 824 |

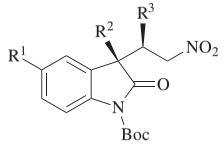
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| Me | TIPSC≡C | (71) | 1.5:1 | 93.0:7.0 |
| Me | 2-$C_4H_3O$ | (95) | 8.4:1 | 93.5:6.5 |
| Me | 3-$C_4H_3O$ | (89) | 12.5:1 | 97.5:2.5 |
| Me | 2-$C_4H_3S$ | (88) | 9.1:1 | 96.0:4.0 |
| Me | 3-$C_4H_3S$ | (93) | 10.3:1 | 95.5:4.5 |
| Me | $Me_2CHCH$=CH | (87) | >19:1 | 96.0:4.0 |
| Me | Ph | (94) | >19:1 | 96.5:3.5 |
| Me | 3-$BrC_6H_4$ | (97) | 11.1:1 | 94.0:6.0 |
| Me | 3,5-$Br_2C_6H_3$ | (83) | 8:1 | 92.5:7.5 |
| Me | 4-$ClC_6H_4$ | (93) | 6.7:1 | 93.0:7.0 |
| Me | 2-$FC_6H_4$ | (72) | 5.4:1 | 85.0:15.0 |
| Me | 4-$MeOC_6H_4$ | (97) | 12.8:1 | 96.5:3.5 |
| Me | 4-$O_2NC_6H_4$ | (76) | 3.1:1 | 82.0:18.0 |
| Me | 3,4-$(OCH_2O)C_6H_3$ | (91) | 16.9:1 | 94.0:6.0 |
| Me | 2-$MeC_6H_4$ | (95) | 15.5:1 | 72.0:28.0 |
| Me | 4-$MeC_6H_4$ | (97) | >19:1 | 96.0:4.0 |
| Me | 4-$NCC_6H_4$ | (89) | 3.4:1 | 87.5:12.5 |
| Me | PhCH=CH | (97) | 12.6:1 | 96.0:4.0 |
| Me | *N*-Boc-3-indolyl | (96) | 11.2:1 | 92.0:8.0 |
| Me | 1-Np | (94) | 9.4:1 | 78.0:22.0 |
| Me | 2-Np | (91) | 16.8:1 | 96.0:4.0 |
| Me | Fe($C_{10}H_9$) | (96) | >19:1 | 99.0:1.0 |
| Et | Ph | (>99) | >19:1 | 96.0:4.0 |
| $MeS(CH_2)_2$ | Ph | (>99) | >19:1 | 96.0:4.0 |
| allyl | Ph | (>99) | >19:1 | 96.5:3.5 |
| allyl | PhCH=CH | (96) | >19:1 | 96.5:3.5 |
| TIPSC≡$CCH_2$ | Ph | (89) | >19:1 | 95.0:5.0 |
| *i*-Bu | Ph | (>99) | >19:1 | 95.0:5.0 |
| Bn | Ph | (95) | >19:1 | 97.0:3.0 |

$C_{11–12}$





**231** (10 mol %),
$CH_2Cl_2$, –20°, 24–36 h



826

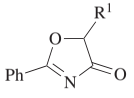
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| H | allyl | Ph | (90) | >30:1 | >99.5:0.5 |
| H | allyl | 4-$BrC_6H_4$ | (89) | >30:1 | 97.0:3.0 |
| H | allyl | 4-$MeOC_6H_4$ | (96) | >30:1 | 97.0:3.0 |
| H | allyl | *n*-$C_7H_{15}$ | (92) | 20:1 | 99.0:1.0 |
| H | allyl | PhCH=CH | (90) | 12:1 | 96.5:3.5 |
| MeO | allyl | Ph | (85) | >20:1 | >99.5:0.5 |
| H | $CH_2$=$CHCH_2CH_2$ | Ph | (85) | 20:1 | >99.5:0.5 |
| H | $CH_2$=$CHCH_2CH_2$ | 4-$MeOC_6H_4$ | (80) | 8:1 | >99.5:0.5 |
| H | $CH_2$=$CHCH_2CH_2$ | 4-$CF_3OC_6H_4$ | (90) | 14:1 | 99.5:0.5 |
| H | $CH_2$=$CHCH_2CH_2$ | 4-$CF_3C_6H_4$ | (90) | >30:1 | >99.5:0.5 |
| H | $CH_2$=$CHCH_2CH_2$ | PhCH=CH | (86) | 10:1 | >99.5:0.5 |

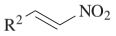
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
A. NITROALKENES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

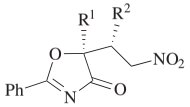
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{13–16}$





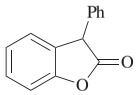
**69b** (5 mol %), toluene, –24°

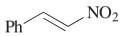


| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| *t*-Bu | Me | (88) | 95:5 | 88.0:12.0 |
| *t*-Bu | $MeS(CH_2)_2$ | (65) | >95:5 | 88.5:11.5 |
| *t*-Bu | $2\text{-}C_4H_3S$ | (91) | 91:9 | 85.0:15.0 |
| *t*-Bu | Ph | (65) | >95:5 | 91.5:8.5 |
| *t*-Bu | $2\text{-}ClC_6H_4$ | (80) | 92:8 | 82.0:18.0 |
| *t*-Bu | $4\text{-}MeOC_6H_4$ | (90) | 93:7 | 86.0:14.0 |
| *t*-Bu | $4\text{-}O_2NC_6H_4$ | (65) | 81:19 | 86.0:14.0 |
| *t*-Bu | 2-Np | (54) | >95:5 | 88.0:12.0 |
| $4\text{-}MeC_6H_4$ | Ph | (98) | 91:9 | 87.0:13.0 |

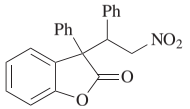
827

$C_{14}$



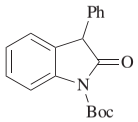


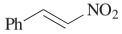
**439** (10 mol %), toluene, 0°, 24 h



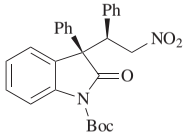
(94) dr 1:1
er 51.0:49.0

828





**439** (10 mol %), solvent



| Solvent | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|
| toluene | 4 | 2 | (99) | 1:1 | 50.0:50.0 |
| $CH_2Cl_2$ | –40 | 8 | (94) | 3:1 | 76.5:23.5 |

822

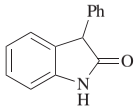
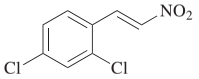
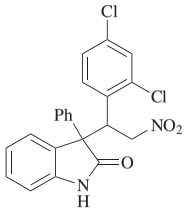
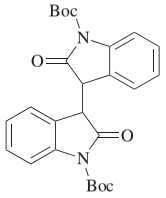
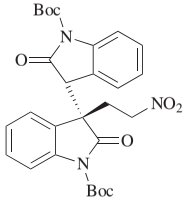
| | | | | | | |
|---|---|---|---|---|---|---|
|  |  | **445** (10 mol %), $CH_2Cl_2$, 0°, 24 h |  | (95) dr 2.2:1<br>er 92.5:7.5 | 829 |
| $C_{16}$  |  | **438** (4.3 mol %), $Mn(4\text{-}FC_6H_4CO_2)_2$ (4.3 mol %), toluene, 5 Å MS, 50°, 5 h |  | (90) er 98.0:2.0 | 830 |

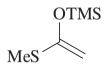
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)

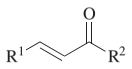
B. ENONES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

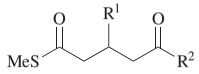
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_2$



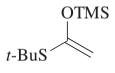



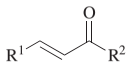

**457** (10 mol %), $Sn(OTf)_2$ (10 mol %), $CH_2Cl_2$, –78°



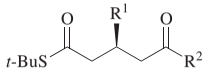

831

| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| 2-$C_4H_3O$ | Me | (82) | 80.0:20.0 |
| Ph | Me | (80) | 85.0:15.0 |
| Ph | Ph | (79) | 70.0:30.0 |



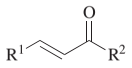




**460a** (*x* mol %), 2,6-(*i*-Pr)$_2$$C_6H_3OH$ (3 eq, syringe pump), $CH_2Cl_2$, –78°, 4 h

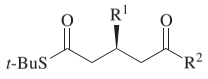



832

| $R^1$ | $R^2$ | *x* | | er |
|---|---|---|---|---|
| Me | Me | 40 | (60) | 92.0:8.0 |
| Ph | Me | 20 | (88) | 89.5:10.5 |
| 3-$ClC_6H_4$ | Me | 20 | (69) | 84.5:15.5 |
| 4-$ClC_6H_4$ | Me | 20 | (94) | 92.5:7.5 |
| 4-$MeC_6H_4$ | Me | 20 | (57) | 77.0:23.0 |
| Ph | Et | 40 | (93) | 80.5:19.5 |
| Ph | *i*-Pr | 40 | (71) | 90.5:9.5 |
| Ph | *t*-Bu | 40 | (72) | 58.0:42.0 |



**460a** (*x* mol %),
2,6-$Me_2C_6H_3OH$ (1–3 eq),
*t*-BuOMe (0–2 eq),
$CH_2Cl_2$, –78°



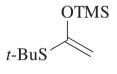
| $R^1$ | $R^2$ | *x* | | er |
|---|---|---|---|---|
| Me | Me | 10 | (28) | 93.0:7.0 |
| 2-$C_4H_3O$ | Me | 10 | (48) | 90.5:9.5 |
| *n*-$C_5H_{11}$ | Me | 10 | (34) | 82.0:18.0 |
| Ph | Me | 10 | (90) | 90.0:10.0 |
| 3-$ClC_6H_4$ | Me | 10 | (82) | 93.0:7.0 |
| 4-$ClC_6H_4$ | Me | 10 | (83) | 93.0:7.0 |
| 4-$ClC_6H_4$ | Me | 20 | (94) | 92.5:7.5 |
| 3-$FC_6H_4$ | Me | 10 | (75) | 87.0:13.0 |
| 4-$FC_6H_4$ | Me | 10 | (78) | 93.0:7.0 |
| 4-$MeOC_6H_4$ | Me | 10 | (50) | 80.0:20.0 |
| Ph | Et | 10 | (53) | 80.5:19.5 |
| 4-$MeC_6H_4$ | Me | 10 | (78) | 87.0:13.0 |
| 3-$CF_3C_6H_4$ | Me | 10 | (71) | 95.0:5.0 |
| 4-$CF_3C_6H_4$ | Me | 10 | (77) | 95.0:5.0 |
| Ph | *i*-Pr | 10 | (74) | 83.0:17.0 |
| Ph | *i*-Pr | 40 | (71) | 90.5:9.5 |
| Ph | *t*-Bu | 40 | (72) | 58.0:42.0 |
| 1-Np | Me | 10 | (90) | 70.5:29.5 |
| 2-Np | Me | 10 | (76) | 90.5:9.5 |
| Ph | Ph | 40 | (90) | 57.0:43.0 |

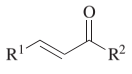
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

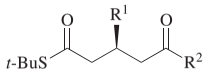
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_2$



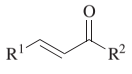




**460b** (*x* mol %), 2,6-$Me_2C_6H_3OH$ (1 eq), *t*-BuOMe (1–2 eq), $CH_2Cl_2$, –78°

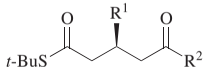



| $R^1$ | $R^2$ | *x* | | er |
|---|---|---|---|---|
| Me | Me | 10 | (75) | 94.5:5.5 |
| 2-$C_4H_3O$ | Me | 10 | (44) | 87.5:12.5 |
| Ph | Me | 10 | (88) | 94.5:5.5 |
| 3-$ClC_6H_4$ | Me | 10 | (80) | 91.5:8.5 |
| 4-$ClC_6H_4$ | Me | 10 | (91) | 92.5:7.5 |
| 4-$ClC_6H_4$ | Me | 20 | (86) | 94.5:5.5 |
| 3-$FC_6H_4$ | Me | 10 | (67) | 86.5:13.5 |
| 4-$FC_6H_4$ | Me | 10 | (76) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | Me | 10 | (78) | 92.5:7.5 |
| Ph | Et | 10 | (63) | 79.5:20.5 |
| 4-$MeC_6H_4$ | Me | 10 | (75) | 93.0:7.0 |
| 4-$MeC_6H_4$ | Me | 20 | (74) | 94.5:5.5 |
| 3-$CF_3C_6H_4$ | Me | 10 | (71) | 94.5:5.5 |
| 4-$CF_3C_6H_4$ | Me | 10 | (70) | 90.0:10.0 |
| 2-Np | Me | 10 | (59) | 87.5:12.5 |
| Ph | *i*-Pr | 10 | (52) | 86.0:14.0 |

833

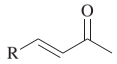



**460b** (10 mol %), 2,6-*i*-$Pr_2C_6H_3OH$ (1 eq, syringe pump), *t*-BuOMe (1 eq), $CH_2Cl_2$, –78°, 12 h

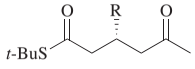



| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | Et | (79) | 97.0:3.0 |
| Ph | Et | (85) | 92.0:8.0 |
| Ph | *i*-Pr | (64) | 94.0:6.0 |
| Ph | *n*-Bu | (82) | 94.0:6.0 |

834

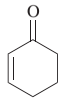


**461** (20 mol %),
2,6-*i*-$Pr_2C_6H_3OH$ (3 eq),
$Ph_3PO$ (0.25 eq),
toluene, –78°, 24 h

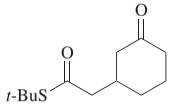


| R | | er |
|---|---|---|
| Me | (94) | 95.0:5.0 |
| Ph | (99) | 92.0:8.0 |

56

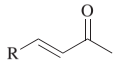


**460a** (40 mol %),
2,6-$Me_2C_6H_3OH$ (3 eq),
$CH_2Cl_2$, –78°

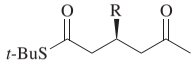


(74) er 54.5:45.5

833



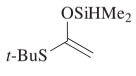
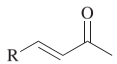
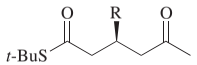
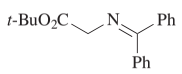
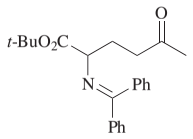
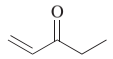
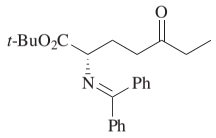
Catalyst (10 mol %),
2,6-$Me_2C_6H_3OH$ (1 eq),
*t*-BuOMe (1 eq),
$CH_2Cl_2$, –78°



833

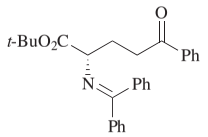
| R | Catalyst | | er |
|---|---|---|---|
| Ph | **460a** | (15) | 94.0:6.0 |
| Ph | **460b** | (20) | 97.0:3.0 |
| 3-$ClC_6H_4$ | **460a** | (7) | 97.5:2.5 |
| 3-$ClC_6H_4$ | **460b** | (12) | 93.0:7.0 |
| 4-$ClC_6H_4$ | **460a** | (7) | 98.0:2.0 |
| 4-$ClC_6H_4$ | **460b** | (20) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | **460a** | (3) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | **460b** | (5) | 97.5:2.5 |
| 4-$MeC_6H_4$ | **460a** | (13) | 94.5:5.5 |
| 4-$MeC_6H_4$ | **460b** | (18) | 97.5:2.5 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_2$ | | | | |
|  |  | **460b** (10 mol %), 2,6-*i*-$Pr_2C_6H_3OH$ (1 eq, syringe pump), *t*-BuOMe (1 eq), $CH_2Cl_2$, –78°, 12 h |  | 834 |
| | | | R (75) er<br>Me (75) 99.0:1.0<br>$BnOCH_2$ (60) 95.0:5.0<br>Ph (83) 97.5:2.5<br>4-$ClC_6H_4$ (72) 97.5:2.5<br>4-$FC_6H_4$ (63) 96.5:3.5<br>4-$MeOC_6H_4$ (54) 96.0:4.0<br>4-$MeC_6H_4$ (75) 97.5:2.5<br>3-$CF_3C_6H_4$ (68) 97.5:2.5<br>4-$CF_3C_6H_4$ (81) 96.0:4.0 | |
|  |  | **300** (10 mol %), $Cs_2CO_3$, toluene, 0°, 24 h |  (99) er 52.5:47.5 | 602 |
| |  | **405b** (10 mol %), $CsOH•H_2O$, $CH_2Cl_2$, –78°, 2 h |  (85) er 95.5:4.5 | 206 |

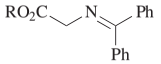


**446** (10 mol %), mesitol (10 mol %), KOH, $CH_2Cl_2$, –78°



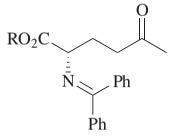
835

| Time (h) | | er |
|---|---|---|
| 1.5 | (63) | 95.5:4.5 |
| 2.5 | (99) | 94.5:5.5 |
| 3 | (49) | 96.0:4.0 |
| 11 | (51) | 93.0:7.0 |





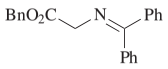
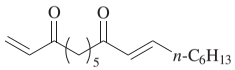
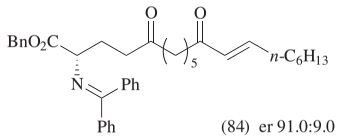
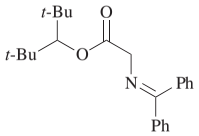
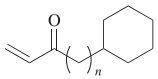
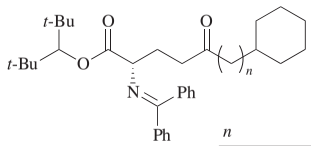
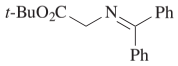
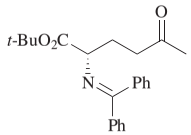
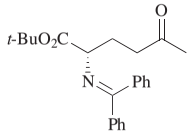
**449** (10 mol %), $Cs_2CO_3$ (50 mol %), $C_6H_5Cl$, –40°

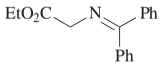


836

| R | Time (h) | | er |
|---|---|---|---|
| *t*-Bu | 48 | (87) | 86.5:13.5 |
| Bn | 36 | (91) | 87.5:12.5 |
| 4-$ClC_6H_4CH_2$ | 24 | (88) | 82.5:17.5 |
| 2-Np | 48 | (89) | 86.0:14.0 |
| $Ph_2CH$ | 48 | (59) | 85.5:14.5 |

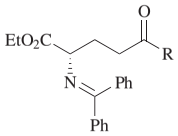
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_2$ | | | | |
|  |  | **449** (10 mol %), $Cs_2CO_3$ (1.5 eq), 3-fluorotoluene, –40°, 66 h |  (84) er 91.0:9.0 | 220 |
|  |  | **450** (1 mol %), CsCl, $K_2CO_3$, $Et_2O$, 0°, 12 h |  | 837 |
| | | | *n* (85) er<br>2 (85) 95.0:5.0<br>3 (88) 97.0:3.0 | |
|  |  | **451a** (10 mol %), $Cs_2CO_3$ (10 eq), $C_6H_5Cl$, –30° |  (79) er 66.5:33.5 | 838 |
| |  | **452** (20 mol %), solvent, 20° |  | 839 |
| | | | Solvent Time (h) (90) er<br>THF 144 (90) 98.0:2.0<br>— 14 (90) 90.0:10.0 | |

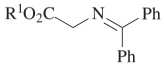




**453** (20 mol %),
*t*-BuOK (0.2 eq),
$CH_2Cl_2$, –78°, 0.25 h

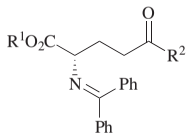


| R | | er | |
|---|---|---|---|
| Me | (80) | 95.0:5.0 | 223 |
| Et | (65) | 98.0:2.0 | |



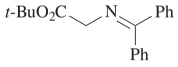


**454** (1 mol %),
$Cs_2CO_3$ (50 mol %),
*i*-$Pr_2O$ , 0°



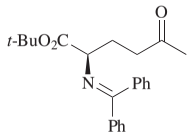
840

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| *t*-Bu | Me | 18 | (45) | 80.0:20.0 |
| Bn | Me | 2 | (94) | 95.5:4.5 |
| $Ph_2CH$ | Me | 2 | (84) | 97.0:3.0 |
| $Ph_2CH$ | Et | 18 | (74) | 96.0:4.0 |
| $Ph_2CH$ | *n*-$C_5H_{11}$ | 18 | (60) | 97.0:3.0 |





**455** (20 mol %),
THF, 12 h



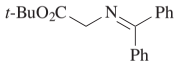
(98) er 58.3:41.7 841

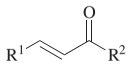
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

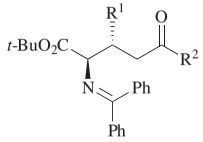
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_2$





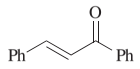
**456** (*x* mol %), $Cs_2CO_3$ (5 eq), mesitylene, –20°



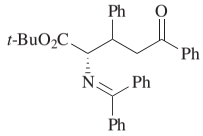
222

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| H | Me | 2 | 3 | (86) | 95.5:4.5 |
| H | Et | 2 | 4 | (92) | 96.5:3.5 |
| H | *n*-Bu | 2 | 1 | (97) | 96.5:3.5 |
| H | Ph | 2 | 1 | (50) | 94.0:6.0 |
| Ph | Me | 2 | 16 | (71) | 93.5:6.5 |
| Ph | 2-$C_4H_3O$ | 2 | 12 | (95) | 95.0:5.0 |
| Ph | 2-$C_4H_3S$ | 2 | 12 | (92) | 95.0:5.0 |
| Ph | Ph | 2 | 12 | (98) | 96.0:4.0 |
| Ph | 4-$ClC_6H_4$ | 2 | 12 | (90) | 96.0:4.0 |
| Ph | 4-$MeOC_6H_4$ | 2 | 18 | (83) | 93.5:6.5 |
| Ph | 4-$O_2NC_6H_4$ | 2 | 12 | (91) | 95.5:4.5 |

| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| 4-$BrC_6H_4$ | Ph | 2 | 15 | (96) | 96.0:4.0 |
| 4-$FC_6H_4$ | Ph | 2 | 18 | (89) | 95.0:5.0 |
| 2-$ClC_6H_4$ | Ph | 2 | 12 | (93) | 97.0:3.0 |
| 4-$ClC_6H_4$ | Ph | 0.05 | 24 | (89) | 96.0:4.0 |
| 4-$ClC_6H_4$ | Ph | 2 | 15 | (98) | 96.0:4.0 |
| 4-$MeOC_6H_4$ | Ph | 2 | 36 | (89) | 92.5:7.5 |
| 4-$O_2NC_6H_4$ | Ph | 2 | 10 | (91) | 97.0:3.0 |
| Ph | 2-Np | 2 | 11 | (80) | 95.5:4.5 |
| 1-Np | Ph | 2 | 12 | (91) | 96.0:4.0 |
| 2-Np | Ph | 2 | 24 | (93) | 95.0:5.0 |
| 4-$PhC_6H_4$ | Ph | 2 | 21 | (88) | 95.5:4.5 |

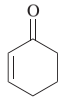


**459** (10 mol %), EtOAc, rt, 1 h

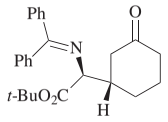


(97) dr 6:1
er 97.5:2.5

842



**405b** (10 mol %), $CsOH•H_2O$, $CH_2Cl_2$, –78°, 2 h

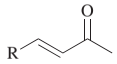


(88) dr 25:1
er 99.5:0.5

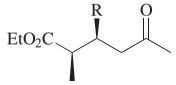
206

$C_3$





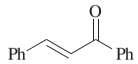
**460b** (30 mol %),
2,6-*i*-$Pr_2C_6H_3OH$ (3 eq),
*t*-BuOMe (4 eq),
$CH_2Cl_2$, –78°, 6 h



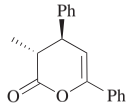
843

| R | | *syn*/*anti* | er |
|---|---|---|---|
| Me | (54) | 8.8:1 | 87.5:12.5 |
| Ph | (62) | 16:1 | 93.0:7.0 |
| 4-$ClC_6H_4$ | (53) | 11:1 | 88.5:11.5 |
| 4-$MeC_6H_4$ | (57) | 8.7:1 | 87.5:12.5 |
| 4-$CF_3C_6H_4$ | (42) | >30:1 | 94.0:6.0 |





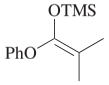
**464** (5 mol %),
solvent, –78°, 0.5 h

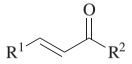


844

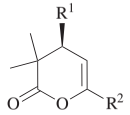
| R | Solvent | | *trans*/*cis* | er (*trans*) | er (*cis*) |
|---|---|---|---|---|---|
| Ph | THF | (91) | 92:8 | 62.5:37.5 | 87.5:12.5 |
| 2-*i*-$PrC_6H_4$ | toluene/$CH_2Cl_2$ | (93) | 98:2 | 78.5:21.5 | — |

