CHAPTER 1

THE SAEGUSA OXIDATION AND RELATED PROCEDURES

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INTRODUCTION

α,β-Unsaturated carbonyl compounds are highly useful synthetic materials in organic synthesis,[1−4] and regioselective dehydrogenation of carbonyl compounds to the corresponding α,β-unsaturated carbonyl compounds is an important transformation in synthetic chemistry.[5,6] One-pot, palladium-mediated dehydrogenation reactions of ketones, aldehydes, esters, lactones, and amides are known, but such reactions are limited primarily to simple substrates.[7−11] Moreover, they suffer from lack of regiocontrol in the case of unsymmetrical ketones. In 1977, Ito, Hirato, and Saegusa reported the conversion of silyl enol ethers to the corresponding α,β-unsaturated ketones and aldehydes using stoichiometric or substoichiometric amounts of palladium(II) salts.[12] Although silyl enol ethers are easily prepared from saturated ketones or aldehydes,[12] several years passed before the first application of the Saegusa Reaction was reported. Studies to improve on the original procedure by using lower catalyst loadings have since appeared. A brief review of the Saegusa Reaction concerning the literature up to 1998 is available,[13] and related methods devised primarily by the Tsuji and Larock groups are discussed in reviews[14−16] and books.[6,17−19]

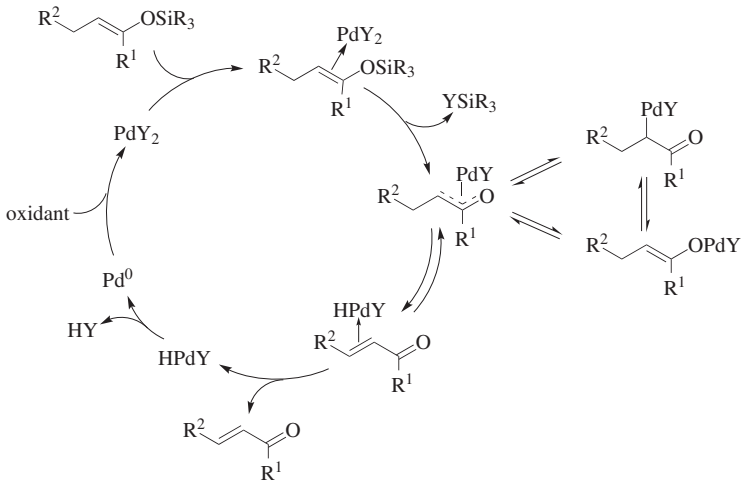
This review concerns the Saegusa Reaction and related methods. In addition to enol silanes, enol acetates, alkyl enol ethers, allyl enol carbonates, allyl β-keto carboxylates, allyl malonates, and α-chloro ketones have been transformed into α,β-unsaturated carbonyl products. This chapter covers the literature through August 2018.

MECHANISM AND STEREOCHEMISTRY

The mechanism of the formation of α,β-unsaturated carbonyl compounds using palladium-mediated procedures related to the Saegusa Reaction is substrate-dependent, but a majority of known examples involve a palladium enolate as the key intermediate. Catalytic reactions have been developed under various conditions.

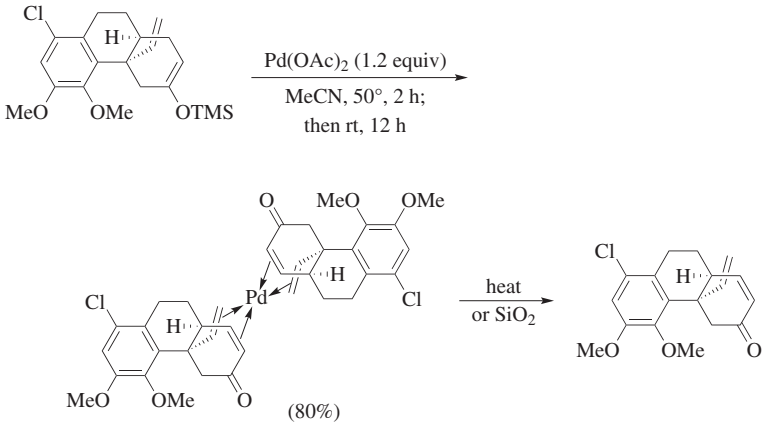
Silyl Enol Ethers or Silyl Ketene Acetals as Substrates

Most palladium-mediated, oxidative dehydrogenation reactions of silyl enol ethers and silyl ketene acetals use a palladium(II) salt. The coordination of the C=C bond to the palladium species results in transmetalation, which leads to loss of the silyl group and formation of a palladium enolate.[13] The latter compound exists as an equilibrium between the oxo-η^3-allyl palladium and the *C*- and *O*-enolate tautomers (Scheme 1).[20] Subsequent β-hydride elimination affords the α,β-unsaturated carbonyl compound and a hydridopalladium complex. Although the stability of palladium hydrides is ligand-dependent,[21] they are converted, in most cases, to palladium(0) species. Because addition/elimination of hydridopalladium species to olefins is reversible, (*E*)-α,β-unsaturated carbonyl compounds are usually produced selectively from acyclic substrates.