$C_4$





**464** (5 mol %),
THF, –78°, 1 h



845, 844

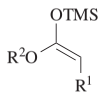
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Me | Ph | (86) | 97.5:2.5 |
| *i*-Pr | Ph | (98) | 96.5:3.5 |
| Ph | Ph | (98) | 95.0:5.0 |
| Ph | 4-$FC_6H_4$ | (94) | 91.0:9.0 |
| Ph | 4-$MeOC_6H_4$ | (98) | 97.5:2.5 |
| 4-$BrC_6H_4$ | 4-$MeOC_6H_4$ | (95) | 94.0:6.0 |
| 4-$FC_6H_4$ | Ph | (98) | 92.0:8.0 |
| 4-$MeOC_6H_4$ | Ph | (98) | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 4-$BrC_6H_4$ | (98) | 94.5:5.5 |

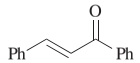
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

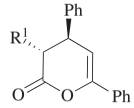
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{4-6}$



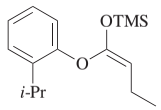

**464** (5 mol %), solvent, –78°, 0.5 h

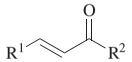



| $R^1$ | $R^2$ | Solvent | | *trans*/*cis* | er |
|---|---|---|---|---|---|
| Et | Ph | THF | (99) | 99:1 | 83.5:16.5 |
| Et | 2-*i*-Pr$C_6H_4$ | toluene/$CH_2Cl_2$ | (99) | >99:1 | 92.0:8.0 |
| Et | 1-Np | THF | (84) | >99:1 | 85.0:15.0 |
| Et | 2-Np | THF | (93) | 98:2 | 77.5:22.5 |
| *i*-Pr | Ph | THF | (99) | >99:1 | 98.0:2.0 |
| *i*-Bu | Ph | THF | (96) | 99:1 | 88.0:12.0 |
| *i*-Bu | 2-*i*-Pr$C_6H_4$ | toluene/$CH_2Cl_2$ | (99) | >99:1 | 94.0:6.0 |
| *t*-Bu | Ph | THF | (96) | >99:1 | 98.0:2.0 |

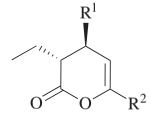
844

$C_4$



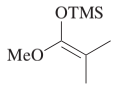



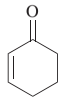

**464** (5 mol %), toluene/$CH_2Cl_2$, –78°, 0.5 h



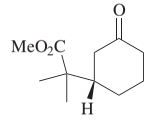

| $R^1$ | $R^2$ | | *trans*/*cis* | er |
|---|---|---|---|---|
| Ph | 4-$MeOC_6H_4$ | (97) | >99:1 | 93.5:6.5 |
| 4-$MeOC_6H_4$ | Ph | (95) | >99:1 | 92.5:7.5 |
| Ph | PhCH=CH | (87) | 97:3 | 93.0:7.0 |

844



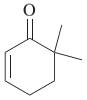




**461** (20 mol %), $Ph_3PO$ (0.25 eq), toluene, –20°, 16 h

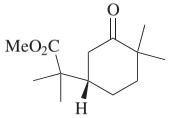



(91) er 95.0:5.0

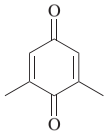
56



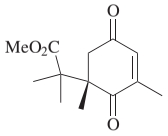
**461** (20 mol %),
2,6-*i*-$Pr_2C_6H_3OH$ (1 eq),
$Ph_3PO$ (0.25 eq),
toluene, –20°, 6 h



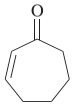
(80) er 96.0:4.0 56



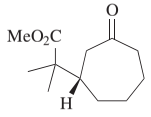
**461** (20 mol %),
2,6-*i*-$Pr_2C_6H_3OH$ (1.5 eq),
$Ph_3PO$ (0.25 eq),
toluene, –20°, 24 h



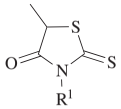
(87) er 95.0:5.0 56

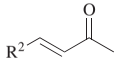


**461** (20 mol %),
2,6-*i*-$Pr_2C_6H_3OH$ (1 eq),
$Ph_3PO$ (0.25 eq),
toluene, –20°, 6 h

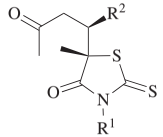


(99) er 99.5:0.5 56





**458** (*x* mol %),
0.5 M in xylene, 40°



846

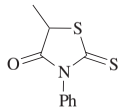
| $R^1$ | $R^2$ | *x* | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *i*-Pr | Ph | 10 | 48 | (97) | 99:1 | 95.0:5.0 |
| Ph | Me | 20 | 96 | (64) | 95:5 | 90.0:10.0 |
| Ph | 2-$C_4H_3O$ | 10 | 48 | (84) | 99:1 | 97.5:2.5 |
| Ph | 2-$C_4H_3S$ | 10 | 48 | (96) | 97:3 | 99.0:1.0 |
| Ph | Ph | 10 | 48 | (95) | 99:1 | 98.0:2.0 |
| Ph | 3-$BrC_6H_4$ | 10 | 48 | (92) | 99:1 | 96.5:3.5 |
| Ph | 4-$ClC_6H_4$ | 20 | 48 | (95) | 99:1 | 98.0:2.0 |
| Ph | 3-$MeOC_6H_4$ | 10 | 96 | (81) | 99:1 | 97.0:3.0 |
| Ph | 2-$O_2NC_6H_4$ | 10 | 24 | (89) | 99:1 | 97.5:2.5 |
| Ph | 4-$MeC_6H_4$ | 10 | 96 | (75) | 97:3 | 96.5:3.5 |
| Ph | $BnCH_2$ | 20 | 96 | (60) | 97:3 | 93.5:6.5 |
| Ph | PhCH=CH | 10 | 72 | (83) | 93:7 | 98.0:2.0 |
| Ph | 1-Np | 10 | 48 | (93) | 98:2 | 95.5:4.5 |
| 4-$MeOC_6H_4$ | Ph | 10 | 48 | (98) | 99:1 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 4-$BrC_6H_4$ | 10 | 48 | (96) | 99:1 | 97.5:2.5 |
| Bn | Ph | 10 | 48 | (94) | 98:2 | 97.5:2.5 |
| Bn | 4-$ClC_6H_4$ | 10 | 48 | (97) | 97:3 | 97.5:2.5 |

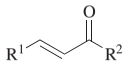
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

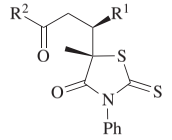
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_4$





Catalyst (20 mol %),
0.5 M in xylene, 40°, 48 h

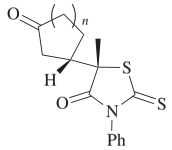


846

| $R^1$ | $R^2$ | Catalyst | | dr | er |
|---|---|---|---|---|---|
| Ph | *n*-Pr | **458** | (82) | 99:1 | 97.5:2.5 |
| Ph | Ph | **447** | (82) | >30:1 | 96.0:4.0 |
| Ph | 4-$BrC_6H_4$ | **447** | (89) | >30:1 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | Ph | **447** | (93) | >30:1 | 96.5:3.5 |



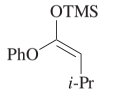
**447** (10 mol %),
0.5 M in xylene, 0°

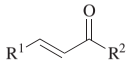


846

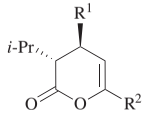
| *n* | Time (h) | | dr | er |
|---|---|---|---|---|
| 1 | 48 | (82) | 5:1 | 97.0:3.0 |
| 2 | 48 | (89) | 6:1 | >99.5:0.5 |
| 3 | 36 | (93) | 1:1 | >99.5:0.5 |

$C_5$



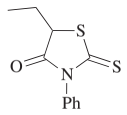



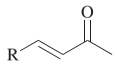

**464** (5 mol %),
THF, –78°, 0.5 h



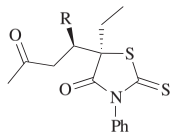

844

| $R^1$ | $R^2$ | | *trans*/*cis* | er |
|---|---|---|---|---|
| Ph | 4-$FC_6H_4$ | (92) | >99:1 | 97.0:3.0 |
| Ph | 4-$MeOC_6H_4$ | (94) | >99:1 | 98.5:1.5 |
| 4-$BrC_6H_4$ | 4-$MeOC_6H_4$ | (98) | >99:1 | 97.5:2.5 |
| 4-$FC_6H_4$ | Ph | (92) | >99:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | Ph | (93) | >99:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | 4-$BrC_6H_4$ | (94) | >99:1 | 96.0:4.0 |




**458** (10 mol %),
0.5 M in xylene, 40°, 48 h




846

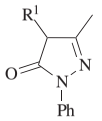
| R | | dr | er |
|---|---|---|---|
| Ph | (91) | 98:2 | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | (98) | 97:3 | 96.0:4.0 |
| 1-Np | (96) | 99:1 | 95.5:4.5 |

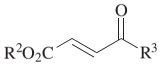
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

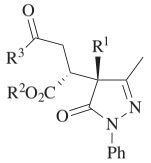
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{5-12}$





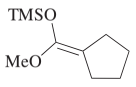
**465** (5.5 mol %), $Sc(OTf)_3$ (5 mol %), EtOH, rt, 24 h

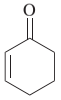


107

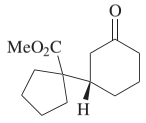
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| Me | *i*-Pr | Ph | (92) | 13.3:1 | 93.0:7.0 |
| Et | *i*-Pr | Ph | (97) | 19:1 | 96.5:3.5 |
| (2-$C_4H_3O$)$CH_2$ | *i*-Pr | Ph | (95) | 19:1 | 97.5:2.5 |
| Bn | Et | Ph | (95) | 4.5:1 | 93.0:7.0 |
| Bn | *i*-Pr | 2-$C_4H_3S$ | (95) | 3:1 | 95.0:5.0 |
| Bn | *i*-Pr | Ph | (83) | 9:1 | 95.0:5.0 |
| Bn | *i*-Pr | 4-$BrC_6H_4$ | (96) | 4.5:1 | 96.5:3.5 |
| Bn | *i*-Pr | 3-$ClC_6H_4$ | (83) | 13.3:1 | 96.0:4.0 |
| Bn | *i*-Pr | 4-$ClC_6H_4$ | (95) | 7.3:1 | 96.5:3.5 |
| Bn | *i*-Pr | 3,4-$Cl_2C_6H_3$ | (89) | 10.1:1 | 95.0:5.0 |
| Bn | *i*-Pr | 4-$FC_6H_4$ | (85) | 6.1:1 | 97.0:3.0 |
| Bn | *i*-Pr | 4-$MeOC_6H_4$ | (85) | 5.7:1 | 96.0:4.0 |
| Bn | *i*-Pr | 4-$MeC_6H_4$ | (91) | 6.7:1 | 96.0:4.0 |
| Bn | *i*-Pr | 2-Np | (97) | 8.1:1 | 95.5:4.5 |
| 3-$MeOC_6H_4CH_2$ | *i*-Pr | Ph | (95) | 6.1:1 | 97.5:2.5 |
| 3-$MeC_6H_4CH_2$ | *i*-Pr | Ph | (97) | 4.9:1 | 95.0:5.0 |
| 4-$MeC_6H_4CH_2$ | *i*-Pr | Ph | (91) | 9:1 | 97.5:2.5 |

$C_6$



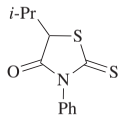


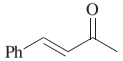
**461** (20 mol %), 2,6-*i*-$Pr_2C_6H_3OH$ (1 eq, slow addition), $Ph_3PO$ (0.25 eq), toluene, –20°, 6 h



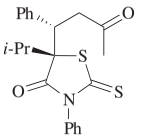
(79) er 91.0:9.0

56





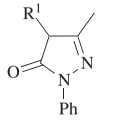
**458** (20 mol %),
0.5 M in xylene, 40°, 96 h

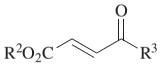


(68) dr 93:7
er 85.5:14.5

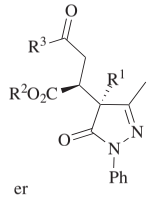
846

$C_{6-12}$





**465** (5.5 mol %),
$Y(OTf)_3$ (5 mol %),
$CH_2Cl_2$, 0°

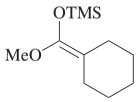
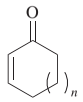
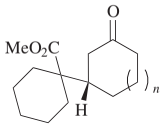
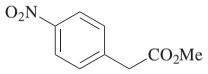
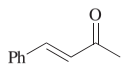
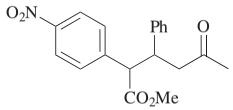
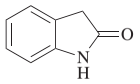
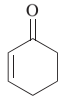
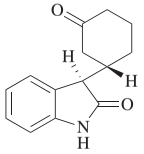
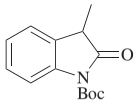
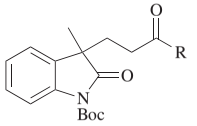
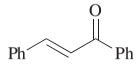
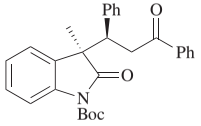


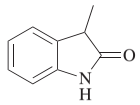
dr >49:1

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| $R^1$ | $R^2$ | $R^3$ | Time (h) | | er |
|---|---|---|---|---|---|
| Et | Et | Ph | 30 | (93) | 91.5:8.5 |
| allyl | *i*-Pr | Ph | 48 | (89) | 96.0:4.0 |
| (2-$C_4H_3O$)$CH_2$ | *i*-Pr | Ph | 48 | (87) | 98.0:2.0 |
| Bn | Me | Ph | 30 | (93) | 95.0:5.0 |
| Bn | Et | Ph | 30 | (95) | 98.0:2.0 |
| Bn | *i*-Pr | 2-$C_4H_3S$ | 48 | (82) | 97.5:2.5 |
| Bn | *i*-Pr | Ph | 48 | (87) | 99.0:1.0 |
| Bn | *i*-Pr | 4-$BrC_6H_4$ | 48 | (95) | 98.5:1.5 |
| Bn | *i*-Pr | 3-$ClC_6H_4$ | 48 | (91) | 99.0:1.0 |
| Bn | *i*-Pr | 4-$ClC_6H_4$ | 48 | (91) | 98.5:1.5 |
| Bn | *i*-Pr | 3,4-$Cl_2C_6H_3$ | 48 | (89) | 98.0:2.0 |
| Bn | *i*-Pr | 4-$FC_6H_4$ | 48 | (84) | 99.0:1.0 |
| Bn | *i*-Pr | 4-$MeOC_6H_4$ | 72 | (75) | 95.5:4.5 |
| Bn | *i*-Pr | 4-$MeC_6H_4$ | 48 | (80) | 98.5:1.5 |
| Bn | *i*-Pr | 2-Np | 48 | (91) | 98.5:1.5 |
| Bn | Bn | Ph | 48 | (82) | 98.5:1.5 |
| 3-$MeOC_6H_4CH_2$ | Et | Ph | 30 | (94) | 95.0:5.0 |
| 4-$MeOC_6H_4CH_2$ | *i*-Pr | Ph | 48 | (82) | 97.5:2.5 |
| 3-$MeC_6H_4CH_2$ | *i*-Pr | Ph | 48 | (84) | 98.5:1.5 |
| 4-$MeC_6H_4CH_2$ | *i*-Pr | Ph | 48 | (90) | 99.0:1.0 |

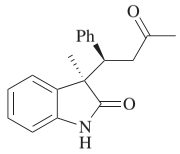
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_7$  |  | **461** (20 mol %), 2,6-*i*-$Pr_2C_6H_3OH$ (1 eq), $Ph_3PO$ (0.25 eq), toluene, –20°, 6 h |  | *n* (%) er<br>1 (86) 95.0:5.0<br>2 (89) 94.0:6.0 | 56 |
| $C_8$  |  | **225a** (20 mol %), 4-$O_2NC_6H_4CO_2H$ (40 mol %), DMF, rt, 18 h |  | (86) dr 65:35<br>er (major) 77.0:23.0; er (minor) 73.0:27.0 | 847 |
|  |  | **1** (30 mol %), **411** (100 mol %), $CHCl_3$, rt, 48 h |  | (63) dr 60:40<br>er (major) 66.0:34.0<br>er (minor) 66.5:33.5 | 848 |
| $C_9$  |  | *ent*-**252b** (20 mol %), toluene, 4 Å MS, 4°, 72 h |  | R (%) er<br>Me (90) 61.0:39.0<br>Et (99) 58.5:41.5<br>Ph (99) 74.0:26.0 | 849 |
| |  | **463** (20 mol %), $Cl_3CCH_3$, rt, 24 h |  | (37) dr 93:7<br>er 88.0:12.0 | 850 |



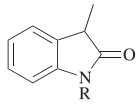


**1** (30 mol %),
**411** (100 mol %),
$CHCl_3$, rt, 48 h



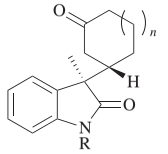
(83) dr 48:52
er (major) 86.0:14.0
er (minor) 85.0:15.0

848





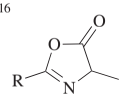
**1** (30 mol %),
**411** (100 mol %),
$CHCl_3$, rt

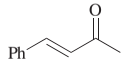


848

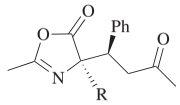
| R | *n* | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|
| H | 0 | 48 | (76) | 60:40 | 57.5:42.5 | 77.5:22.5 |
| H | 1 | 48 | (99) | 53:47 | 80.0:20.0 | 95.5:4.5 |
| Me | 1 | 192 | (75) | 50:50 | 71.5:28.5 | 51.0:49.0 |
| Ph | 1 | 72 | (96) | 51:49 | 83.0:17.0 | 59.0:41.0 |
| Cbz | 1 | 24 | (81) | 61:39 | 75.0:25.0 | 57.0:43.0 |

$C_{10–16}$





**362** (1 mol %),
AgOTs/MeCN (6 mol %),
$Ac_2O$/AcOH (70:30), rt, 20 h



dr >98:2

851

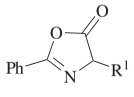
| R | | er |
|---|---|---|
| 4-$ClC_6H_4$ | (79) | 81.0:19.0 |
| 4-$FC_6H_4$ | (40) | 84.5:15.5 |
| 4-$MeOC_6H_4$ | (20) | 85.5:14.5 |
| 3,4,5-$(MeO)_3C_6H_2$ | (58) | 72.5:27.5 |
| 4-$O_2NC_6H_4$ | (86) | 76.0:24.0 |
| 4-$MeC_6H_4$ | (75) | 87.5:12.5 |
| 4-$CF_3C_6H_4$ | (52) | 72.0:28.0 |
| 3,5-$Me_2C_6H_3$ | (70) | 82.0:18.0 |
| 4-*t*-$BuC_6H_4$ | (89) | 75.0:25.0 |
| 1-Np | (29) | 79.0:21.0 |
| 2-Np | (34) | 80.5:19.5 |
| 4-$PhC_6H_4$ | (34) | 79.5:20.5 |

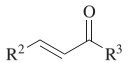
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

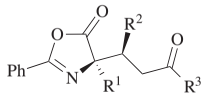
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{10-16}$



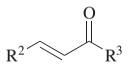


**362** (2 mol %),
AgOTf (8 mol %),
AcONa (10 mol %),
$Ac_2O$/AcOH (30:70), 30°, 23 h

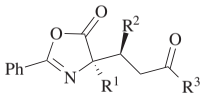


852, 851

| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| Me[a] | Ph | Me | (95) | >98:2 | 88.0:12.0 |
| Et[a] | Me | Et | (92) | >98:2 | 93.5:6.5 |
| Et[a] | *n*-Pr | Me | (90) | >98:2 | 95.0:5.0 |
| Et[a] | Ph | Me | (92) | >98:2 | 96.5:3.5 |
| Et[a] | 4-$BrC_6H_4$ | Me | (88) | >98:2 | 96.0:4.0 |
| Et[a] | 4-$HOC_6H_4$ | Me | (43)[b] | >98:2 | 94.0:6.0 |
| Et[a] | 3,4-$(MeO)_2C_6H_3$ | Me | (81) | >98:2 | 95.5:4.5 |
| *n*-Pr[a] | 2-$C_4H_3O$ | Me | (88) | >98:2 | 98.0:2.0 |
| *n*-Pr[a] | *i*-Pr | Me | (64) | >98:2 | >98.5:1.5 |
| *n*-Pr[a] | Ph | Me | (89) | >98:2 | 99.0:1.0 |
| *n*-Pr[a] | 2-$ClC_6H_4$ | Me | (82) | >98:2 | 99.5:0.5 |
| *n*-Pr[a] | 4-$ClC_6H_4$ | Me | (85) | >98:2 | 99.0:1.0 |
| *n*-Pr[a] | 4-$MeOC_6H_4$ | Me | (81) | >98:2 | 98.0:2.0 |
| *n*-Pr[a] | 4-$O_2NC_6H_4$ | Me | (76) | >98:2 | 99.0:1.0 |
| *n*-Pr[a] | Ph | Ph | (87) | 98:2 | 95.0:5.0 |
| Bn[a] | Ph | Me | (41) | >98:2 | 90.5:9.5 |



**362** (2 mol %),
AgOTf (8 mol %),
AcONa (10 mol %),
$Ac_2O$/AcOH (30:70), 30°, 24 h



dr >98:2

851

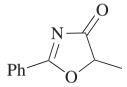
| $R^1$ | $R^2$ | $R^3$ | | er |
|---|---|---|---|---|
| Me | Ph | Me | (96) | 87.5:12.5 |
| Et | Me | Et | (94) | 94.0:6.0 |
| Et | *n*-Pr | Me | (93) | 95.0:5.0 |
| Et | Ph | Me | (95) | 98.0:2.0 |
| Et | 4-$BrC_6H_4$ | Me | (86) | 95.5:4.5 |
| Et | 4-$HOC_6H_4$ | Me | (42)[b] | 92.0:8.0 |
| Et | 3,4-$(MeO)_2C_6H_3$ | Me | (89) | 95.5:4.5 |
| *n*-Pr | *i*-Pr | Me | (65) | >98.5:1.5 |
| *n*-Pr | 2-$C_4H_3O$ | Me | (96) | 98.0:2.0 |
| *n*-Pr | Ph | Me | (86) | 99.0:1.0 |
| *n*-Pr | 2-$ClC_6H_4$ | Me | (94) | 99.5:0.5 |
| *n*-Pr | 4-$ClC_6H_4$ | Me | (80) | 98.5:1.5 |
| *n*-Pr | 4-$MeOC_6H_4$ | Me | (80) | 97.5:2.5 |
| *n*-Pr | 4-$O_2NC_6H_4$ | Me | (80) | 98.5:1.5 |
| *n*-Pr | Ph | Ph | (92) | 95.0:5.0 |
| Bn | Ph | Me | (73) | 91.0:9.0 |

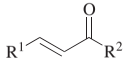
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

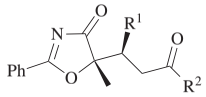
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{10}$





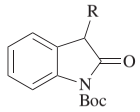
**462** (*x* mol %), DCE, 50°

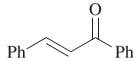


| $R^1$ | $R^2$ | *x* | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| *n*-$C_6H_{13}$ | Me | 15 | 96 | (85) | 10:1 | 96.5:3.5 |
| Ph | Me | 10 | 72 | (84) | >30:1 | 98.0:2.0 |
| Ph | Ph | 10 | 72 | (87) | >30:1 | >99.5:0.5 |
| 4-$FC_6H_4$ | Me | 10 | 72 | (94) | >30:1 | 98.0:2.0 |
| 3-$MeC_6H_4$ | Me | 10 | 72 | (90) | >30:1 | 98.5:1.5 |
| PhCH=CH | Me | 10 | 72 | (94) | >30:1 | 98.5:1.5 |

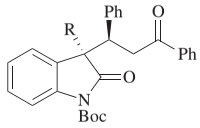
853

$C_{10-12}$





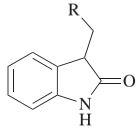
**463** (20 mol %), $Cl_3CCH_3$



| R | Temp | Time (h) | | dr | er |
|---|---|---|---|---|---|
| $EtO_2CCH_2$ | –30° | 36 | (97) | 93:7 | 92.0:8.0 |
| *n*-Bu | rt | 24 | (70) | 98:2 | 89.0:11.0 |

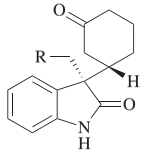
850

$C_{10-15}$



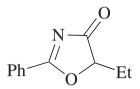


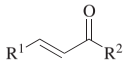
**1** (30 mol %),
**411** (1 eq),
$CHCl_3$, rt, 48 h



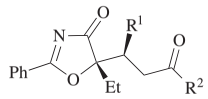
848

$C_{11}$





**462** (*x* mol %), DCE, 50°



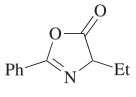
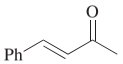
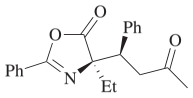
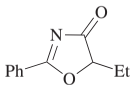
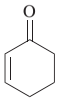
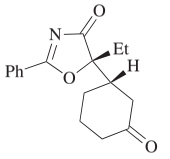
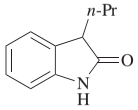
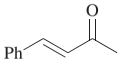
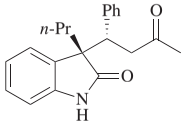
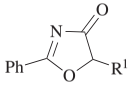
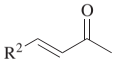
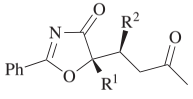
dr >30:1

853

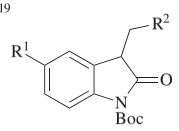
| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| $MeO_2C$ | (99) | 64:37 | 59.5:40.5 | 84.0:16.0 |
| Ph | (99) | 61:39 | 68.5:31.5 | 92.0:8.0 |
| 4-$BrC_6H_4$ | (99) | 62:38 | 65.0:35.0 | 90.5:9.5 |
| 4-$MeOC_6H_4$ | (99) | 61:39 | 70.0:30.0 | 91.0:9.0 |
| 4-$O_2NC_6H_4$ | (99) | 62:38 | 62.0:38.0 | 86.0:14.0 |

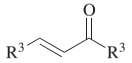
| $R^1$ | $R^2$ | *x* | Time (h) | | er |
|---|---|---|---|---|---|
| Me | Me | 15 | 72 | (90) | 98.0:2.0 |
| Me | *n*-Bu | 15 | 96 | (81) | 99.0:1.0 |
| 2-$C_4H_3O$ | Me | 10 | 72 | (84) | 98.5:1.5 |
| Ph | Me | 10 | 72 | (95) | 98.5:1.5 |
| 3-$BrC_6H_4$ | Me | 10 | 72 | (98) | 98.5:1.5 |
| 2-$ClC_6H_4$ | Me | 10 | 72 | (85) | 95.0:5.0 |
| 4-$ClC_6H_4$ | Me | 10 | 72 | (95) | 98.5:1.5 |
| 2-$FC_6H_4$ | Me | 10 | 72 | (96) | 97.0:3.0 |
| 2-$MeOC_6H_4$ | Me | 10 | 72 | (83) | 97.0:3.0 |
| 2,3-$(MeO)_2C_6H_3$ | Me | 10 | 72 | (86) | 96.0:4.0 |
| 4-$O_2NC_6H_4$ | Me | 10 | 72 | (88) | 98.5:1.5 |
| 3-$MeC_6H_4$ | Me | 10 | 72 | (90) | 98.5:1.5 |
| Ph | *i*-Pr | 10 | 72 | (86) | 99.5:0.5 |
| 2-Np | Me | 10 | 72 | (97) | 99.0:1.0 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

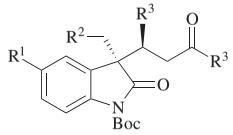
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{11}$ | | | | |
|  |  | **362** (2 mol %), AgOTf (8 mol %), AcONa (10 mol %) $Ac_2O$/AcOH (30:70), 30° |  dr >98:2 | 851 |
| | | | Catalyst Recycling<br>Run / Time (h) / er<br>1 / 22 / (88)[a] / 99.0:1.0<br>2 / 24 / (86)[a] / 98.5:1.5<br>3 / 24 / (89)[a] / 98.5:1.5<br>4 / 23 / (87)[a] / 98.5:1.5<br>5 / 24 / (86)[a] / 98.0:2.0<br>6 / 23 / (80)[a] / 97.5:2.5<br>7 / 23 / (70)[a] / 96.5:3.5<br>8 / 23 / (45)[a] / 95.0:5.0 | |
|  |  | **462** (15 mol %), DCE, 50°, 96 h |  (81) dr 13:1 er 95.0:5.0 | 853 |
|  |  | **80d** (20 mol %), *N*-Boc-D-phenylglycine (40 mol %), toluene, rt, 48 h |  (95) dr 2:1 er 97.5:2.5 | 854 |
| $C_{12}$ | | | | |
|  |  | **462** (10 mol %), DCE, 50°, 72 h |  dr >30:1 | 853 |

$C_{13–19}$





**463** (20 mol %), $Cl_3CCH_3$



| $R^1$ | $R^2$ | $R^3$ | Temp (°) | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|
| H | 2-$C_4H_3S$ | Ph | –30 | 36 | (95) | 98:2 | 95.0:5.0 |
| H | Ph | 2-$C_4H_3S$ | rt | 24 | (93) | 93:7 | 78.0:22.0 |
| H | Ph | Ph | –30 | 36 | (94) | 98:2 | 94.0:6.0 |
| H | Ph | 4-$BrC_6H_4$ | –30 | 36 | (88) | 92:8 | 89.0:11.0 |
| H | Ph | 2-$ClC_6H_4$ | –30 | 36 | (92) | 97:3 | 87.0:13.0 |
| H | Ph | 3-$ClC_6H_4$ | –30 | 36 | (88) | 95:5 | 87.0:13.0 |
| H | Ph | 4-$ClC_6H_4$ | –30 | 36 | (93) | 97:3 | 94.0:6.0 |
| H | Ph | 4-$FC_6H_4$ | –30 | 36 | (96) | 95:5 | 90.0:10.0 |
| H | Ph | 3-$MeOC_6H_4$ | –30 | 36 | (95) | 97:3 | 91.0:9.0 |
| H | Ph | 2-Np | rt | 24 | (61) | 91:9 | 76.0:24.0 |
| F | Ph | Ph | –30 | 36 | (93) | 98:2 | 94.0:6.0 |
| H | 2-$FC_6H_4$ | Ph | –30 | 36 | (90) | 96:4 | 90.0:10.0 |
| H | 3-$FC_6H_4$ | Ph | –30 | 36 | (93) | 98:2 | 93.0:7.0 |
| H | 4-$FC_6H_4$ | Ph | –30 | 36 | (95) | 98:2 | 93.0:7.0 |
| H | 2-$MeOC_6H_4$ | Ph | –30 | 36 | (88) | 96:4 | 84.0:16.0 |
| H | 4-$MeOC_6H_4$ | Ph | –30 | 36 | (94) | 98:2 | 92.0:8.0 |
| H | 3,4-$(MeO)_2C_6H_3$ | Ph | –30 | 36 | (96) | 98:2 | 92.0:8.0 |
| H | 3-$MeC_6H_4$ | Ph | –30 | 36 | (95) | 97:3 | 87.0:13.0 |
| Me | Ph | Ph | –30 | 36 | (82) | 96:4 | 89.0:11.0 |
| H | 1-Np | Ph | –30 | 36 | (95) | 98:2 | 93.0:7.0 |

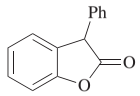
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| *n*-Pr | 2-$C_4H_3S$ | (94) | 98.5:1.5 |
| *n*-Pr | 4-$BrC_6H_4$ | (98) | 98.0:2.0 |
| *n*-Pr | 3-$MeOC_6H_4$ | (87) | 98.5:1.5 |
| *n*-Pr | 3-$O_2NC_6H_4$ | (93) | 97.5:2.5 |
| *i*-Pr | Ph | (85) | 99.0:1.0 |
| *i*-Pr | 4-$ClC_6H_4$ | (91) | 99.0:1.0 |
| *i*-Pr | 3-$MeOC_6H_4$ | (87) | 99.0:1.0 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

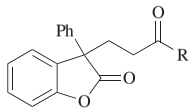
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{14}$



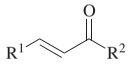


*ent*-**252b** (10 mol %), $CHCl_3$, –20°

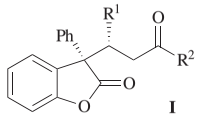


| R | Time (h) | | er |
|---|---|---|---|
| Me | 72 | (95) | 63.5:36.5 |
| Et | 96 | (82) | 53.5:46.5 |
| Ph | 96 | (78) | 50.0:50.0 |

828

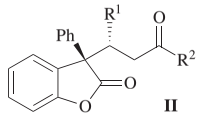


**439** (10 mol %), toluene, 4 Å MS, –20°



**I**

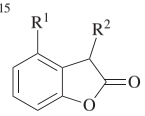
| $R^1$ | $R^2$ | Time (h) | | **I**/**II** | er **I** | er **II** |
|---|---|---|---|---|---|---|
| Ph | Ph | 48 | (95) | 3:2 | 98.5:1.5 | 97.0:3.0 |
| Ph | 4-$BrC_6H_4$ | 48 | (91) | 3:2 | 98.5:1.5 | 93.0:7.0 |
| Ph | 3-$ClC_6H_4$ | 48 | (99) | 2:1 | 98.5:1.5 | 97.0:3.0 |
| Ph | 4-$ClC_6H_4$ | 48 | (94) | 2:1 | 98.0:2.0 | 90.5:9.5 |
| Ph | 4-$FC_6H_4$ | 54 | (91) | 2:1 | 98.0:2.0 | 96.0:4.0 |
| 2-$BrC_6H_4$ | Ph | 60 | (91) | 1:1 | 89.0:11.0 | 91.5:8.5 |
| 2-$ClC_6H_4$ | Ph | 60 | (92) | 1:1 | 94.5:5.5 | 92.0:8.0 |
| 3-$ClC_6H_4$ | Ph | 60 | (98) | 3:2 | 99.0:1.0 | 95.5:4.5 |
| 3-$ClC_6H_4$ | 4-$BrC_6H_4$ | 48 | (95) | 3:1 | 98.5:1.5 | 97.0:3.0 |
| 3-$ClC_6H_4$ | 3-$ClC_6H_4$ | 48 | (96) | 2:1 | 99.0:1.0 | 95.5:4.5 |
| 4-$ClC_6H_4$ | Ph | 48 | (93) | 1:1 | 99.0:1.0 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | Ph | 84 | (80) | 1:1 | 98.5:1.5 | 96.5:3.5 |
| Ph | 4-$CF_3C_6H_4$ | 72 | (80) | 2:1 | 98.5:1.5 | 97.0:3.0 |
| 4-$MeC_6H_4$ | Ph | 72 | (89) | 3:2 | 97.0:3.0 | 96.0:4.0 |
| 4-$PhC_6H_4$ | Ph | 72 | (85) | 3:2 | 98.5:1.5 | 97.5:2.5 |

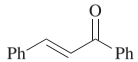
+ 

**II**

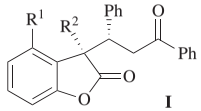
828

$C_{14–15}$



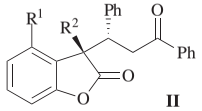


**439** (10 mol %),
toluene, 4 Å MS, –20°, 36 h



**I**

+

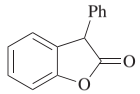


**II**

| $R^1$ | $R^2$ | | **I/II** | er **I** | er **II** |
|---|---|---|---|---|---|
| H | 4-$ClC_6H_4$ | (91) | 3:2 | 99.0:1.0 | 98.0:2.0 |
| Me | Ph | (92) | 3:1 | 98.5:1.5 | 95.0:5.0 |

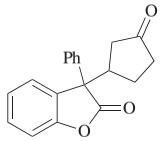
828

$C_{14}$





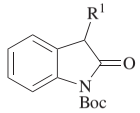
**164b** (10 mol %),
$CH_2Cl_2$, 4 Å MS, –20°, 48 h



(87) dr 6:1
er 91.5:9.5

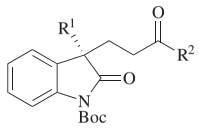
855

$C_{14–16}$





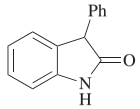
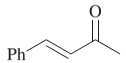
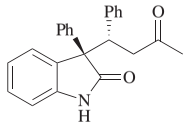
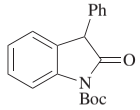
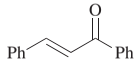
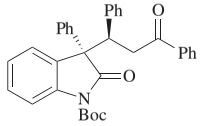
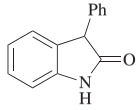
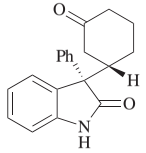
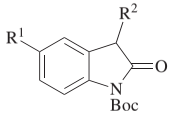
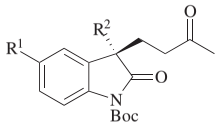
*ent*-**252b** (20 mol %),
toluene, 4 Å MS, –60°



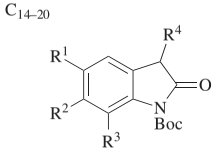
849

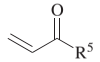
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| Ph | Me | 36 | (98) | 91.0:9.0 |
| Ph | Et | 36 | (99) | 80.5:19.5 |
| Ph | Ph | 48 | (99) | 88.0:12.0 |
| 4-$MeOC_6H_4$ | Me | 48 | (92) | 82.5:17.5 |
| 4-$MeOC_6H_4$ | Et | 72 | (93) | 73.0:27.0 |
| 4-$MeOC_6H_4$ | Ph | 60 | (96) | 92.5:7.5 |
| 4-$MeC_6H_4$ | Me | 36 | (99) | 90.5:9.5 |
| 4-$MeC_6H_4$ | Et | 36 | (99) | 81.5:18.5 |
| 4-$MeC_6H_4$ | Ph | 48 | (99) | 86.0:14.0 |
| 3,5-$Me_2C_6H_3$ | Me | 36 | (98) | 94.0:6.0 |
| 3,5-$Me_2C_6H_3$ | Et | 36 | (99) | 88.0:12.0 |
| 3,5-$Me_2C_6H_3$ | Ph | 48 | (99) | 80.0:20.0 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

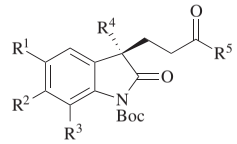
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_{14}$  |  | **80d** (20 mol %), *N*-Boc-D-phenylglycine (40 mol %), toluene, rt, 48 h |  | (96) dr 2:1 er 50.0:50.0 | 854 |
|  |  | **164b** (5 mol %), $CH_2Cl_2$, rt, 6 h |  | (92) dr 88:12 er 74.0:26.0 | 850 |
|  |  | **1** (30 mol %), **411** (100 mol %), $CHCl_3$, rt, 48 h |  | (76) dr 55:45 er (major) 50.5:49.5 er (minor) 50.5:49.5 | 848 |
| $C_{14-18}$  |  | **468** (2.5 mol %), *i*-PrOAc, 0° |  | | 856 |

| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| H | Ph | 23 | (97) | 95.0:5.0 |
| F | Ph | 22 | (96) | 97.5:2.5 |
| H | 4-$MeC_6H_4$ | 34 | (96) | 95.0:5.0 |
| H | 2-Np | 34 | (95) | 97.5:2.5 |




**466** (3 mol %),
$PhCO_2K$ (5 eq),
toluene




221

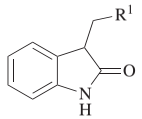
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|---|---|---|
| H | H | H | Ph | Me | –60 | 24 | (97) | 99.5:0.5 |
| H | H | H | Ph | Et | –40 | 45 | (97) | 98.0:2.0 |
| H | H | H | 3-$ClC_6H_4$ | Me | –60 | 24 | (98) | 99.0:1.0 |
| H | H | H | 3-$ClC_6H_4$ | Et | –40 | 45 | (98) | 98.0:2.0 |
| H | H | H | 4-$ClC_6H_4$ | Me | –60 | 24 | (99) | 99.0:1.0 |
| H | H | H | 4-$FC_6H_4$ | Me | –60 | 24 | (99) | 99.5:0.5 |
| H | H | H | 4-$MeOC_6H_4$ | Me | –40 | 45 | (96) | 97.0:3.0 |
| H | H | F | Ph | Me | –60 | 24 | (99) | 98.0:2.0 |
| H | Cl | H | Ph | Me | –60 | 24 | (96) | 99.0:1.0 |
| F | H | H | Ph | Me | –60 | 24 | (99) | >99.5:0.5 |
| MeO | H | H | Ph | Et | –60 | 24 | (95) | >99.5:0.5 |
| H | H | H | 3-$MeC_6H_4$ | Me | –60 | 24 | (99) | 99.0:1.0 |
| H | H | H | 4-$MeC_6H_4$ | Me | –60 | 24 | (94) | 99.5:0.5 |
| H | $CF_3$ | H | Ph | Me | –60 | 24 | (91) | 99.0:1.0 |
| Me | H | H | Ph | Me | –60 | 24 | (99) | 99.5:0.5 |
| H | H | H | 2-Np | Me | –60 | 24 | (99) | 99.5:0.5 |
| H | H | H | 4-$PhC_6H_4$ | Me | –60 | 24 | (95) | 98.0:2.0 |

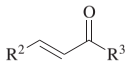
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
B. ENONES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

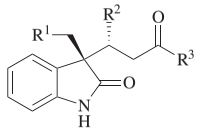
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{15}$



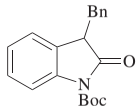
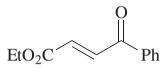
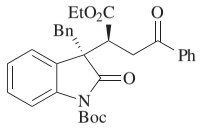
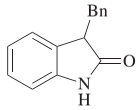
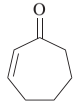
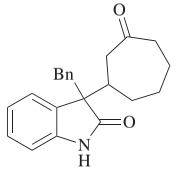


**80d** (20 mol %),
*N*-Boc-D-phenylglycine
(40 mol %),
toluene, rt, 48 h



854

| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| Ph | *n*-Pr | Me | (75) | >20:1 | >99.5:0.5 |
| Ph | *n*-$C_5H_{11}$ | Me | (71) | >20:1 | 99.5:0.5 |
| Ph | Ph | Me | (97) | 2:1 | 98.5:1.5 |
| Ph | 4-$BrC_6H_4$ | Me | (97) | 2:1 | 99.0:1.0 |
| Ph | 3-$ClC_6H_4$ | Me | (94) | 2:2 | 99.0:1.0 |
| Ph | 4-$ClC_6H_4$ | Me | (97) | 2:1 | 98.5:1.5 |
| Ph | 4-$FC_6H_4$ | Me | (93) | 2:1 | 99.0:1.0 |
| Ph | 2-$MeOC_6H_4$ | Me | (91) | 2:1 | 99.0:1.0 |
| Ph | 3-$MeOC_6H_4$ | Me | (94) | 2:1 | 97.0:3.0 |
| Ph | 4-$MeOC_6H_4$ | Me | (96) | 2:1 | 98.0:2.0 |
| Ph | Ph | Et | (80) | 2:1 | >99.5:0.5 |
| 3-$ClC_6H_4$ | Ph | Me | (95) | 2:1 | >99.5:0.5 |
| 4-$ClC_6H_4$ | Ph | Me | (96) | 2:1 | 99.0:1.0 |
| 2-$MeOC_6H_4$ | Ph | Me | (95) | 2:1 | 98.5:1.5 |

| | | | | | |
|---|---|---|---|---|---|
|  |  | **463** (20 mol %), $Cl_3CCH_3$, –30°, 36 h |  | (81) dr 75:25<br>er 87.0:13.0 | 850 |
|  |  | **42** (20 mol %), *N*-Boc-D-phenylglycine (40 mol %), toluene, rt, 48 h |  | (71) dr >20:1<br>er 99.5:0.5 | 854 |

[a] The azlactones are prepared in situ from their corresponding *N*-protected amino acids.

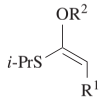
[b] The OH group is acylated during the reaction.

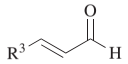
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

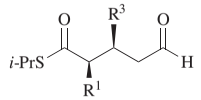
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{2-4}$



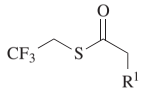

Catalyst (20 mol %),
$H_2O$ (1–1.2 eq),
solvent, –78°, 22–24 h

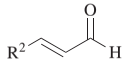



857

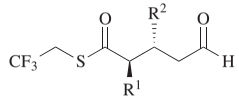
| $R^1$ | $R^2$ | $R^3$ | Catalyst | Solvent | | *syn/anti* | er |
|---|---|---|---|---|---|---|---|
| BnO | TBS | Me | **146**•TFA | $CH_2Cl_2$ | (82) | >20:1 | 95.0:5.0 |
| Me | TMS | Ph | **146**•TCA | acetone/cyclohexane | (50) | 20:1 | 95.0:5.0 |
| Me | TBS | Me | **146**•TCA | acetone | (76) | 10:1 | 95.0:5.0 |
| Me | TBS | $MeO_2C$ | **146**•TCA | acetone | (73) | 4:1 | 95.5:4.5 |
| Me | TBS | *n*-Pr | **146**•TCA | acetone | (62) | 6:1 | 95.0:5.0 |
| Et | TBS | Me | **146**•TCA | BnOMe | (76) | 4:1 | 97.0:3.0 |

$C_{6-12}$



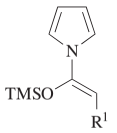

**145b** (*x* mol %),
$PhCO_2H$ (10 mol %),
solvent

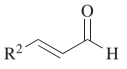



152

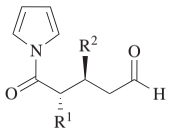
| $R^1$ | $R^2$ | *x* | Solvent | Temp | Time (h) | | *anti/syn* | er |
|---|---|---|---|---|---|---|---|---|
| 2-$C_4H_3S$ | Ph | 10 | MeOH | rt | 24 | (57) | 81:19 | 92.0:8.0 |
| Ph | Ph | 10 | MeOH | rt | 16 | (71) | 67:33 | 91.0:9.0 |
| 2-$ClC_6H_4$ | Ph | 10 | MeOH | rt | 19 | (75) | 65:35 | 94.5:5.5 |
| 4-$ClC_6H_4$ | Me | 10 | DMF | rt | 36 | (51) | 63:37 | 77.0:23.0 |
| 4-$ClC_6H_4$ | Ph | 10 | MeOH | rt | 17 | (70) | 65:35 | 95.0:5.0 |
| 4-$ClC_6H_4$ | 2-$MeOC_6H_4$ | 10 | MeOH | rt | 72 | (63) | 71:29 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | Ph | 20 | MeOH | rt | 48 | (46) | 64:36 | 92.0:8.0 |
| 4-$O_2NC_6H_4$ | Ph | 10 | MeOH | 4° | 2 | (84) | 61:39 | 95.5:4.5 |
| 4-$O_2NC_6H_4$ | Ph | 10 | MeOH | rt | 1 | (88) | 57:43 | 83.0:17.0 |
| 4-$O_2NC_6H_4$ | Ph | 10 | MeOH | rt | 16 | (45) | 60:40 | 66.5:33.5 |
| 4-$CF_3C_6H_4$ | Ph | 10 | MeOH | rt | 18 | (74) | 74:26 | 96.5:3.5 |
| PhCH=CH | Ph | 10 | MeOH | rt | 24 | (70) | 78:22 | 99.0:1.0 |
| 1-Np | Ph | 20 | MeOH | rt | 48 | (66) | 63:37 | 83.5:16.5 |

$C_{7–12}$





**146** (20 mol %),
$H_2O$ (1 eq),
solvent, 21–24 h

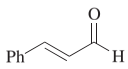


587

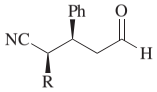
| $R^1$ | $R^2$ | Solvent | Temp (°) | | *anti*/*syn* | er |
|---|---|---|---|---|---|---|
| BnO | Me | $CHCl_3$ | –65 | (78) | 3:1 | 93.5:6.5 |
| Me | Me | toluene | –78 | (92) | 17:1 | 91.5:8.5 |
| Me | *n*-Pr | DME | –40 | (55) | 4:1 | 96.5:3.5 |
| Me | 4-$ClC_6H_4$ | cyclohexane | –60 | (74) | 3:1 | 99.0:1.0 |
| *c*-$C_5H_9CH_2$ | Me | $CH_2Cl_2$ | –78 | (68) | 10:1 | 94.0:6.0 |
| Ph | Me | THF | –78 | (69) | >20:1 | 96.5:3.5 |

$C_{8–9}$





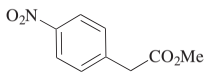
**145b** (10 mol %),
4-$O_2NC_6H_4CO_2H$ (10 mol %)
MeOH, rt

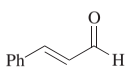


858

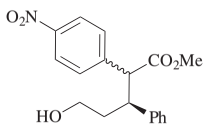
| R | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| 2-$MeO_2CC_6H_4$ | 72 | (76) | 51:49 | 95.0:5.0 | 94.0:6.0 |
| 4-$MeO_2CC_6H_4$ | 72 | (88) | 54:46 | 94.5:5.5 | 97.5:2.5 |
| 2-$O_2NC_6H_4$ | 24 | (92) | 64:36 | 85.5:14.5 | 98.5:1.5 |
| 4-$O_2NC_6H_4$ | 36 | (78) | 51:49 | 85.5:14.5 | — |
| 2-$NCC_6H_4$ | 24 | (98) | 61:39 | 94.0:6.0 | 96.5:3.5 |
| 4-$NCC_6H_4$ | 24 | (88) | 60:40 | 86.5:13.5 | — |

$C_8$





1. *ent*-**145b** (10 mol %),
   TBAB (1 eq), $CH_2Cl_2$, 24 h
2. $NaBH_4$, $CeCl_3$, EtOH
3. KOH, $H_2O$, DMF,
   ultrasonic bath, 9 h



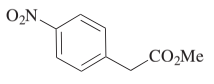
(90) dr 1:1 er 95.0:5.0 859

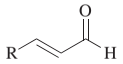
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

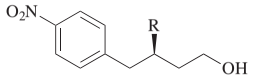
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_8$





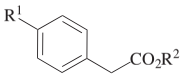
1. *ent*-**145b** (10 mol %), TBAB (1 eq), $CH_2Cl_2$
2. $NaBH_4$, $CeCl_3$, EtOH
3. KOH, $H_2O$, DMF, ultrasonic bath, 9h