Scheme 1

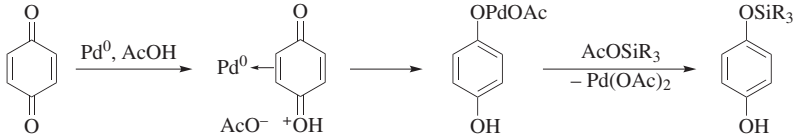
To achieve a catalytic process, the Saegusa Reaction is carried out in the presence of an oxidant—often 1,4-benzoquinone or oxygen—to regenerate the active palladium(II) species. The proposed catalytic cycle generates $AcOSiR_3$ and acetic acid (i.e., $YSiR_3$ and HY of Scheme 1) as the byproducts of the first turnover and hydroquinone or peroxides as the stoichiometric byproducts. However, palladium(0) species can form relatively stable palladium(0)–alkene complexes, which can impede the catalytic cycle (Scheme 2).[22] Such complexes can be decomposed on heating or treatment with silica gel.



Scheme 2

1,4-Benzoquinone as the Oxidant. Coordination of 1,4-benzoquinone to palladium(0) in the presence of acetic acid generates 4-hydroxyphenoxypalladium acetate

(Scheme 3).[23,24] This intermediate reacts with $AcOSiR_3$ to regenerate palladium(II) acetate. A mixture of 4-trimethylsilyloxyphenol and 1,4-bis(trimethylsilyloxy)benzene has been isolated.[12] It is also possible that HPdOAc reacts directly with 1,4-benzoquinone, rather than undergoing reductive elimination to form palladium(0) first.[25]

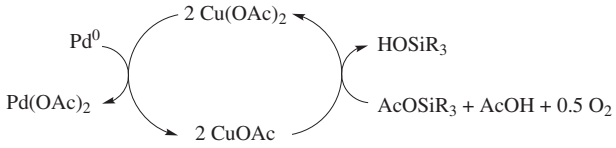


Scheme 3

Oxygen, Oxygen and a Copper Salt, or Oxygen and Oxone as the Oxidant. The use of oxygen as the oxidant in DMSO leads to formation of a peroxopalladacycle.[26] Addition of acetic acid affords a hydroperoxypalladium complex, which reacts with $AcOSiR_3$ to regenerate palladium(II) acetate (Scheme 4).[27] The mechanism of the formation of active palladium(II) species from hydridopalladium intermediates and oxygen remains unknown.[28–31]

Scheme 4

In the presence of both oxygen and a copper salt, the catalyst can be regenerated in a manner analogous to the Wacker oxidation (Scheme 5).[32]

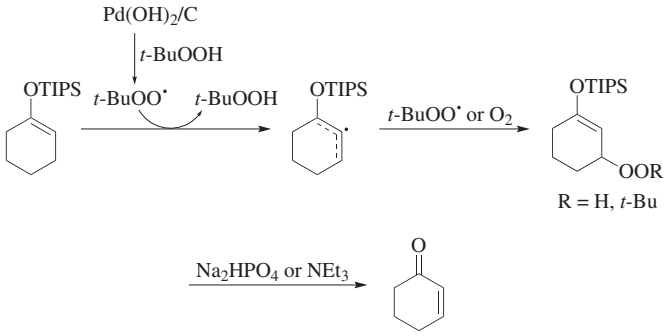


Scheme 5

A recently developed catalytic procedure involves the use of Oxone under an oxygen or air atmosphere.[33] The exact role of oxygen under these conditions has not been elucidated.

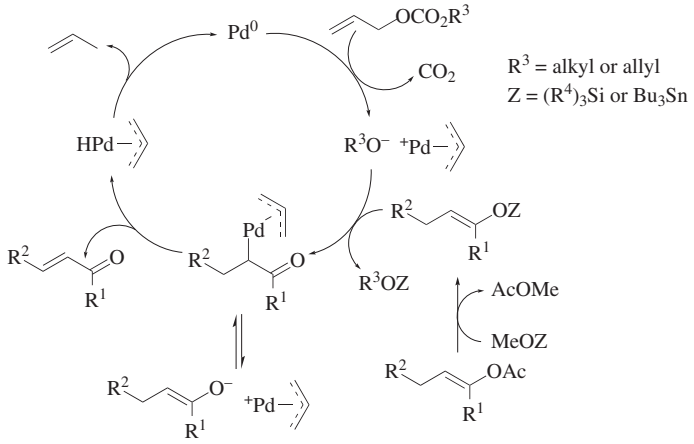
Silica-supported palladium(0) has been used as a catalyst under an oxygen atmosphere primarily in NMP; acetonitrile is a poor solvent for this method.[34,35] The dispersion of oxygen on palladium(0) is proposed to oxidize part of the supported palladium(0) into palladium(II), and the silyl ether is adsorbed onto the catalytic surface.[35]

Oxygen and *tert*-Butyl Hydroperoxide as the Oxidant. Cycloalkenyloxy triisopropylsilyl ethers can be used to prepare cyclic α,β-enones; this process employs palladium(II) hydroxide on carbon as the catalyst and is performed in the presence of oxygen, a base (disodium hydrogen phosphate or triethylamine), and excess amounts of *tert*-butyl hydroperoxide.[36,37] The catalyst is believed to initiate a radical process by palladium-mediated homolytic cleavage of the O–H bond of the hydroperoxide (Scheme 6). However, because *tert*-butyl hydroperoxide is capable of generating active palladium(II) species from palladium(0),[38] a catalytic cycle similar to that shown in Scheme 1 cannot be ruled out.