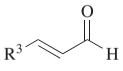


859

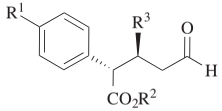
| R | Time (h) | | er |
|---|---|---|---|
| Me | 24 | (71) | 95.0:5.0 |
| Et | 24 | (61) | 95.0:5.0 |
| *n*-Pr | 66 | (52) | 95.5:4.5 |
| *i*-Pr | 66 | (59) | 97.0:3.0 |
| *n*-Bu | 96 | (55) | 98.0:2.0 |
| Ph | 2 | (66) | 94.0:6.0 |
| 4-$MeOC_6H_4$ | 48 | (68) | 95.0:5.0 |
| 4-$O_2NC_6H_4$ | 48 | (55) | 82.0:18.0 |

$C_{8-9}$





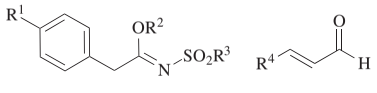
**145b** (10 mol %), 4-$O_2NC_6H_4CO_2H$ (10 mol %), MeOH, rt



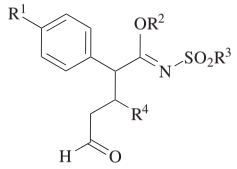
858

| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|---|
| $O_2N$ | Me | 2-$C_4H_3O$ | 96 | (96) | 55:45 | 90.5:9.5 | 91.0:9.0 |
| $O_2N$ | Me | Ph | 48 | (86) | 52:48 | 98.0:2.0 | 98.0:2.0 |
| $O_2N$ | Me | 4-$BrC_6H_4$ | 72 | (78) | 52:48 | 92.0:8.0 | 98.0:2.0 |
| $O_2N$ | Me | 4-$ClC_6H_4$ | 72 | (99) | 53:47 | 91.5:8.5 | 97.0:3.0 |
| $O_2N$ | Me | 3,4-$Cl_2C_6H_3$ | 72 | (98) | 56:44 | 91.5:8.5 | 98.5:1.5 |
| $O_2N$ | Me | 4-$FC_6H_4$ | 72 | (62) | 54:46 | 98.0:2.0 | 83.0:17.0 |
| $O_2N$ | Me | 3-$MeOC_6H_4$ | 72 | (86) | 52:48 | 90.5:9.5 | 93.5:6.5 |
| $O_2N$ | Me | 3,4-$(MeO)_2C_6H_3$ | 72 | (89) | 74:26 | 95.5:4.5 | 90.0:10.0 |
| $O_2N$ | Me | 2-$O_2NC_6H_4$ | 72 | (89) | 55:45 | 96.5:3.5 | 98.0:2.0 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $O_2N$ | Me | 4-$O_2NC_6H_4$ | 60 | (99) | 55:45 | 96.5:3.5 | 96.5:3.5 |
| $O_2N$ | Me | 4-$MeC_6H_4$ | 72 | (92) | 55:45 | 98.0:2.0 | 90.5:9.5 |
| $O_2N$ | Et | Ph | 72 | (91) | 61:39 | 91.0:9.0 | 90.0:10.0 |
| $O_2N$ | Bn | Ph | 72 | (45) | 63:37 | 97.5:2.5 | 97.5:2.5 |
| $MeO_2C$ | Me | Ph | 72 | (32) | 53:47 | 97.0:3.0 | 95.5:4.5 |



**207c** (10 mol %),
$PhCO_2H$ (10 mol %),
MeOH, rt, 16 h

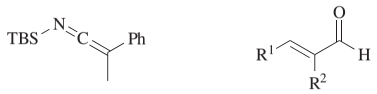


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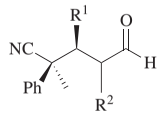
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|---|---|
| H | Me | 4-$MeC_6H_4$ | Ph | (38) | 57:43 | — | 71.5:28.5 |
| H | Bn | Me | Ph | — | 55:45 | — | — |
| H | Bn | 4-$MeC_6H_4$ | Me | (66) | 58:42 | 76.0:24.0 | 72.5:27.5 |
| H | Bn | 4-$MeC_6H_4$ | Ph | (85) | 55:45 | 98.5:1.5 | 99.0:1.0 |
| MeO | Bn | 4-$MeC_6H_4$ | Ph | (50) | 57:43 | — | — |
| Me | Bn | 4-$MeC_6H_4$ | Ph | (50) | 57:43 | 97.5:2.5 | 97.0:3.0 |
| $CF_3$ | Bn | 4-$MeC_6H_4$ | Ph | (87) | 60:40 | 93.5:6.5 | 97.0:3.0 |



$C_9$



**498** (5 mol %),
$SiCl_4$ (1 eq),
DIPEA (1.1 eq),
$CH_2Cl_2$, –78°, 2 h



861

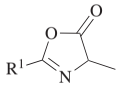
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | H | (78) | 81:19 | 79.0:21.0 |
| Ph | H | (84) | 90:10 | 70.0:30.0 |
| Ph | Me | (86) | 84:10:4:2 | 69.0:31.0 |
| 2-$MeOC_6H_4$ | H | (83) | 68:32 | 86.0:14.0 |
| 4-$MeOC_6H_4$ | H | (79) | 91:9 | 72.0:28.0 |
| 4-$Me_2NC_6H_4$ | H | (94) | 68:32 | 59.0:41.0 |

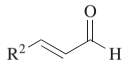
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

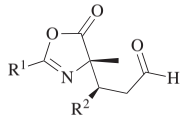
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{10}$





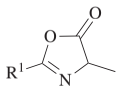
**145d** (10 mol %), toluene, 0°

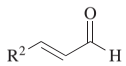


862

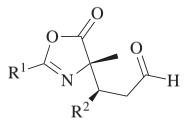
| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Ph | Me | 5 | (72) | >20:1 | 98.5:1.5 |
| Ph | Et | 5 | (77) | >20:1 | 99.5:0.5 |
| Ph | *i*-Pr | 9 | (70) | 14:1 | 99.5:0.5 |
| Ph | *i*-Bu | 7 | (74) | >20:1 | 96.0:4.0 |
| Ph | *c*-$C_6H_{11}$ | 30 | (66) | 7.6:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | Me | 6 | (74) | >20:1 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | *c*-$C_6H_{11}$ | 30 | (63) | 9.2:1 | 99.0:1.0 |
| 4-$MeOC_6H_4$ | Ph | 18 | (73) | 2.2:1 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | 4-$ClC_6H_4$ | 16 | (83) | 2.2:1 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | 4-$MeOC_6H_4$ | 17 | (76) | 1.7:1 | 86.5:13.5 |
| 4-$MeOC_6H_4$ | 2-Np | 18 | (73) | 2.0:1 | 98.5:1.5 |

$C_{10-17}$





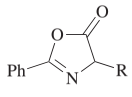
**207c** (10 mol %), toluene, rt

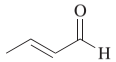


166

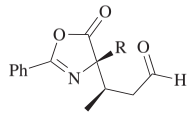
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| Ph | Et | (78) | 5:1 | 96.5:3.5 |
| $Ph_2CH$ | Me | (59) | 5:1 | 95.0:5.0 |
| $Ph_2CH$ | Et | (70) | >10:1 | 98.0:2.0 |
| $Ph_2CH$ | *n*-Pr | (40) | >10:1 | 96.5:3.5 |
| $Ph_2CH$ | (*E*)-$CH_3CH$=CH | (55) | >10:1 | 96.0:4.0 |
| $Ph_2CH$ | *n*-$C_6H_{13}$ | (52) | >10:1 | 97.0:3.0 |
| $Ph_2CH$ | (*Z*)-EtCH=$CH(CH_2)_2$ | (38) | >10:1 | 97.0:3.0 |
| $Ph_2CH$ | Ph | (47) | 6:1 | 97.0:3.0 |

$C_{11–18}$





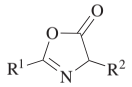
**145d** (10 mol %), toluene, 0°

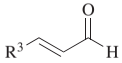


862

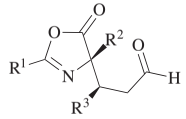
| R | Time (h) | | dr | er |
|---|---|---|---|---|
| $MeSCH_2CH_2$ | 3 | (89) | >20:1 | 96.0:4.0 |
| *i*-Bu | 3 | (74) | 9.3:1 | 95.5:4.5 |
| Bn | 2 | (83) | 11:1 | 98.0:2.0 |
| $C_8H_6NCH_2$ | 2 | (62) | 5.2:1 | 98.5:1.5 |

$C_{11–16}$





**207c** (10 mol %), toluene, rt



166

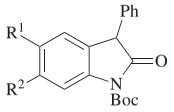
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| Ph | $MeS(CH_2)_2$ | Et | (73) | 3:1 | 97.0:3.0 |
| Ph | *i*-Pr | Et | (81) | 1.2:1 | 98.0:2.0 |
| *t*-Bu | Ph | Et | (71) | 5:2 | 95.5:4.5 |
| Ph | *i*-Bu | Me | (82) | 3:1 | 95.5:4.5 |
| Ph | *i*-Bu | $BnOCH_2$ | (53) | 2:1 | 92.0:8.0 |
| Ph | *i*-Bu | Et | (91) | 4:1 | 97.0:3.0 |
| Ph | *i*-Bu | *n*-Pr | (88) | 7:3 | 91.5:8.5 |
| Ph | *i*-Bu | (Z)-EtCH=CH$(CH_2)_2$ | (76) | 2:1 | 96.5:3.5 |
| Ph | *i*-Bu | Ph | (46) | 1:1 | 96.0:4.0 |
| Ph | *i*-Bu | 2-$HOC_6H_4$ | (36) | >20:1 | 93.0:7.0 |
| Ph | *i*-Bu | 2-$O_2NC_6H_4$ | (72) | 3:1 | 96.5:3.5 |
| Ph | *i*-Bu | *n*-$C_7H_{15}$ | (87) | 3:1 | 96.0:4.0 |
| 2-$ClC_6H_4$ | *i*-Bu | Et | (54) | 2:1 | 94.0:6.0 |
| Ph | Bn | Et | (75) | 3:1 | 98.0:2.0 |
| 4-$MeC_6H_4$ | Ph | Et | (85) | 7:3 | 96.5:3.5 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
C. α,β-UNSATURATED ALDEHYDES AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

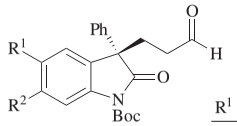
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{14}$





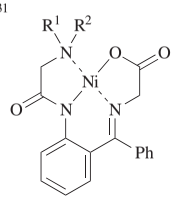
**466** (3 mol %), $PhCO_2K$ (5 eq), toluene, –60°, 24 h

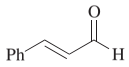


| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| H | H | (93) | 95.0:5.0 |
| H | Cl | (98) | 95.0:5.0 |
| F | H | (99) | 95.0:5.0 |

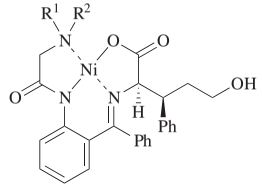
221

$C_{19–31}$





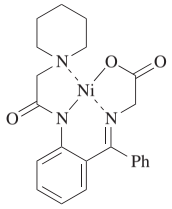
1. **145b** (10 mol %), $PhCO_2Li$ (20 mol %), $CH_2Cl_2$/MeOH (1:5), rt, 24 h
2. $NaBH_4$, MeOH

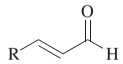


| $R^1$ | $R^2$ | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| Me | Me | (92) | 1.6:1 | 90.5:9.5 | 99.5:0.5 |
| *i*-Pr | *i*-Pr | (83) | 1.3:1 | 98.0:2.0 | 98.5:1.5 |
| Me | Bn | (44) | 1.3:1 | 94.5:5.5 | 99.5:0.5 |
| Bn | Bn | (25) | 1.6:1 | 87.5:12.5 | 89.0:11.0 |

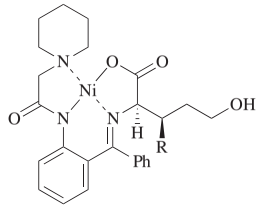
863

$C_{22}$





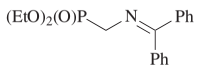
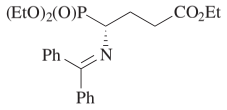
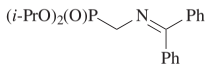
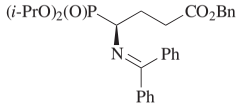
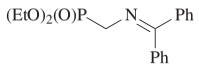
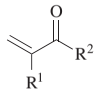
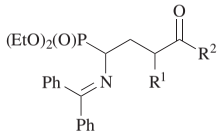
1. **145b** (10 mol %), $PhCO_2Li$ (20 mol %), $CH_2Cl_2$/MeOH (1:5), rt
2. $NaBH_4$, MeOH



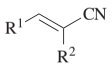
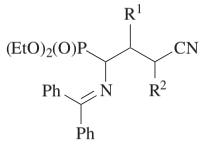
863

| R | Time (h) | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| Ph | 24 | (98) | 2:1 | 97.5:2.5 | 97.5:2.5 |
| 4-$BrC_6H_4$ | 48 | (94) | 2.2:1 | 94.5:5.5 | 94.5:5.5 |
| 2-$ClC_6H_4$ | 72 | (52) | 1.9:1 | 97.5:2.5 | 96.0:4.0 |
| 4-$ClC_6H_4$ | 48 | (88) | 2.3:1 | 95.5:4.5 | 99.5:0.5 |
| 4-$FC_6H_4$ | 72 | (59) | 1.5:1 | 96.0:4.0 | 98.0:2.0 |
| 2-$MeOC_6H_4$ | 24 | (96) | 49:1 | 95.5:4.5 | — |
| 3-$MeOC_6H_4$ | 24 | (99) | 2.6:1 | 95.0:5.0 | >99.5:0.5 |
| 4-$MeOC_6H_4$ | 24 | (85) | 6.7:1 | 95.0:5.0 | — |
| 2,3-$(MeO)_2C_6H_3$ | 24 | (93) | 19:1 | 97.5:2.5 | — |
| 2,4-$(MeO)_2C_6H_3$ | 24 | (95) | 24:1 | 94.0:6.0 | — |
| 2-$MeC_6H_4$ | 24 | (99) | 10:1 | 95.5:4.5 | 95.5:4.5 |
| 3-$MeC_6H_4$ | 48 | (93) | 2.4:1 | 96.0:4.0 | 97.5:2.5 |
| 4-$MeC_6H_4$ | 24 | (94) | 5.7:1 | 94.5:5.5 | 91.0:9.0 |
| 2-Np | 24 | (98) | 3.8:1 | 93.56.5 | 85.5:14.5 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS

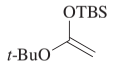
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_1$ | | | | |
|  |  | **472a** (10 mol %), *t*-BuONa (2 eq), toluene, –78°, 0.25 h |  (46) er 57.5:42.5 | 864 |
|  |  | **456** (2 mol %), $CsOH•H_2O$ (2 eq), mesitylene, –20° |  (93) er 92.5:7.5 | 222 |
|  |  | **470** (10 mol %), *t*-BuONa (1.3 eq), toluene, –75° |  | 865 |

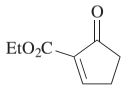
| $R^1$ | $R^2$ | | dr | er (major) | er (minor) |
|---|---|---|---|---|---|
| H | *t*-BuO | (92) | — | 60.5:29.5 | — |
| H | $Me_2N$ | (93) | — | 72.0:28.0 | — |
| Me | *t*-BuO | (80) | 68:32 | 66.5:33.5 | 65.5:34.5 |

| | | | | | |
|---|---|---|---|---|---|
|  | **470** (10 mol %), *t*-BuONa (1.3 eq), toluene, –75° |  | | | 865 |

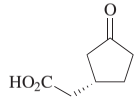
| $R^1$ | $R^2$ | | dr | er (major) | er (minor) | Config. |
|---|---|---|---|---|---|---|
| H | H | (75) | — | 97.5:2.5 | — | (*S*) |
| H | Me | (86) | 99.3:0.7 | 98.0:2.0 | 73.0:27.0 | (1*S*,3*R*) |
| Ph | H | (91) | 89:11 | 85.5:14.5 | 69.0:31.0 | — |

$C_2$

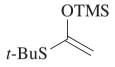


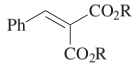




1. **472a** (10 mol %), $TiCl_2(Oi\text{-}Pr)_2$, toluene, 4 Å MS, rt
2. HCl, reflux

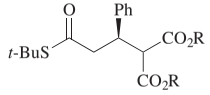



866



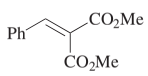




**151** (10 mol %), HFIP (2 eq), $CH_2Cl_2$

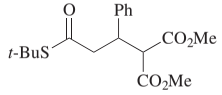



404

| R | Temp | Time | Conv. (%) | er |
|---|---|---|---|---|
| Me | –78° | 16 h | >98 | 95.5:4.5 |
| Me | –20° | 10 h | >98 | 89.0:11.0 |
| Me | rt | 15 s | >98 | 80.0:20.0 |
| Et | –78° | 16 h | 30 | 96.5:3.5 |
| Et | –20° | 10 h | >98 | 94.0:6.0 |
| Et | rt | 15 s | >98 | 85.0:15.0 |
| *i*-Pr | rt | 15 s | 80 | 90.0:10.0 |
| *i*-Bu | –78° | 16 h | 24 | 97.0:3.0 |
| *i*-Bu | –20° | 10 h | 50 | 94.0:6.0 |
| *i*-Bu | rt | 15 s | 70 | 89.5:10.5 |



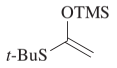
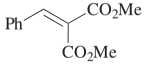
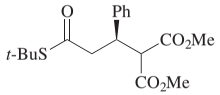
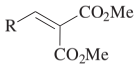
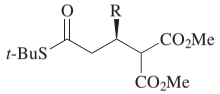

Catalyst (20 mol %), HFIP, $CH_2Cl_2$/toluene –78°, 2 h



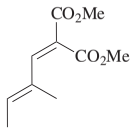

867

| Catalyst | | er | Config. |
|---|---|---|---|
| **151** | (99) | >95.0:5.0 | (*R*) |
| **479a** | (67) | 78.0:22.0 | (*S*) |
| **479b** | (55) | 85.0:15.0 | (*S*) |
| **479c** | (–) | 89.5:10.5 | (*S*) |

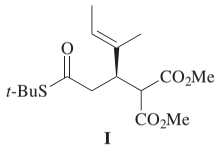
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_2$ | | | | |
|  |  | **479b** (10 mol %), HFIP (2 eq), toluene/$CH_2Cl_2$ (3:1), –78° |  (55) er 85.0:15.0 | 868 |
| |  | **151** (*x* mol %), HFIP (2 eq), toluene/$CH_2Cl_2$ (3:1), –78° |  | |

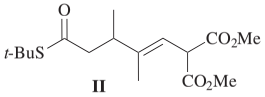
| R | *x* | Time (h) | | er | Refs. |
|---|---|---|---|---|---|
| Me | 10 | 5 | (91) | 71.5:28.5 | 404, 869 |
| Et | 10 | 5 | (82) | 61.0:39.0 | 404 |
| *n*-Pr | 10 | 5 | (87) | 63.5:36.5 | 404 |
| *i*-Pr | 10 | 6 | (93) | 96.5:3.5 | 404, 869 |
| *i*-Bu | 10 | 8 | (99) | 66.5:33.5 | 404 |
| *t*-Bu | 10 | 8 | (89) | 95.0:5.0 | 404, 869 |
| 2-$C_4H_3O$ | 10 | 5 | (88) | 97.0:3.0 | 404, 869 |
| *c*-$C_6H_{11}$ | 5 | 12 | (96) | 96.5:3.5 | 404, 869 |
| *c*-$C_6H_{11}$ | 10 | 5 | (95) | 97.5:2.5 | 404, 869 |
| Ph | 10 | 3 | (91) | 96.5:3.5 | 404, 869 |
| 2-$MeOC_6H_4$ | 10 | 12 | (92) | 99.5:0.5 | 404, 869 |
| *N*-Ts-3-indolyl | 20 | 48 | (99) | 93.0:7.0 | 404, 869 |
| 1-Np | 10 | 16 | (82) | 50.0:50.0 | 404 |
| 2-Np | 10 | 10 | (90) | 96.5:3.5 | 404, 869 |



**151** (10 mol %), HFIP (2 eq), toluene/$CH_2Cl_2$ (3:1), –78°



**I**

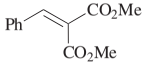


**II**

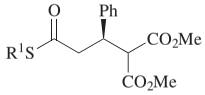
(92) **I/II** = 90:10
er **I** 97.0:3.0

404



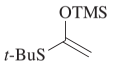


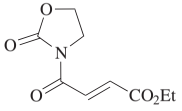
**151** (10 mol %), HFIP (2 eq), $CH_2Cl_2$, –78°



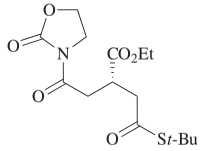
404

| $R^1$ | $R^2$ | Conv. (%) | er |
|---|---|---|---|
| *t*-Bu | TES | 10 | 96.0:4.0 |
| Ph | TMS | 60 | 86.5:13.5 |



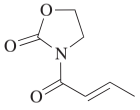


**151** (10 mol %), $CH_2Cl_2$

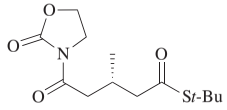


(86) er 94.5:5.5

55



**151** (10 mol %), HFIP, $CH_2Cl_2$, –20°, 4 d



(13) er 72.0:28.0

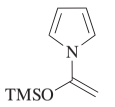
55

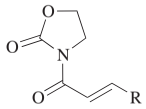
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

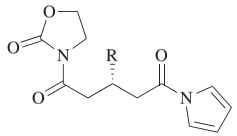
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_2$



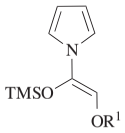



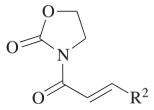

**151** (10 mol %), HFIP, $CH_2Cl_2$, –20°



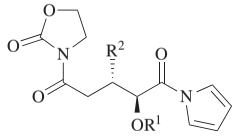

| R | Time (min) | | er |
|---|---|---|---|
| Me | 26 | (90) | 95.5:4.5 |
| $EtO_2C$ | 68 | (92) | 97.5:2.5 |
| Ph | 120 | (94) | 95.0:5.0 |

55



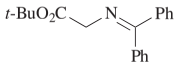



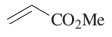

**151** (10 mol %), HFIP, $CH_2Cl_2$, –20°



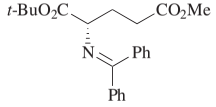

| $R^1$ | $R^2$ | | *anti*/*syn* | er |
|---|---|---|---|---|
| TBS | Me | (75) | 98:2 | 97.5:2.5 |
| Bn | Me | (86) | 98:2 | 99.5:0.5 |
| Bn | $EtO_2C$ | (93) | 92:8 | 99.5:0.5 |

55



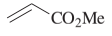




**405b** (10 mol %), $CsOH•H_2O$, $CH_2Cl_2$, –78°

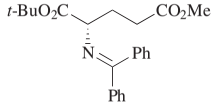



(95) er 92.5:7.5

206

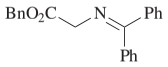



**446** (10 mol %), mesitol (10 mol %), KOH, $CH_2Cl_2$, –78°, 8 h



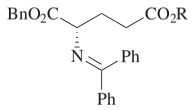

(95) er 99.0:1.0

870



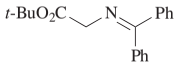


**449** (10 mol %), $Cs_2CO_3$ (50 mol %), $C_6H_5Cl$ , –30°



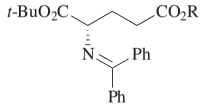
| R | Time (h) | | er |
|---|---|---|---|
| Me | 12 | (96) | 94.0:6.0 |
| Et | 13 | (92) | 94.0:6.0 |
| *n*-Bu | 24 | (44) | 94.0:6.0 |
| Bn | 11 | (96) | 93.5:6.5 |

836





**451a** (10 mol %), $Cs_2CO_3$ (10 eq), $C_6H_5Cl$, –30°

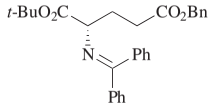


| R | Time (h) | | er |
|---|---|---|---|
| Me | 20 | (86) | 87.5:12.5 |
| Et | 26 | (88) | 91.0:9.0 |
| *n*-Bu | 22 | (85) | 89.0:11.0 |

838, 871



**451b** (10 mol %), $Cs_2CO_3$ (50 mol %), $C_6H_5Cl$, –30°

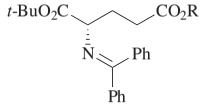


(87) er 90.5:9.5

872, 838



**452** (20 mol %), 20°, 3 d



| R | | er |
|---|---|---|
| Me | (98) | 96.5:3.5 |
| Et | (85) | 98.5:1.5 |

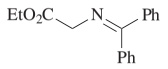
839

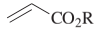
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

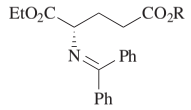
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_2$



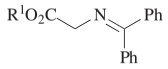


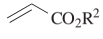
**453** (20 mol %), *t*-BuOK (0.2 eq), $CH_2Cl_2$, –78°



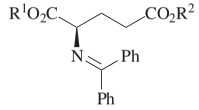
| R | Time (h) | | er |
|---|---|---|---|
| Me | 24 | (77) | 90.0:10.0 |
| Et | 24 | (76) | 93.5:6.5 |
| *t*-Bu | 3 | (80) | 91.0:9.0 |

223



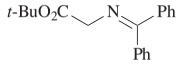


**455** (20 mol %), THF, –78 to –10°, 48 h



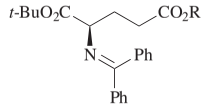
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| Et | Et | (99) | 53.2:46.8 |
| *t*-Bu | Me | (95) | 57.8:42.2 |
| *t*-Bu | Et | (99) | 65.2:34.8 |
| *t*-Bu | *t*-Bu | (98) | 65.0:35.0 |

841





**456** (*x* mol %), $Cs_2CO_3$ (5 eq), mesitylene, –20°

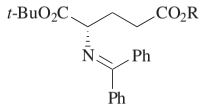


| R | *x* | Time (h) | | er |
|---|---|---|---|---|
| Et | 2 | 6 | (71) | 98.5:1.5 |
| Bn | 0.03 | 12 | (75) | 95.5:4.5 |
| Bn | 0.1 | 6 | (77) | 96.5:3.5 |
| Bn | 2 | 4 | (80) | 98.0:2.0 |

222



**459** (10 mol %), EtOAc, rt

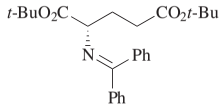


| R | Time (h) | | er |
|---|---|---|---|
| Me | 1 | (99) | 99.0:1.0 |
| *n*-Bu | 1.5 | (99) | 99.0:1.0 |
| *t*-Bu | 12 | (98) | 99.5:0.5 |
| Bn | 1 | (97) | 99.0:1.0 |

842



**473** (10 mol %), *t*-BuOMe (50 mol %), $C_6H_5Cl$ , –60°, 26 h

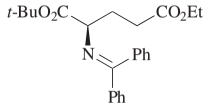


(73) er 88.5:11.5

873

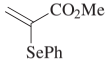


**475** (20 mol %), 20°, 5 d

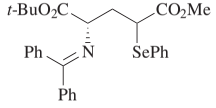


(79) er 98.5:1.5

874



**476** (10 mol %), 50% of KOH, $CH_2Cl_2$, –20°, 1 h



(99) er 98.0:2.0

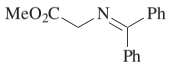
875

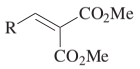
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

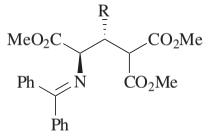
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_2$



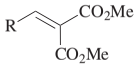


**471** (11 mol %), $Cu(OAc)_2$ (10 mol %), *t*-BuOK (10 mol %), THF, 4 Å MS, rt

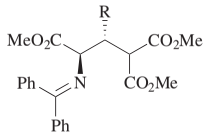


876

| R | Time (h) | | *anti*/*syn* | er (*anti*) | er (*syn*) |
|---|---|---|---|---|---|
| 2-$C_4H_3O$ | 10 | (93) | 82:18 | 90.5:9.5 | 93.0:7.0 |
| 3-$C_5H_4N$ | 10 | (88) | 80:20 | 89.0:11.0 | 90.0:10.0 |
| Ph | 10 | (89) | 88:12 | 91.5:8.5 | 95.0:5.0 |
| 4-$BrC_6H_4$ | 10 | (98) | 87:13 | 90.5:9.5 | 94.0:6.0 |
| 3-$ClC_6H_4$ | 10 | (90) | 85:15 | 89.5:10.5 | 94.5:5.5 |
| 4-$ClC_6H_4$ | 10 | (86) | 87:13 | 90.5:9.5 | 93.5:6.5 |
| 4-$MeOC_6H_4$ | 10 | (82) | 87:13 | 90.5:9.5 | 93.0:7.0 |
| 4-$O_2NC_6H_4$ | 24 | (83) | 82:18 | 90.0:10.0 | 93.0:7.0 |
| 2-$MeC_6H_4$ | 10 | (82) | 82:18 | 90.0:10.0 | 95.0:5.0 |
| 4-$MeC_6H_4$ | 10 | (93) | 89:11 | 91.0:9.0 | 91.5:8.5 |
| 4-$CF_3C_6H_4$ | 10 | (96) | 89:11 | 90.0:10.0 | 94.0:6.0 |

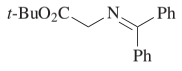


**474** (11 mol %),
$Cu(OAc)_2$ (10 mol %),
*t*-BuOK, THF, 4 Å MS, rt



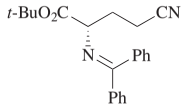
877

| R | | *anti*/*syn* | er (*anti*) | er (*syn*) |
|---|---|---|---|---|
| *i*-Bu | (94) | 83:17 | 95.5:4.5 | 90.5:9.5 |
| 2-$C_4H_3O$ | (95) | 67:33 | 96.5:3.5 | 95.5:4.5 |
| 3-$C_5H_4N$ | (91) | 77:33 | 95.0:5.0 | 92.0:8.0 |
| Ph | (85) | 85:15 | 95.0:5.0 | 77.5:22.5 |
| 4-$BrC_6H_4$ | (98) | 96:4 | 97.5:2.5 | 97.5:2.5 |
| 3-$ClC_6H_4$ | (91) | 87:13 | 94.5:4.5 | 92.0:8.0 |
| 4-$ClC_6H_4$ | (94) | 91:9 | 96.5:3.5 | 78.5:21.5 |
| 4-$MeOC_6H_4$ | (82) | 88:12 | 94.5:4.5 | — |
| 4-$O_2NC_6H_4$ | (94) | 85:15 | 95.0:5.0 | 77.5:22.5 |
| 4-$MeC_6H_4$ | (87) | 87:13 | 95.0:5.0 | — |
| 4-$CF_3C_6H_4$ | (92) | 94:6 | 95.5:4.5 | 81.5:18.5 |





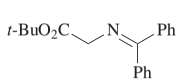
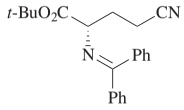
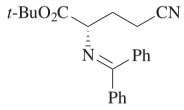
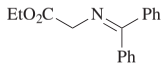
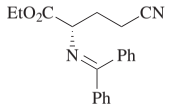
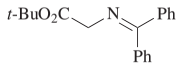
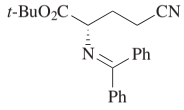
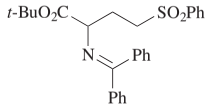
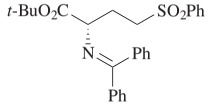
**405b** (10 mol %),
50% of KOH,
$CH_2Cl_2$, −55°, 15 h



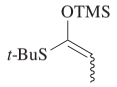
(85) er 95.5:4.5

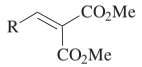
94

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

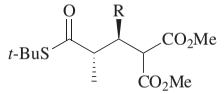
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_2$ | | | | |
|  |  | **446** (10 mol %), mesitol (10 mol %), KOH, $CH_2Cl_2$, –78°, 8 h |  (77) er 98.0:2.0 | 870 |
| |  | **452** (20 mol %), 20°, 5 d |  (79) er 77.5:22.5 | 839 |
|  |  | **453** (20 mol %), *t*-BuOK (0.2 eq), $CH_2Cl_2$, –78°, 1 d |  (70) er 73.0:27.0 | 223 |
|  |  | **459** (10 mol %), EtOAc, rt, 30 h |  (97) er 88.5:11.5 | 842 |
| |  | **446** (10 mol %), mesitol (10 mol %), KOH, $CH_2Cl_2$, –78°, 1.5 h |  (90) er 96.0:4.0 | 870 |
| |  | **459** (10 mol %), EtOAc, rt, 24 h |  (89) er 70.5:29.5 | 842 |

$C_3$



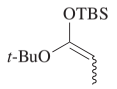



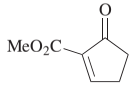

**151** (10 mol %),
HFIP (2 eq),
$CH_2Cl_2$, –78°



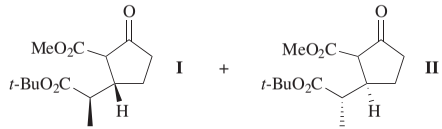

404

| R | (*E*)/(*Z*) | | *anti*/*syn* | er (*anti*) | er (*syn*) |
|---|---|---|---|---|---|
| Me | 97:3 | (—) | 29:71 | 84.0:16.0 | 65.0:35.0 |
| Me | 5:95 | (—) | 95:5 | 55.0:45.0 | 81.0:19.0 |
| Ph | 97:3 | (—) | 55:45 | <52.5:47.5 | <52.5:47.5 |
| Ph | 5:95 | (—) | 92:8 | 90.0:10.0 | 85.0:15.0 |



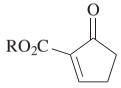




**140** (10 mol %),
$Cu(R)_2$ (10 mol %),
solvent, –78°, 2 h

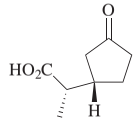



878

| R | Solvent | | *syn*/*anti* | er **I**/**II** |
|---|---|---|---|---|
| OTf | toluene | (63) | 9:1 | 83.0:17.0 |
| $SbF_6$ | $CH_2Cl_2$ | (45) | 60:1 | 20.0:80.0 |




1. Catalyst (10 mol %),
$TiCl_2(O\textit{i}\text{-Pr})_2$,
toluene, 4 Å MS, rt
2. HCl, reflux




866

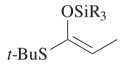
| R | Catalyst | | *syn*/*anti* | er |
|---|---|---|---|---|
| Me | **472a** | (38) | 97:3 | 71.5:28.5 |
| Me | **472b** | (50) | 98:2 | 73.5:26.5 |
| Et | **472a** | (55) | 96:4 | 58.0:42.0 |

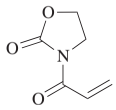
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

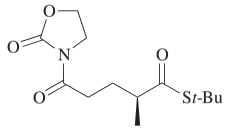
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



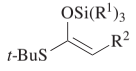
**151** (10 mol %), HFIP, $CH_2Cl_2$

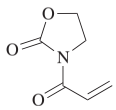



55

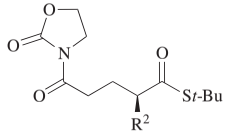
| R | Temp (°) | | er |
|---|---|---|---|
| Me | –70 | (80) | 84.5:15.5 |
| Et | –78 | (80) | 94.5:5.5 |
| Et | –70 | (80) | 94.5:5.5 |
| *i*-Pr | –70 | (61) | 94.0:6.0 |
| *i*-Pr | –20 | (80) | 93.0:7.0 |

$C_{4-5}$



**151** (10 mol %), HFIP, $CH_2Cl_2$

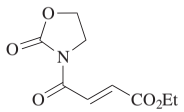



55

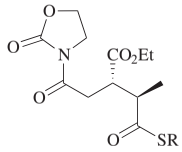
| $R^1$ | $R^2$ | Enol silane (*E*)/(*Z*) | Temp (°) | | er |
|---|---|---|---|---|---|
| *i*-Pr | Et | 90:10 | –78 | (94) | 83.0:17.0 |
| *i*-Pr | *i*-Pr | 95:5 | –20 | (84) | 96.0:4.0 |
| Ph | Et | 97:3 | –78 | (83) | 91.5:8.5 |
| Ph | *i*-Pr | 92:8 | –20 | (93) | 70.0:30.0 |

$C_3$



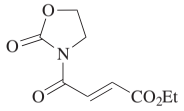




**151** (10 mol %),
additive, $CH_2Cl_2$

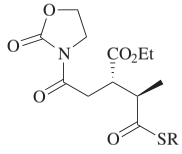



55

| R | Additive | Temp (°) | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|---|
| Me | none | –78 | 96 | (90) | 66:34 | 95.0:5.0 |
| Et | none | –78 | 96 | (91) | 75:25 | 96.0:4.0 |
| *t*-Bu | none | –78 | 96 | (73) | 99:1 | 98.5:1.5 |
| *t*-Bu | HFIP | –78 | 36 | (94) | 99:1 | 99.5:0.5 |
| *t*-Bu | HFIP | –20 | 2 | (95) | 93:7 | 94.5:5.5 |




**151** (10 mol %),
additive (1 eq), $CH_2Cl_2$




54

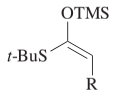
| R | Additive | Temp (°) | Time (h) | | *syn/anti* | er |
|---|---|---|---|---|---|---|
| Me | HFIP | –78 | 36 | (94) | >99:1 | 99.5:0.5 |
| Me | HFIP | –20 | 2 | (95) | 93:7 | 94.5:5.5 |
| *t*-Bu | none | –78 | 96 | (73) | >99:1 | 98.5:1.5 |

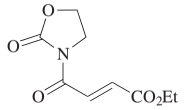
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

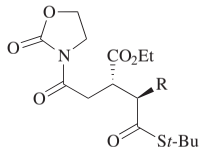
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{3-8}$



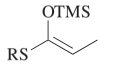

**151** (10 mol %), $CH_2Cl_2$, HFIP

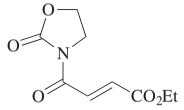



55

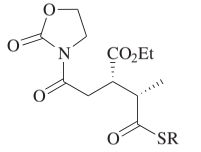
| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Me | –78 | 36 | (94) | 99:1 | 95.5:4.5 |
| Et | –78 | 96 | (67) | 91:9 | 95.0:5.0 |
| *c*-$C_5H_9CH_2$ | –20 | 48 | (92) | 73:27 | 99.5:0.5 |

$C_3$



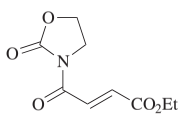




**151** (10 mol %), $CH_2Cl_2$, –78°

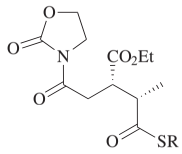



55

| R | | *anti*/*syn* | er |
|---|---|---|---|
| Me | (90) | 95:5 | 95.0:5.0 |
| Et | (77) | 86:14 | 95.5:4.5 |
| *t*-Bu | (65) | 78:22 | 98.0:2.0 |



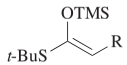
**151** (10 mol %),
additive (1 eq),
$CH_2Cl_2$, –78°

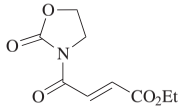


54

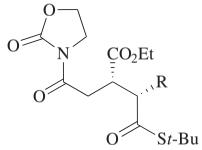
| R | Additive | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|---|
| Me | none | 48 | (97) | 5:95 | 95.0:5.0 |
| Me | HFIP | 2 | (93) | 10:90 | 91.5:8.5 |
| *t*-Bu | none | — | (61) | 22:78 | 98.0:2.0 |

$C_{3-8}$





**151** (10 mol %),
$CH_2Cl_2$, HFIP, –78°



55

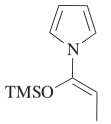
| R | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|
| Me | 2 | (93) | 90:10 | 91.5:8.5 |
| Et | 2 | (89) | 95:5 | 95.0:5.0 |
| *i*-Pr | 4.5 | (93) | 99:1 | 99.0:1.0 |
| *c*-$C_5H_9CH_2$ | 20 | (84) | 96.0:4.0 | 98.5:1.5 |

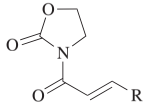
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

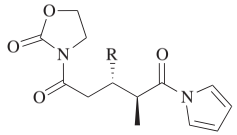
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_3$



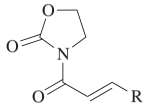




**151** (5 mol %), HFIP (1 eq), $CH_2Cl_2$, –78°

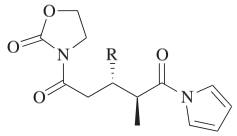



| R | | *syn*/*anti* | er |
|---|---|---|---|
| Me | (90) | >99:1 | 95.5:4.5 |
| $MeO_2C$ | (94) | 98:2 | 98.5:1.5 |

54



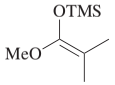

**151** (10 mol %), HFIP, $CH_2Cl_2$, –20°

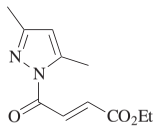



| R | Time | | *anti*/*syn* | er |
|---|---|---|---|---|
| Me | 5 min | (88) | 99:1 | 99.0:1.0 |
| $EtO_2C$ | 1 h | (91) | 97:3 | 97.0:3.0 |
| *i*-Pr | 24 h | (40) | 99:1 | 99.0:1.0 |
| (*E*)-MeCH=CH | 20 h | (85) | 99:1 | 97.0:3.0 |
| $MeCH{=}CHO_2C$ | 1 h | (80) | 98:2 | 98.5:1.5 |
| Ph | 16 h | (97) | 99:1 | 97.0:3.0 |

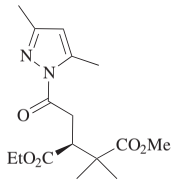
55

$C_4$



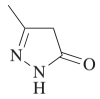



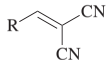

**158** (11 mol %), $Cu(OTf)_2$ (10 mol %), MeCN, –20°, 13 h



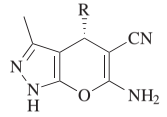

(91) er 93.0:7.0

408



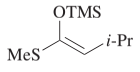


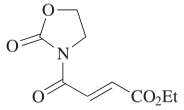
**1** (5 mol %),
**268** (5 mol %),
$CH_2Cl_2$, rt, 24h



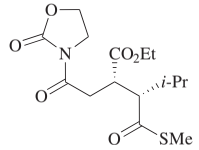
| R | | er | |
|---|---|---|---|
| *n*-$C_5H_{11}$ | (54) | 66.0:34.0 | 879 |
| Ph | (72) | 86.0:14.0 | |
| 2-$BrC_6H_4$ | (89) | 88.5:11.5 | |
| 3-$BrC_6H_4$ | (87) | 55.5:44.5 | |
| 4-$BrC_6H_4$ | (87) | 63.0:37.0 | |
| 2-$ClC_6H_4$ | (79) | 77.0:23.0 | |
| 4-$ClC_6H_4$ | (89) | 63.0:27.0 | |
| 2-$FC_6H_4$ | (66) | 79.5:20.5 | |
| 4-$FC_6H_4$ | (81) | 58.0:42.0 | |
| 4-$MeOC_6H_4$ | (89) | 67.0:33.0 | |
| 4-$O_2NC_6H_4$ | (86) | 67.0:33.0 | |
| 2-$MeC_6H_4$ | (85) | 60.5:39.5 | |
| 4-$MeC_6H_4$ | (85) | 56.5:43.5 | |
| 4-$NCC_6H_4$ | (89) | 63.0:37.0 | |

$C_5$





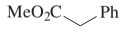
**170** (10 mol %),
HFIP (1 eq),
$CH_2Cl_2$, –78°, 4.5 h



(93) *anti*/*syn* > 99:1
er 99.0:1.0

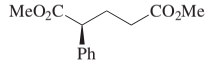
54

$C_8$





**480** (6.4 mol %),
*t*-BuOK (34 mol %),
toluene, –78°, 1 min

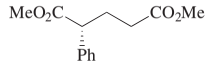


(82.3) er 92.2:7.8

880, 881



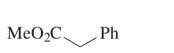
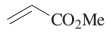
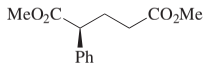
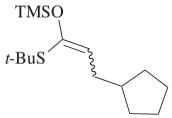
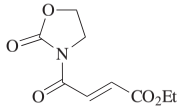
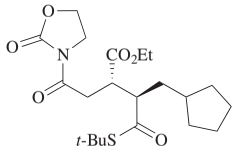
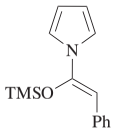
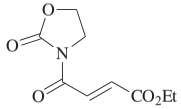
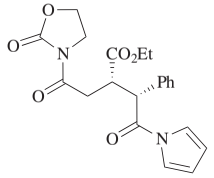
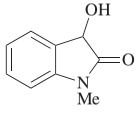
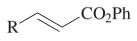
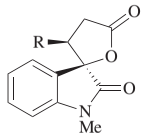
**482** (10 mol %),
*t*-BuOK (20 mol %),
toluene, –78°, 8 h



(83) er 91.0:9.0

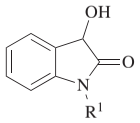
882

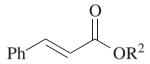
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | | Refs. |
|---|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | | |
| $C_8$ | | | | | |
|  |  | **486**, *t*-BuOK |  | (94) er 82.5:17.5 | 883 |
|  (*Z*)/(*E*) = 88:12 |  | **151** (10 mol %), HFIP (1 eq), $CH_2Cl_2$, –20° |  | (56) *anti*/*syn* = 73:27 er 99.5:0.5 | 54 |
|  |  | **151** (10 mol %), HFIP, $CH_2Cl_2$, –20° |  | (60) *anti*/*syn* = 75:25 er 99.5:0.5 | 55 |
|  |  | **434a** (5 mol %), $Et_2Zn$ (10 mol %), 0.6 M in toluene/MeCN, 40°, 36 h |  | | 884 |

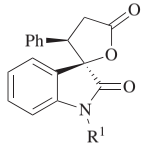
| R | | dr | er |
|---|---|---|---|
| H | (67) | — | 73.5:26.5 |
| Me | (67) | 4.3:1 | 77.0:23.0 |
| TIPSC≡C | (84) | 11.4:1 | 88.0:12.0 |
| *c*-$C_3H_5$ | (38) | 2.3:1 | 87.5:12.5 |
| MeCH=CH | (83) | 2.5:1 | 98.5:1.5 |
| 2-$C_4H_3O$ | (72) | 6.2:1 | 99.0:1.0 |
| 3-$C_4H_3O$ | (73) | 3.7:1 | 97.5:2.5 |

| | | | |
|---|---|---|---|
| 2-$C_4H_3S$ | (98) | 5.5:1 | 98.5:1.5 |
| 3,5-$Br_2C_6H_3$ | (65) | 3.2:1 | 98.5:1.5 |
| 2-$ClC_6H_4$ | (81) | 7.6:1 | 98.0:2.0 |
| 4-$ClC_6H_4$ | (85) | 3.2:1 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | (85) | 13:1 | 98.0:2.0 |
| 3,5-$(MeO)_2C_6H_3$ | (86) | 5.5:1 | 96.0:4.0 |
| 4-$NCC_6H_4$ | (84) | 4:1 | 99.5:0.5 |
| PhCH=CH | (82) | 6.6:1 | 99.0:1.0 |
| 1-Np | (84) | 4.5:1 | 97.5:2.5 |
| Ferrocenyl | (55) | 11.5:1 | 98.0:2.0 |



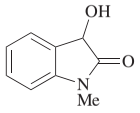


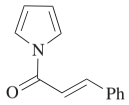
**434a** (5 mol %),
$Et_2Zn$ (10 mol %),
0.6 M in toluene/MeCN,
40°



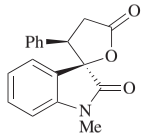
884

| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Me | Me | 37 | (72) | 6.7:1 | 97.5:2.5 |
| Me | Ph | 24 | (89) | 9.2:1 | 98.0:2.0 |
| allyl | Ph | 36 | (88) | 7.4:1 | 98.5:1.5 |
| MOM | Ph | 36 | (81) | 6.8:1 | 99.5:0.5 |
| Bn | Ph | 36 | (84) | 6.1:1 | 98.0:2.0 |
| PMB | Ph | 36 | (60) | 6.7:1 | 97.5:2.5 |



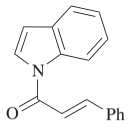


**434a** (5 mol %),
$Et_2Zn$ (10 mol %),
0.6 M in toluene/MeCN,
40°, 14 h

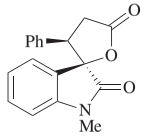


(91) dr 4.4:1
er 86.5:13.5

884



**434a** (5 mol %),
$Et_2Zn$ (10 mol %),
0.6 M in toluene/MeCN,
40°, 14 h



(92) dr 6:1
er 89.5:10.5

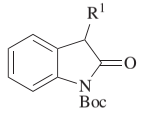
884

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

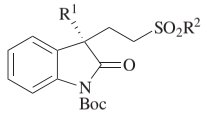
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{9-16}$





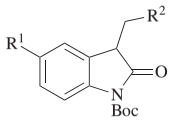
*ent*-**252b** (20 mol %), toluene, 4 Å MS



849

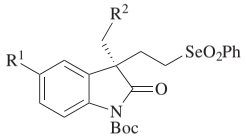
| $R^1$ | $R^2$ | Temp (°) | Time (d) | | er |
|---|---|---|---|---|---|
| Me | Ph | 4 | 4 | (48) | 92.0:8.0 |
| Ph | Me | –20 | 6 | (51) | 95.5:4.5 |
| Ph | Ph | –20 | 6 | (80) | 93.5:6.5 |
| 4-$MeOC_6H_4$ | Ph | –20 | 6 | (60) | 94.0:6.0 |
| 4-$MeC_6H_4$ | Me | –20 | 8 | (48) | 93.0:7.0 |
| 4-$MeC_6H_4$ | Ph | –20 | 6 | (75) | 91.0:9.0 |
| 3,5-$Me_2C_6H_3$ | Me | –20 | 8 | (55) | 93.5:6.5 |
| 3,5-$Me_2C_6H_3$ | Ph | –20 | 6 | (72) | 95.0:5.0 |

$C_{9-19}$





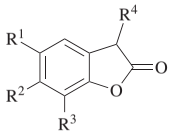
**389** (10 mol %), [bpy][$BF_4$], rt, 4 h

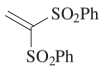


885

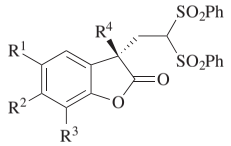
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| H | H | (88) | 97.5:2.5 |
| H | Me | (86) | 97.0:3.0 |
| Me | H | (84) | 95.5:4.5 |
| H | Et | (86) | 94.0:6.0 |
| H | Ph | (91) | 94.0:6.0 |
| H | 2-$MeOC_6H_4$ | (80) | 95.0:5.0 |
| H | 3-$MeOC_6H_4$ | (80) | 95.0:5.0 |
| H | 2-$MeC_6H_4$ | (86) | 95.5:4.5 |
| H | 3-$MeC_6H_4$ | (90) | 95.5:4.5 |
| H | 4-$MeC_6H_4$ | (86) | 92.5:7.5 |
| H | 1-Np | (86) | 94.0:6.0 |

$C_{9–20}$




**69b** (10 mol %),
$CH_2Cl_2$, –80°



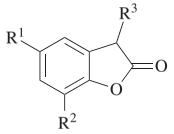

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Time (h) | | er |
|---|---|---|---|---|---|---|
| H | H | H | Me | 24 | (99) | 75.0:25.0 |
| H | H | H | Ph | 48 | (95) | 91.0:9.0 |
| H | H | H | 4-$ClC_6H_4$ | 32 | (99) | 72.5:27.5 |
| Br | H | H | Ph | 40 | (98) | 75.0:5.0 |
| I | H | H | Ph | 20 | (92) | 88.0:12.0 |
| MeO | H | H | Ph | 44 | (99) | 85.5:14.5 |
| H | H | H | Bn | 24 | (95) | 61.5:38.5 |
| H | H | Me | Ph | 24 | (96) | 99.5:0.5 |
| H | Me | H | Ph | 24 | (99) | 94.0:6.0 |
| Me | H | H | Ph | 40 | (99) | 85.5:14.5 |
| Me | H | H | 4-$ClC_6H_4$ | 40 | (99) | 88.5:11.5 |
| H | H | Et | Ph | 24 | (95) | 95.0:5.0 |
| Et | H | H | Ph | 36 | (90) | 91.5:8.5 |
| Et | H | H | 4-$ClC_6H_4$ | 48 | (95) | 82.0:18.0 |
| H | H | *i*-Pr | Ph | 24 | (96) | 95.0:5.0 |
| H | H | *i*-Bu | Ph | 24 | (93) | 96.0:4.0 |
| H | H | *t*-Bu | Ph | 24 | (95) | 98.5:1.5 |
| *t*-Bu | H | H | Ph | 40 | (99) | 87.5:12.5 |
| Ph | H | H | Ph | 24 | (98) | 92.5:7.5 |

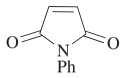
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

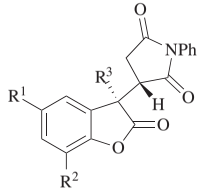
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{9–15}$





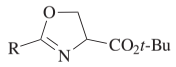
**164b** (10 mol %), $CH_2Cl_2$, 4 Å MS, 24–60 h



855

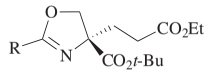
| $R^1$ | $R^2$ | $R^3$ | Temp (°) | | dr | er |
|---|---|---|---|---|---|---|
| H | H | Me | –40 | (90) | >20:1 | 86.5:13.5 |
| H | H | 4-$ClC_6H_4$ | –80 | (98) | >20:1 | 97.5:2.5 |
| H | MeO | Ph | –80 | (95) | >20:1 | 98.5:1.5 |
| Cl | H | Ph | –80 | (96) | >20:1 | 96.5:3.5 |
| MeO | H | Ph | –80 | (96) | 13:1 | 97.0:3.0 |
| Me | H | Ph | –80 | (95) | >20:1 | 98.5:1.5 |

$C_{10–18}$





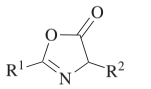
**377** (2.5 mol %), base (5 eq), $CH_2Cl_2$

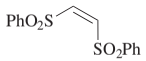


887

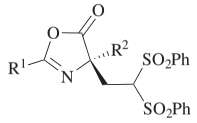
| R | Base | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| Ph | 50% of KOH | 0 | 2 | (95) | 71.5:28.5 |
| 1-Np | 50% of KOH | 0 | 2 | (90) | 90.0:10.0 |
| 1-Np | KOH | –40 | 5 | (77) | 87.5:12.5 |
| 1-Np | CsOH | –78 | 20 | (70) | 68.0:32.0 |
| 1-Np | BEMP | –60 | 20 | (93) | 98.5:1.5 |
| 1-Np | BTPP | –60 | 2 | (90) | 90.5:9.5 |
| 2-Np | 50% of KOH | 0 | 2 | (84) | 69.5:30.5 |
| 2-$PhC_6H_4$ | 50% of KOH | 0 | 6 | (94) | 53.5:46.5 |
| 1-$C_{14}H_9$ | 50% of KOH | 0 | 2 | (81) | 89.0:11.0 |
| 9-$C_{14}H_9$ | 50% of KOH | 0 | 20 | (32) | 69.0:31.0 |

$C_{10-13}$





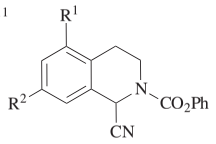
**164b** (10 mol %), toluene, 0°

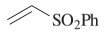


888

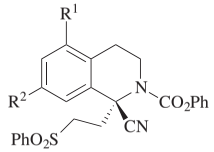
| $R^1$ | $R^2$ | Time (h) | | er |
|---|---|---|---|---|
| 2,4-$F_2C_6H_3$ | Me | 72 | (73) | 87.5:12.5 |
| Ph | *i*-Pr | 48 | (76) | 94.0:6.0 |
| 2-$ClC_6H_4$ | *i*-Pr | 48 | (63) | 87.5:12.5 |
| 2-$FC_6H_4$ | *i*-Pr | 48 | (81) | 87.0:13.0 |
| 2,4-$F_2C_6H_3$ | *i*-Pr | 48 | (73) | 97.5:2.5 |
| 2,6-$F_2C_6H_3$ | *i*-Pr | 24 | (50) | 77.0:23.0 |
| *t*-Bu | Ph | 96 | (45) | 87.5:12.5 |
| Ph | *t*-Bu | 48 | (82) | 84.0:16.0 |
| 2,4-$F_2C_6H_3$ | *i*-Bu | 72 | (97) | 87.0:13.0 |

$C_{10-11}$





**469** (1 mol %), 50% of $Cs_2CO_3$ toluene



889

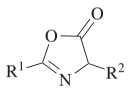
| $R^1$ | $R^2$ | Temp (°) | Time (h) | | er |
|---|---|---|---|---|---|
| H | H | 0 | 48 | (67) | 92.0:8.0 |
| H | Cl | –20 | 72 | (64) | 97.5:2.5 |
| H | F | 0 | 72 | (73) | 95.5:4.5 |
| Cl | H | –20 | 72 | (73) | 96.5:3.5 |
| Cl | Cl | –20 | 72 | (59) | 97.5:2.5 |
| H | Me | 0 | 72 | (47) | 94.0:6.0 |

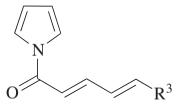
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

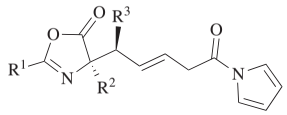
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{11–16}$





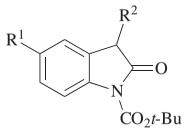
**483** (5 mol %),
toluene, 0°, 1–3 h

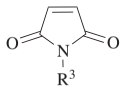


890

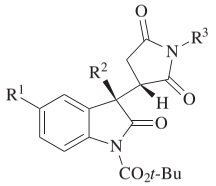
| $R^1$ | $R^2$ | $R^3$ | | dr | er |
|---|---|---|---|---|---|
| 2,6-$(MeO)_2C_6H_3$ | $MeS(CH_2)_2$ | Me | (95) | >20:1 | 95.0:5.0 |
| 2,6-$(MeO)_2C_6H_3$ | *i*-Bu | Me | (97) | >20:1 | 97.0:3.0 |
| Ph | Bn | Me | (99) | 12:1 | 97.0:3.0 |
| 2-$MeOC_6H_4$ | Bn | Me | (96) | 14:1 | 95.5:4.5 |
| 2,6-$(MeO)_2C_6H_3$ | Bn | Me | (97) | >20:1 | 99.0:1.0 |
| 2,6-$(MeO)_2C_6H_3$ | Bn | $BnOCH_2$ | (93) | >20:1 | 98.5:1.5 |
| 2,6-$(MeO)_2C_6H_3$ | Bn | $BzOCH_2$ | (96) | >20:1 | 97.0:3.0 |
| 2,6-$(MeO)_2C_6H_3$ | Bn | *n*-Pr | (94) | >20:1 | 99.0:1.0 |
| 2,6-$(MeO)_2C_6H_3$ | Bn | *i*-Bu | (95) | >20:1 | 99.0:1.0 |
| 2,6-$(MeO)_2C_6H_3$ | Bn | $CH_2=CH(CH_2)_3$ | (98) | >20:1 | 99.0:1.0 |
| 2,6-$(MeO)_2C_6H_3$ | Bn | *n*-$C_7H_{15}$ | (84) | >20:1 | 99.0:1.0 |
| 2,6-$(MeO)_2C_6H_3$ | Bn | $BnCH_2$ | (99) | >20:1 | 99.0:1.0 |
| 2,6-$(MeO)_2C_6H_3$ | 4-$MeOC_6H_4CH_2$ | Me | (98) | >20:1 | 99.0:1.0 |

$C_{11–20}$





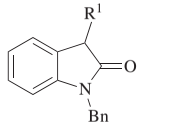
**252b** (20 mol %),
$CH_2Cl_2$, rt

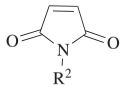


891

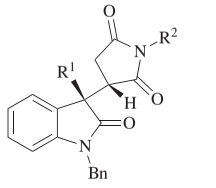
| $R^1$ | $R^2$ | $R^3$ | Time (h) | | dr | er |
|---|---|---|---|---|---|---|
| H | *i*-Pr | Ph | 36 | (67) | 99:1 | 97.0:3.0 |
| H | *n*-Bu | 4-$ClC_6H_4$ | 24 | (65) | 95:5 | 98.5:1.5 |
| F | Ph | Ph | 10 | (90) | 92:8 | 98.0:2.0 |
| H | 4-$FC_6H_4$ | Ph | 10 | (80) | 94:6 | 97.5:2.5 |
| H | 4-$MeOC_6H_4$ | 4-$ClC_6H_4$ | 10 | (75) | 90:10 | 97.0:3.0 |
| Me | Ph | 4-$ClC_6H_4$ | 10 | (73) | 90:10 | 98.0:2.0 |
| H | 4-$MeC_6H_4$ | Ph | 10 | (86) | 92:8 | 97.5:2.5 |
| H | Bn | 4-$ClC_6H_4$ | 10 | (87) | 63:37 | 97.0:3.0 |
| H | 3,5-$Me_2C_6H_3$ | Ph | 10 | (81) | 92:8 | 99.5:0.5 |
| H | 4-$PhC_6H_4$ | Ph | 10 | (87) | 94:6 | 98.5:1.5 |

$C_{12–18}$





**160b** (10 mol %),
toluene, –50°, 40–48 h



892

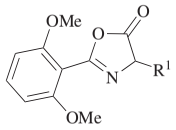
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3S$ | Bn | (97) | >99:1 | 97.0:3.0 |
| Bn | Et | (84) | >99:1 | 95.5:4.5 |
| Bn | Ph | (89) | 32:1 | 96.5:3.5 |
| Bn | 3-$BrC_6H_4$ | (89) | 32:1 | 96.0:4.0 |
| Bn | 4-$BrC_6H_4CH_2$ | (78) | >99:1 | 96.5:3.5 |
| Bn | 2-$ClC_6H_4CH_2$ | (88) | 18:1 | 96.0:4.0 |
| Bn | 2-$MeOC_6H_4CH_2$ | (92) | 32:1 | 96.0:4.0 |
| Bn | 4-$MeOC_6H_4CH_2$ | (81) | >99:1 | 96.0:4.0 |
| Bn | 4-*t*-$BuC_6H_4$ | (90) | 19:1 | 95.0:5.0 |
| 2-Np | Bn | (93) | >99:1 | 99.5:0.5 |

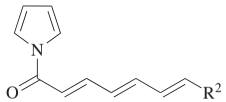
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

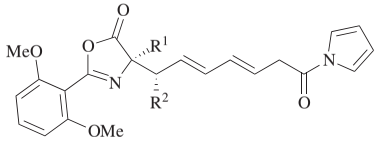
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{13–16}$





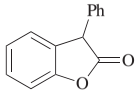
**483** (5 mol %), toluene, 0°, 1–3 h



890

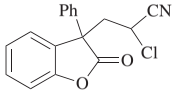
| $R^1$ | $R^2$ | | rr | dr | er |
|---|---|---|---|---|---|
| *i*-Bu | Me | (90) | >20:<1:1 | 8:1 | 99.5:0.5 |
| Bn | Me | (89) | >20:<1:1 | >20:1 | 99.5:0.5 |
| Bn | $BnOCH_2$ | (98) | 14:1:<1 | >20:1 | 99.0:1.0 |
| Bn | $n$-$C_7H_{15}$ | (94) | >20:<1:1 | 18:1 | 99.5:0.5 |
| 4-$MeOC_6H_4CH_2$ | Me | (90) | >20:<1:1 | >20:1 | 99.5:0.5 |

$C_{14}$





**439** (10 mol %), DCE, 0°, 6 h

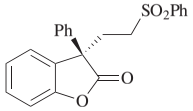


(80) dr 3:2 er 80.0:20.0

828



**69b** (10 mol %), $CH_2Cl_2$, –80°, 24 h

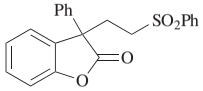


(48) er 62.0:38.0

886

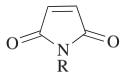


**439** (10 mol %), toluene, 0°, 7 d

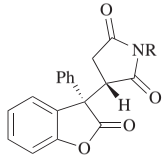


(80) er 67.5:32.5

828



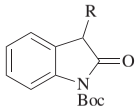
**164b** (10 mol %),
$CH_2Cl_2$, 4 Å MS,
24–60 h

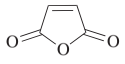


855

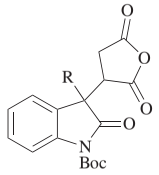
| R | Temp (°) | | dr | er |
|---|---|---|---|---|
| *c*-$C_6H_{11}$ | –40 | (97) | 15:1 | 98.5:1.5 |
| Ph | –80 | (98) | >20:1 | 98.0:2.0 |
| 3-$BrC_6H_4$ | –80 | (98) | >20:1 | 97.5:2.5 |
| 4-$BrC_6H_4$ | –80 | (99) | >20:1 | 96.0:4.0 |
| 3-$ClC_6H_4$ | –80 | (99) | >20:1 | 97.0:3.0 |
| 4-$ClC_6H_4$ | –80 | (98) | >20:1 | 97.0:3.0 |
| 4-$FC_6H_4$ | –80 | (98) | >20:1 | 97.0:3.0 |
| 4-$MeOC_6H_4$ | –80 | (91) | 16:1 | 96.5:3.5 |
| 4-$MeC_6H_4$ | –80 | (95) | >20:1 | 97.5:2.5 |
| 3-Cl-4-$MeC_6H_3$ | –80 | (94) | 15:1 | 95.5:4.5 |
| Bn | –40 | (92) | 7:1 | 95.5:4.5 |
| *n*-$C_8H_{17}$ | –40 | (95) | 16:1 | 97.5:2.5 |
| 2,4,6-$Me_3C_6H_2$ | –40 | (88) | 6:1 | 87.0:13.0 |
| 4-*t*-$BuC_6H_4$ | –80 | (96) | >20:1 | 96.0:4.0 |

$C_{14–15}$





**252b** (5 mol %),
$CH_2Cl_2$, rt, 6 h



891

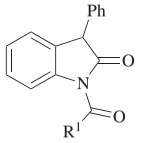
| R | | dr | er |
|---|---|---|---|
| 4-$FC_6H_4$ | (71) | 94:6 | 92.5:7.5 |
| 4-$MeC_6H_4$ | (76) | 95:5 | 92.5:7.5 |

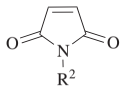
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

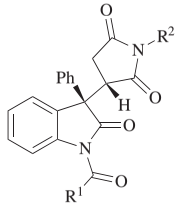
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{14}$





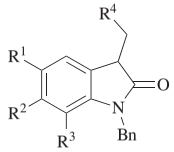
**252b** (20 mol %), $CH_2Cl_2$, rt, 10 h

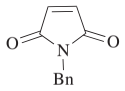


891

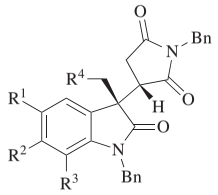
| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| EtO | Ph | (60) | 63:37 | 58.0:42.0 |
| *t*-BuO | *i*-Pr | (45) | 94:6 | 92.5:7.5 |
| *t*-BuO | $CH_2$=$CHCH_2$ | (64) | 89:11 | 95.5:4.5 |
| *t*-BuO | *c*-$C_6H_{11}$ | (65) | 89:11 | 98.0:2.0 |
| *t*-BuO | Ph | (58) | 90:10 | 98.0:2.0 |
| *t*-BuO | 3-$BrC_6H_4$ | (68) | 82:18 | 96.0:4.0 |
| *t*-BuO | 4-$BrC_6H_4$ | (89) | 91:9 | 99.0:1.0 |
| *t*-BuO | 3-$ClC_6H_4$ | (82) | 92:8 | 97.0:3.0 |
| *t*-BuO | 4-$ClC_6H_4$ | (74) | 94:6 | 98.0:2.0 |
| *t*-BuO | 3,4-$Cl_2C_6H_3$ | (50) | 87:13 | 97.0:3.0 |
| *t*-BuO | 4-$MeOC_6H_4$ | (92) | 95:5 | 98.0:2.0 |
| *t*-BuO | 3-$MeC_6H_4$ | (92) | 96:4 | 98.5:1.5 |
| Me | Ph | (36) | 53:47 | 50.5:49.5 |

$C_{15-16}$





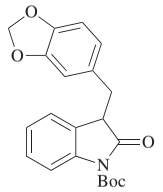
**160b** (10 mol %),
toluene, –50°, 40–48 h

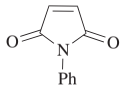


892

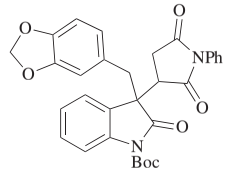
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | | dr | er |
|---|---|---|---|---|---|---|
| H | H | H | Ph | (97) | 49:1 | 97.5:2.5 |
| H | H | H | 2-$BrC_6H_4$ | (93) | >99:1 | >99.5:0.5 |
| H | H | H | 3-$BrC_6H_4$ | (88) | >99:1 | 96.5:3.5 |
| H | H | H | 4-$BrC_6H_4$ | (77) | >99:1 | 95.0:5.0 |
| H | H | H | 4-$ClC_6H_4$ | (75) | >99:1 | 95.0:5.0 |
| H | H | H | 2-$MeOC_6H_4$ | (88) | >99:1 | 98.0:2.0 |
| H | H | H | 3-$MeOC_6H_4$ | (77) | >99:1 | >99.5:0.5 |
| H | H | F | Ph | (92) | 32:1 | 95.0:5.0 |
| H | Br | H | Ph | (99) | >99:1 | 98.5:1.5 |
| Cl | H | H | Ph | (93) | >99:1 | 97.0:3.0 |
| Me | H | H | Ph | (83) | >99:1 | >99.5:0.5 |

$C_{15}$





**441** (20 mol %),
$Et_2O$, –60°, 24 h



(98) dr >99:1
er 94.5:5.5

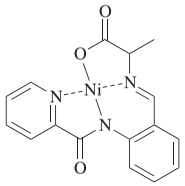
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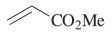
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
D. α,β-UNSATURATED CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS ACCEPTORS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

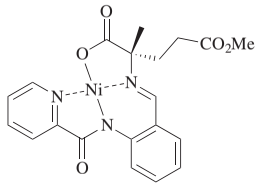
*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_{16}$





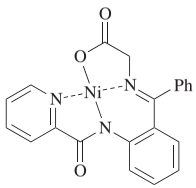
Catalyst (15 mol %),
NaH (1 eq), solvent, rt

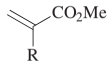


893

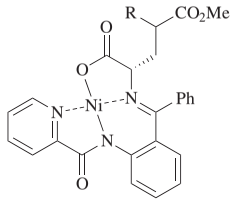
| Catalyst | Solvent | Time (min) | | er |
|---|---|---|---|---|
| **478b** | $CH_2Cl_2$ | 2 | (52) | 69.5:30.5 |
| **478b** | toluene | 5 | (20) | 94.0:6.0 |
| **478d** | $CH_2Cl_2$ | 15 | (62) | 66.0:34.0 |

$C_{21}$

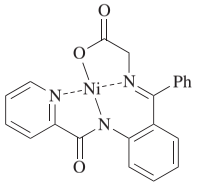




**478b** (*x* mol %),
NaH (1 eq), $CH_2Cl_2$

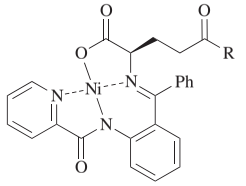


| R | *x* | Temp | Time (min) | | dr | er (major) | er (minor) | |
|---|---|---|---|---|---|---|---|---|
| H | 10 | 20° | 2 | (65) | — | 96.0:4.0 | — | 894 |
| H | 15 | rt | 2 | (70) | — | 95.0:5.0 | — | 893 |
| H | 15 | rt | 20 | (96) | — | 91.5:8.5 | — | 893 |
| Me | 15 | 20° | 9 | (50) | 86:14 | 90.5:9.5 | 83.0:17.0 | 894 |
| Me | 15 | rt | 9 | (60) | 7:1 | 80.5:19.5 | 77.0:23.0 | 893 |





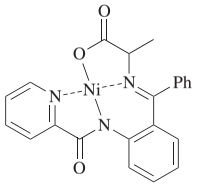
Catalyst (15 mol %),
NaOH (1 eq),
$CH_2Cl_2$, rt



893

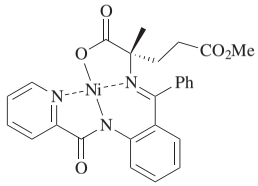
| R | Catalyst | Time (min) | | er |
|---|---|---|---|---|
| $H_2N$ | **478a** | 60 | (85) | 55.0:45.0 |
|  | **478c** | 3 | (90) | 93.0:7.0 |

$C_{22}$





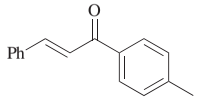
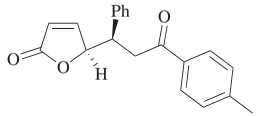
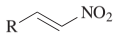
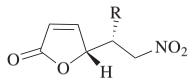
**478b** (15 mol %),
NaH (1 eq),
$CH_2Cl_2$, rt, 4 h



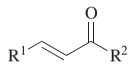
(9) er 56.5:43.5

893

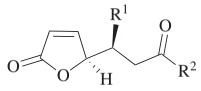
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **125** (20 mol %), hexanedioic acid (20 mol %), MeOH/$CH_2Cl_2$, rt, 6 d |  | (67) dr 1:1<br>er 91.5:8.5 | 895 |
| |  | **434a** (10 mol %), $Et_2Zn$ (20 mol %), 0.25 M in solvent, 4 Å MS, rt, 19 h |  | | 896 |

| R | Solvent | | dr | er |
|---|---|---|---|---|
| 2-$C_4H_3O$ | THF | (77) | 18:1 | 97.5:2.5 |
| 3-$C_4H_3O$ | THF | (65) | 14:1 | 97.5:2.5 |
| 2-$C_4H_3S$ | THF | (69) | >20:1 | 97.0:3.0 |
| 3-$C_4H_3S$ | THF | (71) | 17:1 | 97.5:2.5 |
| Ph | THF | (76) | 10:1 | 95.5:4.5 |
| 3-$BrC_6H_4$ | THF | (72) | 7:1 | 93.5:6.5 |
| 4-$ClC_6H_4$ | THF | (70) | 9:1 | 95.0:5.0 |
| 4-$MeOC_6H_4$ | THF | (78) | 20:1 | 98.0:2.0 |
| 2-$MeC_6H_4$ | THF | (74) | 8:1 | 96.0:4.0 |
| 4-$MeC_6H_4$ | THF | (70) | 17:1 | 97.5:2.5 |
| $BnCH_2$ | toluene | (47) | 4:1 | 93.0:7.0 |
| PhCH=CH | toluene | (52) | 3:1 | 95.5:4.5 |
| *N*-Boc-3-indolyl | THF | (73) | 6:1 | 92.5:7.5 |
| *N*-Boc-3-indolyl | toluene | (60) | 7:1 | 81.0:19.0 |
| 1-Np | THF | (75) | >20:1 | 97.0:3.0 |



**164b** (20 mol %),
LiOAc (20 mol %),
DCE, rt





| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| Ph | Me | 10 | (<5) | — | — |
| 2-$C_4H_3S$ | 2-$C_4H_3S$ | 10 | (26) | 20:1 | 90.0:10.0 |
| Ph | Ph | 10 | (40) | >30:1 | 91.0:9.0 |
| Ph | 2-$ClC_6H_4$ | 8 | (49) | >30:1 | 87.0:13.0 |
| Ph | 4-$O_2NC_6H_4$ | 6 | (83) | >30:1 | 83.5:16.5 |
| 2-$ClC_6H_4$ | Ph | 8 | (80) | >30:1 | 89.5:10.5 |
| 4-$ClC_6H_4$ | Ph | 10 | (52) | >30:1 | 90.0:10.0 |
| 3-$O_2NC_6H_4$ | Ph | 6 | (81) | >30:1 | 91.0:9.0 |
| 4-$O_2NC_6H_4$ | Ph | 6 | (92) | >30:1 | 92.0:8.0 |
| 4-$O_2NC_6H_4$ | 4-$MeOC_6H_4$ | 8 | (65) | >30:1 | 89.5:10.5 |
| 3-$MeOC_6H_4$ | 4-$O_2NC_6H_4$ | 10 | (63) | 20:1 | 77.0:23.0 |
| 4-$CF_3C_6H_4$ | Ph | 10 | (69) | >30:1 | 90.0:10.0 |
| 4-$CF_3C_6H_4$ | 4-$FC_6H_4$ | 10 | (60) | >30:1 | 87.5:12.5 |
| 4-$NCC_6H_4$ | Ph | 10 | (95) | >30:1 | 91.5:8.5 |
| 4-$NCC_6H_4$ | 3,4-$F_2C_6H_3$ | 6 | (69) | >30:1 | 86.0:14.0 |
| 4-$NCC_6H_4$ | 3-$BrC_6H_4$ | 6 | (90) | 20:1 | 88.5:11.5 |
| 4-$NCC_6H_4$ | 4-$MeOC_6H_4$ | 10 | (66) | 25:1 | 90.0:10.0 |

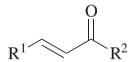
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

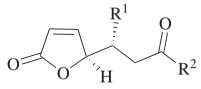
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_4$





**477** (10 mol %), *N*-Boc-L-Phe (30 mol %), $CHCl_3$, 50°, 72 h



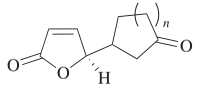
897

| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| *n*-Pr | Me | (75) | >20:1 | 99.0:1.0 |
| Me | *n*-Bu | (65) | 7:1 | 99.5:0.5 |
| *n*-Bu | Me | (74) | >20:1 | 98.0:2.0 |
| 2-$C_4H_3O$ | Me | (79) | >30:1 | 98.5:1.5 |
| 2-$C_4H_3S$ | Me | (83) | 15:1 | 99.0:1.0 |
| *n*-$C_5H_{11}$ | Me | (82) | >20:1 | 98.5:1.5 |
| *n*-$C_6H_{13}$ | Me | (78) | >20:1 | 98.5:1.5 |
| Ph | Me | (84) | 15:1 | 99.0:1.0 |
| 3-$BrC_6H_4$ | Me | (75) | 10:1 | 98.5:1.5 |
| 4-$BrC_6H_4$ | Me | (78) | 8:1 | 97.5:2.5 |
| 2-$ClC_6H_4$ | Me | (78) | 11:1 | 97.5:2.5 |
| 3-$ClC_6H_4$ | Me | (81) | 10:1 | 98.5:1.5 |

| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| 2-$FC_6H_4$ | Me | (80) | 10:1 | 98.5:1.5 |
| 3-$FC_6H_4$ | Me | (75) | 15:1 | 98.0:2.0 |
| 4-$FC_6H_4$ | Me | (79) | 15:1 | 99.0:1.0 |
| 2-$MeOC_6H_4$ | Me | (85) | 13:1 | 99.0:1.0 |
| 3-$MeOC_6H_4$ | Me | (73) | 19:1 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | Me | (84) | 10:1 | 98.0:2.0 |
| 2,3-$(MeO)_2C_6H_3$ | Me | (86) | 11:1 | 98.5:1.5 |
| 2,4-$(MeO)_2C_6H_3$ | Me | (85) | 11:1 | 99.0:1.0 |
| 3-$MeC_6H_4$ | Me | (73) | 19:1 | 98.5:1.5 |
| 4-$MeC_6H_4$ | Me | (85) | 19:1 | 98.0:2.0 |
| $BnCH_2$ | Me | (76) | 19:1 | 98.5:1.5 |
| 2-Np | Me | (86) | 13:1 | 99.0:1.0 |
| Ph | Ph | (79) | 7:1 | 98.5:1.5 |



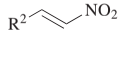
**477** (20 mol %), *N*-Boc-L-Phe (30 mol %), $CHCl_3$, 50°, 72 h



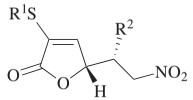
| *n* | | dr | er |
|---|---|---|---|
| 1 | (51) | 2:1 | 98.5:1.5 |
| 3 | (67) | 7:1 | 98.5:1.5 |

897





**487** (5 mol %), THF, –40°

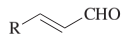


898

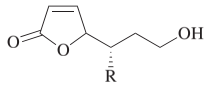
| $R^1$ | $R^2$ | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Et | Ph | 20 | (7) | 90:10 | 95.5:4.5 |

| | | | | | |
|---|---|---|---|---|---|
| *t*-Bu | *i*-Bu | 48 | (93) | 97:3 | 91.0:9.0 |
| *t*-Bu | 2-$C_4H_3S$ | 40 | (75) | 98:2 | 94.0:6.0 |
| *t*-Bu | *c*-$C_6H_{11}$ | 48 | (61) | 98:2 | 93.0:7.0 |
| *t*-Bu | Ph | 16 | (81) | 98:2 | 97.0:3.0 |
| *t*-Bu | 2-$BrC_6H_4$ | 40 | (62) | 97:3 | 95.5:4.5 |
| *t*-Bu | 3-$BrC_6H_4$ | 40 | (60) | 99:1 | 97.0:3.0 |
| *t*-Bu | 4-$BrC_6H_4$ | 16 | (65) | 98:2 | 97.0:3.0 |
| *t*-Bu | 4-$ClC_6H_4$ | 16 | (63) | 98:2 | 96.5:3.5 |
| *t*-Bu | 2-$MeOC_6H_4$ | 40 | (73) | 97:3 | 91.0:9.0 |
| Ph | Ph | 2 | (78) | 90:10 | 71.5:28.5 |



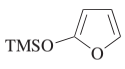
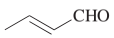
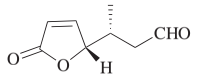
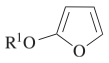
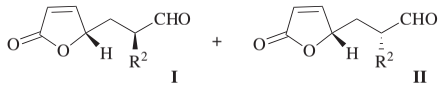


1. **145b** (10 mol %), LiOAc (20 mol %), MeOH, rt, 36 h
2. $NaBH_4$, MeOH

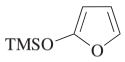
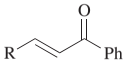
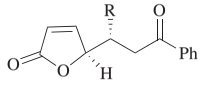


| R | | dr | er (major) | er (minor) |
|---|---|---|---|---|
| Me | (56) | 2:1 | 97.0:3.0 | 88.5:11.5 |
| Et | (43) | 2.1 | 91.0:9.0 | 92.0:8.0 |
| *n*-Pr | (57) | 2:1 | 98.5:1.5 | 93.0:7.0 |
| *i*-Pr | (68) | 2:1 | >99.5:0.5 | 97.5:2.5 |
| Ph | (94) | 2.2:1 | 99.0:1.0 | 91.5:8.5 |
| 4-$BrC_6H_4$ | (74) | 2.3:1 | 98.0:2.0 | 92.0:8.0 |
| 2-$ClC_6H_4$ | (71) | 1.6:1 | 96.5:3.5 | 94.0:6.0 |
| 4-$ClC_6H_4$ | (77) | 2.2:1 | 97.5:2.5 | 94.5:5.5 |
| 4-$FC_6H_4$ | (69) | 2.5:1 | 99.0:1.0 | 94.0:6.0 |
| 2-$MeOC_6H_4$ | (81) | 2.2:1 | 98.5:1.5 | 94.0:6.0 |
| 3-$MeOC_6H_4$ | (75) | 2.1:1 | 97.0:3.0 | 91.5:8.5 |
| 4-$MeOC_6H_4$ | (93) | 2.5:1 | 98.0:2.0 | 92.0:8.0 |
| 2,3-$(MeO)_2C_6H_3$ | (93) | 2.3:1 | 97.0:3.0 | 98.5:1.5 |
| 2,4-$(MeO)_2C_6H_3$ | (92) | 2.8:1 | 99.0:1.0 | 96.0:4.0 |
| 2-$MeC_6H_4$ | (90) | 1.6:1 | 99.0:1.0 | 98.0:2.0 |
| 3-$MeC_6H_4$ | (88) | 2.2:1 | 99.0:1.0 | 100.0:0.0 |
| 4-$MeC_6H_4$ | (92) | 2.5:1 | 99.0:1.0 | 93.5:6.5 |
| 2-Np | (87) | 2.7:1 | 98.5:1.5 | 95.5:4.5 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

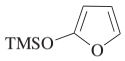
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **146** (20 mol %), 2,4-$(O_2N)_2C_6H_3CO_2H$ (20 mol %), $CH_2Cl_2/H_2O$ |  (87) *syn/anti* = 8:1, er 95.0:5.0 | 169 |
|  |  | **494** (20 mol %), 4-$O_2NC_6H_4CO_2H$, $CH_2Cl_2/H_2O$, rt |  **I** + **II** | 900 |

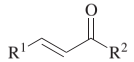
| $R^1$ | $R^2$ | | **I/II** | er | er |
|---|---|---|---|---|---|
| TBS | H | (56) | — | 95.5:4.5 | — |
| TBS | Me | (65) | 50:50 | 97.0:3.0 | 96.5:3.5 |
| TIPS | H | (71) | — | 96.0:4.0 | — |

| | | | | | |
|---|---|---|---|---|---|
|  |  | **399b** (5 mol %), $Sc(OTf)_3$ (5 mol %), *t*-BuOH/$EtCO_2Et$ (1:1), 0° |  *anti/syn* > 99:1 | 901 |

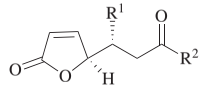
| R | Time (h) | | er | er[a] |
|---|---|---|---|---|
| 2-$C_4H_3S$ | 3 | (99) | 96.0:4.0 | >99.5:0.5 |
| 3-$C_4H_3S$ | 16 | (99) | 95.0:5.0 | — |
| Ph | 3 | (99) | 95.0:5.0 | >99.5:0.5 |
| 3-$BrC_6H_4$ | 8 | (96) | 96.0:4.0 | — |
| 4-$BrC_6H_4$ | 15 | (99) | 95.5:4.5 | >99.5:0.5 |
| 3-$ClC_6H_4$ | 8 | (95) | 96.0:4.0 | — |
| 4-$ClC_6H_4$ | 3 | (92) | 95.0:5.0 | >99.5:0.5 |
| 3,4-$Cl_2C_6H_3$ | 48 | (99) | 96.0:4.0 | >99.5:0.5 |
| 4-$FC_6H_4$ | 3 | (98) | 95.0:5.0 | >99.5:0.5 |
| 3-$MeOC_6H_4$ | 3 | (99) | 95.5:4.5 | — |

| | | | | |
|---|---|---|---|---|
| 4-$MeOC_6H_4$ | 6 | (98) | 95.0:5.0 | — |
| 3-$PhOC_6H_4$ | 3 | (99) | 95.5:4.5 | — |
| 3,4-$(OCH_2O)C_6H_3$ | 18 | (99) | 95.5:4.5 | — |
| 2-$MeC_6H_4$ | 2.5 | (99) | 95.0:5.0 | — |
| 3-$MeC_6H_4$ | 3 | (97) | 95.0:5.0 | — |
| 4-$MeC_6H_4$ | 3 | (99) | 93.5:6.5 | 96.5:3.5 |
| 3-$CF_3C_6H_4$ | 5 | (98) | 97.0:3.0 | >99.5:0.5 |
| 4-$NCC_6H_4$ | 18 | (99) | 96.0:4.0 | >99.5:0.5 |
| 4-$PhC_6H_4$ | 24 | (94) | 95.5:4.5 | >99.5:0.5 |



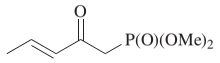

**399b** (5 mol %),
$Sc(OTf)_3$ (5 mol %),
*t*-BuOH/$EtCO_2Et$ (1:1), 0°



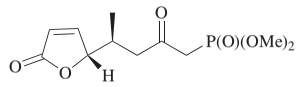

*anti*/*syn* > 99:1

901

| $R^1$ | $R^2$ | Time (h) | | er | er[a] |
|---|---|---|---|---|---|
| Ph | 4-$MeOC_6H_4$ | 24 | (99) | 91.5:8.5 | >99.5:0.5 |
| Ph | 3,4-$(OCH_2O)C_6H_3$ | 36 | (99) | 91.5:8.5 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | 4-$MeOC_6H_4$ | 36 | (92) | 94.0:6.0 | — |
| Ph | 3-$MeC_6H_4$ | 5 | (96) | 92.0:8.0 | >99.5:0.5 |
| Ph | 4-$MeC_6H_4$ | 3 | (99) | 94.0:6.0 | — |
| 3-$BrC_6H_4$ | 4-$MeC_6H_4$ | 18 | (99) | 95.5:4.5 | — |
| 4-$BrC_6H_4$ | 4-$MeC_6H_4$ | 18 | (92) | 94.0:6.0 | — |
| 3-$CF_3C_6H_4$ | 4-$MeC_6H_4$ | 48 | (99) | 94.5:5.5 | — |



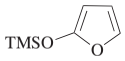
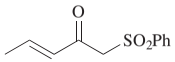
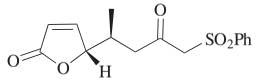
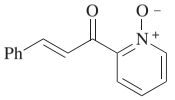
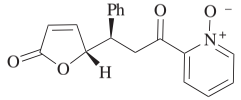

Catalyst (5 mol %),
$Cu(OTf)_2$ (5 mol %),
$CH_2Cl_2$, 0°, 0.2 h




902

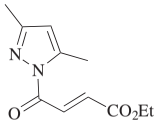
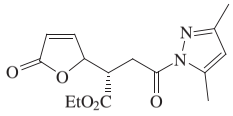
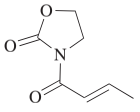
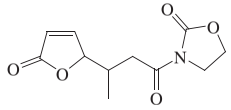
| Catalyst | | dr | er |
|---|---|---|---|
| **140** | (92) | 97:3 | 91.0:9.0 |
| **491** | (88) | 94:6 | 92.0:8.0 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

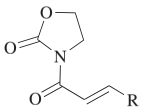
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.* | | | | |
| $C_4$ | | | | |
|  |  | **496** (5 mol %), $Cu(OTf)_2$ (5 mol %), $CHCl_3$, 0°, 2 h |  | (90) dr >99:1, er 99.5:0.5 — 902 |
| |  | Ligand (5 mol %), $Cu(OTf)_2$ (5 mol %), HFIP (1 eq), $CH_2Cl_2$, 3 Å MS |  | 385 |

Only diastereomer

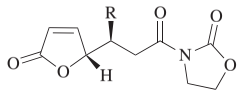
| Ligand | Temp | Time (h) | | er |
|---|---|---|---|---|
| **140** | –20° | 24 | (75) | 93.0:7.0 |
| **140** | rt | 18 | (99) | 89.5:10.5 |
| **141** | –20° | 24 | (72) | 90.0:10.0 |

| | | | | |
|---|---|---|---|---|
| |  | **158** (11 mol %), $Cu(OTf)_2$ (10 mol %), MeCN, –20°, 2 h |  | (97) dr 86:14, er 99.0:1.0 — 408 |
| |  | Ligand (6 mol %), metal salt (5 mol %), HFIP, $CH_2Cl_2$, 0° |  | 903 |

| Ligand | Metal salt | | *anti*/*syn* | er |
|---|---|---|---|---|
| *ent*-**143** | $Sc(OTf)_3$ | (80) | >50:1 | 82.5:17.5 |
| **202b** | $Cu(OTf)_2$ | (89) | 8.5:1 | 97.5:2.5 |

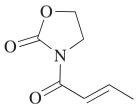


**143** (6 mol %),
$Cu(OTf)_2$ (5 mol %),
HFIP, $CH_2Cl_2$,
4 Å MS, 0°, 3 d

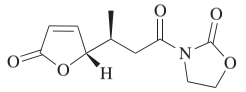


904

| R | | *anti*/*syn* | er |
|---|---|---|---|
| H | (71) | — | 82.0:18.0 |
| Me | (89) | 8.5:1 | 97.5:2.5 |



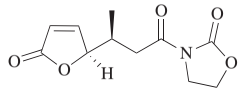
**488** (10 mol %),
$Sc(OTf)_3$ (5 mol %),
alcohol (1 eq),
$CH_2Cl_2$, 4 Å MS, –20°

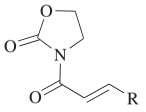


905

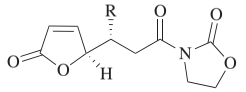
| Alcohol | | *anti*/*syn* | er (*anti*) | er (*syn*) |
|---|---|---|---|---|
| TFE | (100) | 98:2 | 97.0:3.0 | >95.0:5.0 |
| HFIP | (100) | 96:4 | 97.0:3.0 | >97.5:2.5 |
| *t*-BuOH | (100) | 98:2 | 97.0:3.0 | >95.0:5.0 |

+





**493** (*x* mol %),
$Ni(ClO_4)_2 \cdot 6\ H_2O$
(10 mol %),
alcohol (1 eq), solvent



906

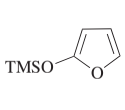
| R | *x* | Alcohol | Solvent | Temp (°) | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|---|---|---|---|
| Me | 10 | HFIP | $CHCl_3$ | –25 | 96 | (93) | 98:2 | 92.5:7.5 |
| Me | 20 | HFIP | $CHCl_3$ | –25 | 42 | (>99) | 98:2 | 94.0:6.0 |
| $EtO_2C$ | 1 | $C_6F_5OH$ | $CHCl_3$ | –40 | 168 | (80) | >99:1 | 94.5:5.5 |
| $EtO_2C$ | 5 | $C_6F_5OH$ | $CHCl_3$ | –40 | 36 | (93) | >99:1 | 95.5:4.5 |
| $EtO_2C$ | 10 | $C_6F_5OH$ | $CHCl_3$ | –40 | 15 | (97) | >99:1 | 96.5:3.5 |
| $EtO_2C$ | 10 | HFIP | $CH_2Cl_2$ | –40 | 3 | (98) | >99:1 | 95.5:4.5 |

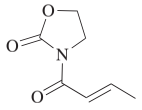
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

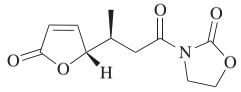
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_4$



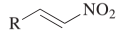


**495** (5 mol %), $La(OTf)_3 \cdot 6H_2O$ or $Ce(OTf)_4 \cdot 6H_2O$ (5 mol %) $CH_2Cl_2$, MS, 0°, 3 d

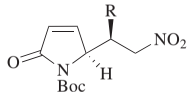


(>99) *anti*/*syn* = >99:1, er >99.5:0.5 — 907

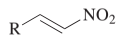




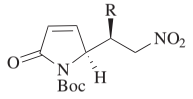
**438** (5 mol %), $Ni(OAc)_2 \cdot 4H_2O$ (10 mol %), 1,4-dioxane, 50° — 908



| R | Time (h) | | dr | er |
|---|---|---|---|---|
| *i*-Pr | 24 | (97) | >30:1 | 99.5:0.5 |
| 2-$C_4H_3O$ | 11 | (98) | >30:1 | 99.0:1.0 |
| 2-$C_4H_3S$ | 15 | (99) | >30:1 | 99.0:1.0 |
| Ph | 13 | (98) | >30:1 | 98.5:1.5 |
| 2-$BrC_6H_4$ | 11 | (98) | 16:1 | 99.0:1.0 |
| 4-$BrC_6H_4$ | 12 | (96) | 29:1 | 99.5:0.5 |
| 4-$MeOC_6H_4$ | 25 | (98) | >30:1 | 99.0:1.0 |
| $BnCH_2$ | 24 | (89) | 26:1 | 98.0:2.0 |
| PhCH=CH | 16 | (83) | 25:1 | 99.5:0.5 |



**481** (10 mol %), 0.5 M in $C_6H_5CF_3$, rt



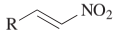
dr >20:1 — 909

| R | Time (h) | | er |
|---|---|---|---|
| *i*-Bu | 58 | (88) | 77.0:23.0 |
| 2-$C_4H_3O$ | 54 | (81) | 85.0:15.0 |
| 2-$C_4H_3S$ | 56 | (81) | 84.0:16.0 |
| Ph | 49 | (81) | 92.0:8.0 |

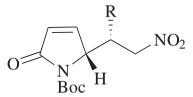
| | | | |
|---|---|---|---|
| 4-$BrC_6H_4$ | 59 | (78) | 78.0:22.0 |
| 3-$ClC_6H_4$ | 62 | (72) | 80.0:20.0 |
| 4-$MeC_6H_4$ | 56 | (82) | 90.0:10.0 |

$C_4$





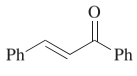
**485** (10 mol %),
0.5 M in $C_6H_5CF_3$, 0°



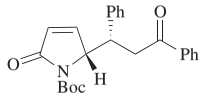
dr >20:1

909

| R | Time (h) | | er |
|---|---|---|---|
| *i*-Pr | 31 | (76) | 86.0:14.0 |
| *i*-Bu | 29 | (79) | 87.0:13.0 |
| 2-$C_4H_3O$ | 32 | (82) | 92.0:8.0 |
| 2-$C_4H_3S$ | 29 | (81) | 92.0:8.0 |
| *c*-$C_6H_{11}$ | 33 | (84) | 82.5:27.5 |
| Ph | 31 | (81) | 94.5:5.5 |
| 4-$BrC_6H_4$ | 31 | (81) | 90.0:10.0 |
| 3-$ClC_6H_4$ | 31 | (81) | 90.0:10.0 |
| 4-$ClC_6H_4$ | 39 | (78) | 82.5:17.5 |
| 2,4-$Cl_2C_6H_3$ | 35 | (79) | 80.0:20.0 |
| 4-$FC_6H_4$ | 36 | (76) | 85.0:15.0 |
| 4-$MeOC_6H_4$ | 39 | (74) | 86.0:14.0 |
| 4-$MeC_6H_4$ | 37 | (79) | 91.0:9.0 |
| *N*-Boc-3-indolyl | 33 | (82) | 92.0:8.0 |
| 2-Np | 36 | (82) | 86.0:14.0 |



**230a** (10 mol %),
$CHCl_3$, 50°



(90) dr >30:1
er 99.0:1.0

910

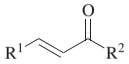
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

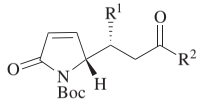
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_4$



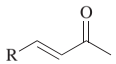


**230a** (10 mol %),
$CHCl_3$, 50°

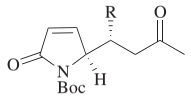


911

| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| 2-$C_4H_3S$ | 2-$C_4H_3S$ | 84 | (78) | 15:1 | 99.5:0.5 |
| Ph | Ph | 72 | (90) | >30:1 | 99.5:0.5 |
| Ph | 4-$BrC_6H_4$ | 60 | (95) | >25:1 | 98.0:2.0 |
| Ph | 4-$MeOC_6H_4$ | 84 | (73) | >30:1 | 97.5:2.5 |
| 2-$ClC_6H_4$ | Ph | 60 | (93) | >30:1 | 98.0:2.0 |
| 3-$ClC_6H_4$ | Ph | 60 | (88) | 15:1 | 98.5:1.5 |
| 4-$ClC_6H_4$ | Ph | 72 | (83) | >25:1 | 98.5:1.5 |
| 2,4-$Cl_2C_6H_3$ | Ph | 48 | (90) | >40:1 | 97.0:3.0 |
| 4-$FC_6H_4$ | Ph | 72 | (86) | 18:1 | 98.5:1.5 |
| 4-$MeOC_6H_4$ | Ph | 84 | (73) | >30:1 | 97.5:2.5 |
| 4-$O_2NC_6H_4$ | Ph | 48 | (90) | 25:1 | 97.5:2.5 |
| 4-$O_2NC_6H_4$ | 4-$MeOC_6H_4$ | 60 | (83) | 10:1 | 99.0:1.0 |
| 4-$MeC_6H_4$ | Ph | 84 | (81) | >25:1 | 98.0:2.0 |
| 4-$CF_3C_6H_4$ | Ph | 48 | (89) | 20:1 | 98.0:2.0 |
| 4-$NCC_6H_4$ | Ph | 48 | (92) | 15:1 | 99.0:1.0 |
| 4-$NCC_6H_4$ | 2-$BrC_6H_4$ | 48 | (93) | >20:1 | 99.0:1.0 |
| 4-$NCC_6H_4$ | 4-$MeOC_6H_4$ | 60 | (88) | 15:1 | 99.0:1.0 |



**477** (15 mol %),
*N*-Boc-L-Trp (15 mol %),
$CHCl_3$, 35°, 72 h





| R | | dr | er |
|---|---|---|---|
| 2-$C_4H_3O$ | (83) | >30:1 | 99.5:0.5 |
| 2-$C_4H_3S$ | (85) | >30:1 | 99.5:0.5 |
| Ph | (86) | 15:1 | 99.0:1.0 |
| 3-$BrC_6H_4$ | (83) | 16:1 | 99.0:1.0 |
| 4-$BrC_6H_4$ | (85) | 14:1 | 99.0:1.0 |
| 2-$ClC_6H_4$ | (82) | 20:1 | 99.5:0.5 |
| 3-$ClC_6H_4$ | (76) | 12:1 | 99.0:1.0 |
| 4-$ClC_6H_4$ | (81) | 12:1 | 96.5:3.5 |
| 2-$FC_6H_4$ | (88) | 16:1 | 99.5:0.5 |
| 3-$FC_6H_4$ | (80) | 13:1 | 99.0:1.0 |
| 4-$FC_6H_4$ | (81) | 12:1 | 99.0:1.0 |
| 2-$MeOC_6H_4$ | (88) | 25:1 | 99.0:1.0 |
| 3-$MeOC_6H_4$ | (86) | 15:1 | 97.5:2.5 |
| 4-$MeOC_6H_4$ | (83) | 14:1 | 99.0:1.0 |
| 2,3-$(MeO)_2C_6H_3$ | (90) | 18:1 | 99.5:0.5 |
| 2,4-$(MeO)_2C_6H_3$ | (88) | 19:1 | 99.0:1.0 |
| 3,4-$(OCH_2O)C_6H_3$ | (82) | 15:1 | 99.0:1.0 |
| 2-$MeC_6H_4$ | (83) | 15:1 | 99.5:0.5 |
| 3-$MeC_6H_4$ | (84) | 17:1 | 99.5:0.5 |
| 4-$MeC_6H_4$ | (75) | 15:1 | 99.0:1.0 |
| 2-Np | (81) | 13:1 | 99.0:1.0 |

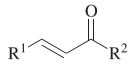
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

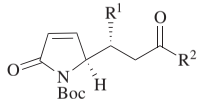
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_4$



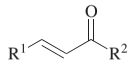


**477** (15 mol %),
*N*-Boc-L-Trp (15 mol %)
$CHCl_3$, 35°, 72 h

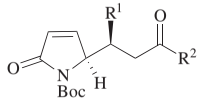


912

| R | R | | dr | er |
|---|---|---|---|---|
| Me | Me | (85) | >20:1 | 99.0:1.0 |
| *n*-Pr | Me | (81) | >20:1 | 99.0:1.0 |
| Me | *n*-Bu | (80) | >20:1 | 99.0:1.0 |
| *n*-Bu | Me | (84) | >20:1 | 99.0:1.0 |
| *n*-$C_5H_{11}$ | Me | (86) | >20:1 | 99.0:1.0 |
| *n*-$C_6H_{13}$ | Me | (83) | >20:1 | 99.0:1.0 |
| $BnCH_2$ | Me | (78) | >20:1 | 99.5:0.5 |
| PhCH=CH | Me | (81) | 18:1 | 99.0:1.0 |



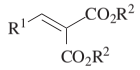
**489** (10 mol %),
*n*-$Bu_2Mg$ (10 mol %),
4 Å MS, 0°, overnight



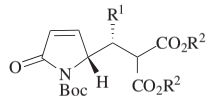
913

| $R^1$ | $R^2$ | | dr | er |
|---|---|---|---|---|
| Me | Ph | (70) | >15:1 | 77.0:23.0 |
| Ph | Me | (62) | 10:1 | 96.0:4.0 |
| 2-$C_4H_3S$ | 1-$C_4H_4N$ | (60) | 10:1 | 96.0:4.0 |
| Ph | 2-$C_4H_3O$ | (81) | >15:1 | 97.0:3.0 |
| Ph | Ph | (83) | 10:1 | 92.0:8.0 |
| Ph | 4-$BrC_6H_4$ | (89) | >15:1 | 95.5:4.5 |
| 4-$BrC_6H_4$ | Ph | (81) | >15:1 | 97.5:2.5 |
| 2-$ClC_6H_4$ | Ph | (82) | >15:1 | 96.0:4.0 |
| 4-$ClC_6H_4$ | Ph | (85) | >15:1 | 96.0:4.0 |
| 2-$FC_6H_4$ | Ph | (72) | >15:1 | 96.0:4.0 |
| 4-$FC_6H_4$ | Ph | (94) | >15:1 | 96.0:4.0 |

| | | | | |
|---|---|---|---|---|
| 2-$MeOC_6H_4$ | Ph | (85) | >20:1 | 97.5:2.5 |
| 3-$MeOC_6H_4$ | Ph | (78) | >15:1 | 96.0:4.0 |
| 4-$MeOC_6H_4$ | Ph | (91) | 12:1 | 98.5:1.5 |
| 3,4-$(OCH_2O)C_6H_3$ | Ph | (87) | >15:1 | 96.5:3.5 |
| Ph | 4-$MeC_6H_4$ | (80) | >15:1 | 98.5:1.5 |
| 3-$MeC_6H_4$ | Ph | (74) | >15:1 | 98.5:1.5 |
| 4-$NCC_6H_4$ | Ph | (86) | 8:1 | 99.0:1.0 |
| 1-Np | Ph | (88) | 8:1 | 95.5:4.5 |
| 2-Np | Ph | (76) | 7:1 | 96.5:3.5 |

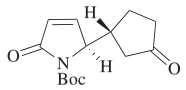
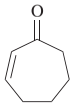
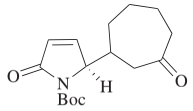
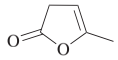
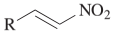
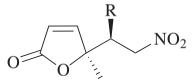
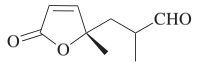


**490** (5 mol %),
$C_6H_5CF_3$, 4 Å MS, 30°



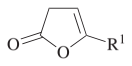
| $R^1$ | $R^2$ | Time (h) | | dr | er |
|---|---|---|---|---|---|
| 2-$C_4H_3S$ | Et | 18 | (72) | 95:5 | 95.0:5.0 |
| 3-$C_4H_3S$ | Et | 18 | (70) | 93:7 | 95.5:4.5 |
| *c*-$C_6H_{11}$ | Et | 18 | (70) | 95:5 | 95.0:5.0 |
| Ph | Me | 18 | (85) | 95:5 | 96.5:3.5 |
| Ph | Et | 18 | (82) | 95:5 | 97.0:3.0 |
| Ph | Bn | 18 | (83) | 95:5 | 95.5:4.5 |
| 3-$BrC_6H_4$ | Et | 12 | (85) | 94:6 | 96.5:3.5 |
| 4-$BrC_6H_4$ | Et | 12 | (86) | 95:5 | 96.5:3.5 |
| 2-$ClC_6H_4$ | Et | 12 | (75) | 95:5 | 96.5:3.5 |
| 3-$ClC_6H_4$ | Et | 12 | (80) | 94:6 | 95.0:5.0 |
| 4-$ClC_6H_4$ | Et | 12 | (85) | 95:5 | 96.0:4.0 |
| 4-$FC_6H_4$ | Et | 12 | (78) | 95:5 | 97.0:3.0 |
| 3-$MeOC_6H_4$ | Et | 18 | (93) | 95:5 | 96.5:3.5 |
| 4-$MeOC_6H_4$ | Et | 24 | (72) | 95:5 | 96.5:3.5 |
| 3,4-$(OCH_2O)C_6H_3$ | Et | 36 | (64) | 90:10 | 95.5:4.5 |
| 3-$PhOC_6H_4$ | Et | 18 | (89) | 95:5 | 94.5:5.5 |
| 3-$MeC_6H_4$ | Et | 18 | (76) | 95:5 | 96.5:3.5 |
| 4-$MeC_6H_4$ | Et | 18 | (82) | 95:5 | 96.5:3.5 |
| PhCH=CH | Et | 12 | (75) | 81:19 | 89.0:11.0 |
| 2-Np | Et | 18 | (82) | 93:7 | 95.5:4.5 |
| 4-$PhC_6H_4$ | Et | 18 | (83) | 95:5 | 95.0:5.0 |

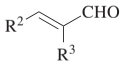
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|
| *Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.* | | | | |
| $C_4$  |  | **477** (15 mol %), *N*-Boc-L-Trp (15 mol %) $CHCl_3$, 35°, 72 h |  (79) dr 4:1 er 99.5:0.5 | 912 |
| |  | **477** (15 mol %), *N*-Boc-L-Trp (15 mol %) $CHCl_3$, 35°, 72 h |  (83) dr 10:1 er 99.5:0.5 | 912 |
| $C_5$  |  | **492** (10 mol %), 0.5 M in $CHCl_3$, –36° |  dr >20:1 | 915 |
| |  | **497** (20 mol %), MeOH, rt, 13 h |  (95) dr 1:1 er 68.0:32.0 er 71.5:28.5 | 916 |

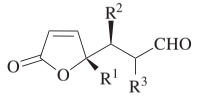
| R | Time (h) | | er |
|---|---|---|---|
| Ph | 34 | (92) | 94.5:5.5 |
| 3-$ClC_6H_4$ | 38 | (86) | 92.0:8.0 |
| 4-$MeOC_6H_4$ | 60 | (94) | 95.5:4.5 |
| 4-$MeC_6H_4$ | 65 | (90) | 95.0:5.0 |
| 4-$CF_3C_6H_4$ | 30 | (88) | 90.0:10.0 |

$C_{5\text{-}6}$





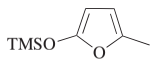
**497** (15 mol %),
toluene, rt, 13 h

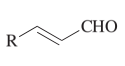


916

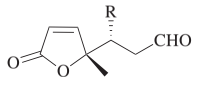
| $R^1$ | $R^2$ | $R^3$ | | er | er |
|---|---|---|---|---|---|
| Me | Me | H | (79) | 4.7:1 | 98.5:1.5 |
| Me | Me | Me | (74) | 17:1:1:1 | 96.5:3.5 |
| Me | Et | H | (88) | 7.6:1 | 97.0:3.0 |
| Me | *n*-Pr | H | (83) | 6.6:1 | 97.0:3.0 |
| Me | *i*-Pr | H | (82) | 7.3:1 | 95.5:4.5 |
| Me | Ph | H | (61) | 2.6:1 | 98.0:2.0 |
| Me | (*E*)-$C_6H_{11}$ | H | (63) | 3.3:1 | 98.0:2.0 |
| Me | *n*-$C_7H_{15}$ | H | (63) | 6.9:1 | 97.5:2.5 |
| Et | Me | H | (60) | 5.6:1 | 94.0:6.0 |

$C_5$





**146** (20 mol %),
2,4-$(O_2N)_2C_6H_3CO_2H$
(20 mol %), $CH_2Cl_2/H_2O$



169

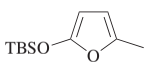
| R | Temp (°) | Time (h) | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Me | –70 | 11 | (81) | 22:1 | 96.0:4.0 |
| $BzOCH_2$ | –70 | 24 | (86) | 20:1 | 95.0:5.0 |
| $MeO_2C$ | –60 | 22 | (84) | 11:1 | 99.5:0.5 |
| *n*-Pr | –50 | 20 | (87) | 31:1 | 92.0:8.0 |
| *i*-Pr | –20 | 30 | (80) | 7:1 | 99.0:1.0 |
| Ph | –40 | 30 | (77) | 1:6 | 99.5:0.5 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

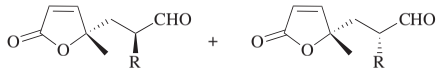
| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

*Please refer to the chart preceding the tables for structures indicated by the* ***bold*** *numbers.*

$C_5$



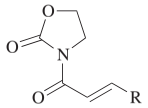

**494** (20 mol %),
4-$O_2NC_6H_4CO_2H$
$CH_2Cl_2/H_2O$, rt



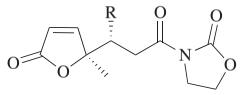

**I** **II**

| R | | I/II | er **I** | er **II** |
|---|---|---|---|---|
| H | (65) | — | 96.5:3.5 | — |
| Me | (90) | 55:45 | 98.5:1.5 | 98.0:2.0 |

900

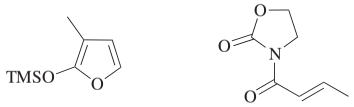



**493** (10 mol %),
$Ni(ClO_4)_2$•6 $H_2O$
(10 mol %),
alcohol (1 eq), $CHCl_3$

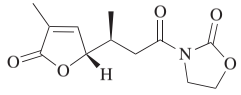



| R | Alcohol | Temp (°) | Time (h) | | *anti/syn* | er |
|---|---|---|---|---|---|---|
| H | $C_6F_5OH$ | –25 | 6 | (>99) | — | 94.0:6.0 |
| $EtO_2C$ | HFIP | –40 | 55 | (95) | 91:9 | 89.0:11.0 |

906

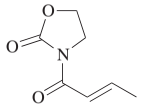



**143** (6 mol %),
$Cu(OTf)_2$ (5 mol %),
HFIP, $CH_2Cl_2$,
4 Å MS, 0°, 3 d

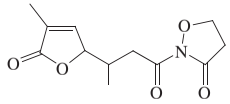



(95) *anti/syn* = 24:1
er 95.5:4.5

904

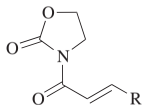



Ligand (6 mol %),
metal salt (5 mol %),
HFIP, $CH_2Cl_2$, 0°

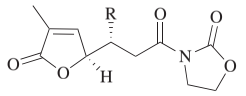



| Ligand | Metal salt | | *anti/syn* | er |
|---|---|---|---|---|
| *ent*-**143** | $Cu(OTf)_2$ | (95) | 24:1 | 95.5:4.5 |
| **202b** | $Sc(OTf)_3$ | (94) | >50:1 | 78.0:22.0 |

903

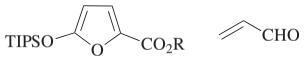


**493** (10 mol %), $Ni(ClO_4)_2$•6 $H_2O$ (10 mol %), alcohol (1 eq), $CHCl_3$

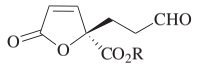


906

| R | Alcohol | Temp (°) | Time (h) | | *anti*/*syn* | er |
|---|---|---|---|---|---|---|
| H | $C_6F_5OH$ | –25 | 18 | (84) | — | 98.5:1.5 |
| Me | HFIP | –25 | 87 | (82) | 99:1 | 96.5:3.5 |
| $EtO_2C$ | HFIP | –40 | 2 | (97) | >99:1 | 98.0:2.0 |
| $EtO_2C$ | HFIP | –25 | 2 | (95) | >99:1 | 98.5:1.5 |



**217** (20 mol %), $H_2O$, $CHCl_3$, rt, 72 h

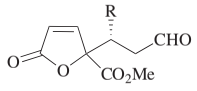


| R | | er |
|---|---|---|
| Me | (24) | 86.5:13.5 |
| Bn | (38) | 90.0:10.0 |

917



**146** (20 mol %), additive (20 mol %), solvent



169

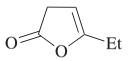
| R | Additive | Solvent | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Me | TFA | $THF/H_2O$ | (86) | 6:1 | 99.0:1.0 |
| Me | TfOH | $CHCl_3/H_2O$ | (83) | 1:7 | 99.0:1.0 |
| $MeO_2C$ | TFA | $THF/H_2O$ | (90) | 11:1 | 94.5:5.5 |
| $MeO_2C$ | TfOH | $CHCl_3/H_2O$ | (—) | 1:22 | 98.5:1.5 |

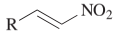
TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

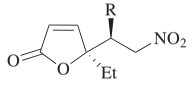
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_6$





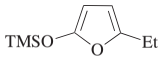
**492** (10 mol %), 0.5 M in $CHCl_3$, –36°

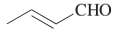


dr >20:1

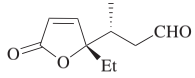
195

| R | Time (h) | | er |
|---|---|---|---|
| *i*-Bu | 96 | (59) | 95.5:4.5 |
| 2-$C_4H_3O$ | 60 | (97) | 93.5:6.5 |
| 2-$C_4H_3S$ | 42 | (92) | 96.0:4.0 |
| Ph | 24 | (94) | 95.5:4.5 |
| 4-$BrC_6H_4$ | 69 | (90) | 94.0:6.0 |
| 3-$ClC_6H_4$ | 30 | (92) | 95.0:5.0 |
| 4-$ClC_6H_4$ | 48 | (94) | 96.0:4.0 |
| 2,4-$Cl_2C_6H_3$ | 60 | (96) | 97.0:3.0 |
| 4-$FC_6H_4$ | 32 | (87) | 95.0:5.0 |
| 4-$MeOC_6H_4$ | 60 | (97) | 96.5:3.5 |
| 4-$MeC_6H_4$ | 60 | (91) | 96.0:4.0 |
| 1-Np | 44 | (90) | 95.0:5.0 |
| 2-Np | 50 | (96) | 95.5:4.5 |



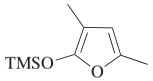


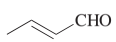
**146** (20 mol %), 2,4-$(O_2N)_2C_6H_3CO_2H$ (20 mol %), $CH_2Cl_2/H_2O$



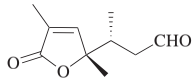
(83) *syn*/*anti* = 16:1, er 95.0:5.0

169



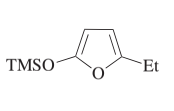


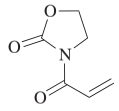
**146** (20 mol %), 2,4-$(O_2N)_2C_6H_3CO_2H$ (20 mol %), $CH_2Cl_2/H_2O$



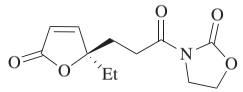
(73) *syn*/*anti* = 24:1, er 95.0:5.0

169



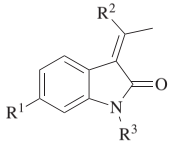


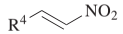
**493** (10 mol %), $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), $C_6F_5OH$ (1 eq), $CHCl_3$, –25°, 21 h



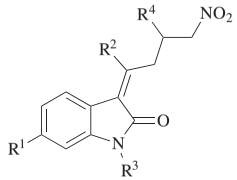
(89) er 93.0:7.0 906

$C_{11-16}$





**323** (5 mol %), 0.1 M in toluene



918

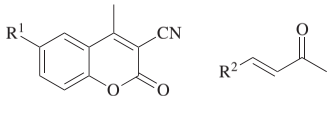
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Temp | Time (h) | | dr | er |
|---|---|---|---|---|---|---|---|---|
| H | Me | Boc | Ph | –15° to rt | 36 | (98) | >20:1 | >99.5:0.5 |
| H | Me | Moc | *n*-Bu | rt | 72 | (72) | 10:1 | >99.5:0.5 |
| H | Me | Moc | 2-$C_4H_3O$ | –15° to rt | 36 | (89) | >20:1 | >99.5:0.5 |
| H | Me | Moc | 2-$C_4H_3S$ | –15° to rt | 36 | (95) | 10:1 | >99.5:0.5 |
| H | Me | Moc | *c*-$C_6H_{11}$ | rt | 72 | (79) | >20:1 | 98.5:1.5 |
| H | Me | Moc | Ph | –15° to rt | 36 | (98) | >20:1 | >99.5:0.5 |
| H | Me | Moc | 4-$BrC_6H_4$ | –15° to rt | 36 | (92) | >20:1 | 99.0:1.0 |
| H | Me | Moc | 4-$MeOC_6H_4$ | –15° to rt | 36 | (89) | >20:1 | 98.5:1.5 |
| H | Me | Moc | 4-$O_2NC_6H_4$ | –15° to rt | 36 | (90) | 18:1 | >99.5:0.5 |
| H | Me | Moc | 4-$MeC_6H_4$ | –15° to rt | 36 | (91) | >20:1 | >99.5:0.5 |
| Cl | Me | Moc | Ph | –15° to rt | 36 | (90) | >20:1 | 99.5:0.5 |
| Cl | Me | Moc | 4-$BrC_6H_4$ | –15° to rt | 36 | (94) | 16:1 | >99.5:0.5 |
| MeO | Me | Moc | Ph | –15° to rt | 36 | (95) | >20:1 | >99.5:0.5 |
| H | Ph | Moc | Ph | –15° to rt | 36 | (93) | >20:1 | 98.5:1.5 |
| H | Ph | Moc | 4-$BrC_6H_4$ | –15° to rt | 36 | (96) | 19:1 | >99.5:0.5 |

TABLE 5. CARBOXYLIC ACIDS AND RELATED COMPOUNDS AS DONORS (*Continued*)
E. VINYLOGOUS REACTIONS (*Continued*)

| Donor | Acceptor | Conditions | Product(s) and Yield(s) (%) | Refs. |
|---|---|---|---|---|

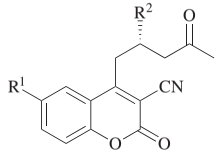
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

$C_{11}$





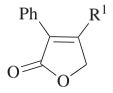
**225c** (20 mol %),
DMSO, rt, 96 h

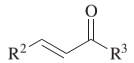


919

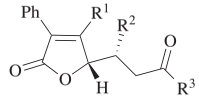
| $R^1$ | $R^2$ | | er |
|---|---|---|---|
| H | 2-$C_4H_3O$ | (75) | 96.0:4.0 |
| H | Ph | (82) | 95.5:4.5 |
| H | 4-$BrC_6H_4$ | (76) | 96.5:3.5 |
| H | 4-$ClC_6H_4$ | (86) | 97.5:2.5 |
| H | 4-$MeOC_6H_4$ | (51) | 95.5:4.5 |
| H | 4-$MeC_6H_4$ | (61) | 95.5:4.5 |
| Cl | 2-$C_4H_3O$ | (73) | 96.0:4.0 |
| Cl | Ph | (91) | 95.5:4.5 |
| Cl | 4-$BrC_6H_4$ | (87) | 96.0:4.0 |
| Cl | 4-$ClC_6H_4$ | (82) | 96.5:3.5 |
| Cl | 4-$MeOC_6H_4$ | (75) | 92.5:7.5 |
| Cl | 4-$MeC_6H_4$ | (88) | 95.5:4.5 |

$C_{16}$




*ent*-**125** (20 mol %), hexanedioic acid (20 mol %), $MeOH/CH_2Cl_2$, rt, 6 d




| $R^1$ | $R^2$ | $R^3$ | | *syn*/*anti* | er |
|---|---|---|---|---|---|
| Ph | 2-$C_4H_3S$ | Ph | (62) | >99:1 | 94.5:5.5 |
| Ph | 2-$C_4H_3S$ | 3-$O_2NC_6H_4$ | (36) | 93:7 | 98.0:2.0 |
| Ph | 2-$C_4H_3S$ | 4-$MeC_6H_4$ | (70) | >99:1 | 95.5:4.5 |
| Ph | Ph | Ph | (65) | 93:7 | 95.5:4.5 |
| Ph | 2-$ClC_6H_4$ | Ph | (63) | >99:1 | 90.0:10.0 |
| Ph | Ph | 4-$MeC_6H_4$ | (69) | >99:1 | 98.0:2.0 |
| Ph | 4-$MeC_6H_4$ | Ph | (61) | 96:4 | 97.0:3.0 |
| 3,4-$Cl_2C_6H_3$ | 2-$C_4H_3S$ | Ph | (71) | 97:3 | 97.5:2.5 |
| 3,4-$Cl_2C_6H_3$ | 2-$C_4H_3S$ | 4-$MeC_6H_4$ | (74) | >99:1 | 95.5:4.5 |
| 3,4-$Cl_2C_6H_3$ | Ph | Ph | (66) | 98:2 | 97.5:2.5 |
| 3,4-$Cl_2C_6H_3$ | 2-$ClC_6H_4$ | Ph | (73) | 98:2 | 91.5:8.5 |
| 3,4-$Cl_2C_6H_3$ | 3-$ClC_6H_4$ | Ph | (78) | 95:5 | 95.5:4.5 |
| 3,4-$Cl_2C_6H_3$ | 4-$ClC_6H_4$ | Ph | (78) | 91:9 | 96.0:4.0 |
| 3,4-$Cl_2C_6H_3$ | Ph | 4-$MeC_6H_4$ | (75) | >99:1 | 98.0:2.0 |
| 3,4-$Cl_2C_6H_3$ | 4-$MeC_6H_4$ | Ph | (69) | >99:1 | 98.0:2.0 |
| 4-$MeOC_6H_4$ | 2-$C_4H_3S$ | Ph | (37) | >99:1 | 96.5:3.5 |
| 3,4-$(MeO)_2C_6H_3$ | Ph | 4-$MeC_6H_4$ | (46) | 98:2 | 97.5:2.5 |

[a] The given er values are after recrystallization.

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