Scheme 6

Allyl Carbonate as the Oxidant. An alkyl allyl carbonate or a diallyl carbonate reacts with a palladium(0) catalyst to afford an η^3-allyl palladium complex (Scheme 7, R^3 = alkyl or allyl, Z = $(R^4)_3Si$).[39] This palladium(II) species reacts with a silyl enol ether to form the η^3-allyl palladium enolate, which provides



Scheme 7

the unsaturated carbonyl compound and an η^3-allyl palladium hydride. The latter complex then releases propene and regenerates palladium(0).

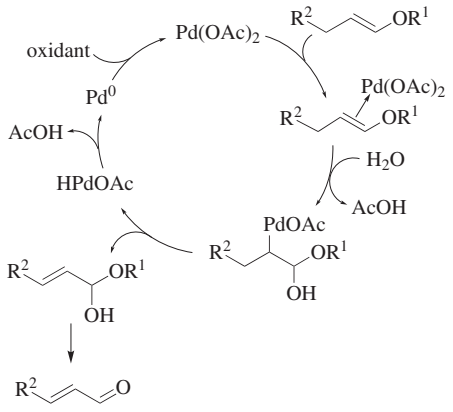
Enol Acetates as Substrates

Enones can also be obtained from enol acetates using an excess of an alkyl allyl carbonate and catalytic amounts of both palladium(II) acetate and tributyltin methoxide. The proposed mechanism is depicted in Scheme 7 (R^3 = alkyl, Z = Bu_3Sn). The role of tributyltin methoxide is to form the tin enolate, which easily transmetalates with the palladium species to afford the η^3-allyl palladium enolate with concomitant generation of the tributyltin alkoxide.

Oxidative dehydroacetoxylation of enol acetates can also be accomplished with silica-supported palladium(0) in the presence of oxygen (9 atm). Under these conditions, oxygen is dispersed over the heterogeneous catalyst and takes part in the reaction.[40]

Alkyl Enol Ethers and Vinyl Halides as Substrates

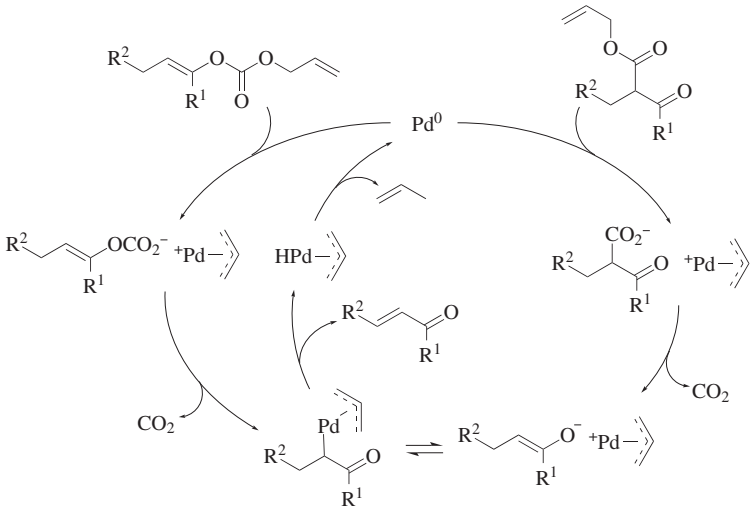
The palladium-mediated formation of enals from alkyl enol ethers is carried out under aqueous conditions with either stoichiometric or catalytic amounts of palladium(II) acetate. Under catalytic conditions, either copper(II) acetate[41] or 1,4-benzoquinone[42] is typically employed as the stoichiometric oxidant. The proposed mechanism parallels the catalytic cycle of the Wacker oxidation,[43] wherein the key step is addition of water to the C=C bond that is activated by coordination to palladium(II) acetate (Scheme 8).[41] The resulting intermediate undergoes regioselective β-hydride elimination, in preference to β-OH or β-OR elimination,[44] to afford the enal. A similar reaction is also possible with vinyl halides.[45]



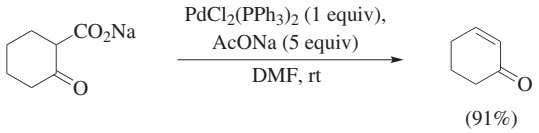
Scheme 8

Allyl Enol Carbonates, Allyl β-Keto Carboxylates, or Allyl Malonates as Substrates

The palladium-catalyzed transformation of allyl enol carbonates, allyl β-keto carboxylates, and allyl malonates into α,β-unsaturated carbonyl compounds also involves a palladium enolate as the key intermediate (Scheme 9).[46] The latter arises from the initial formation of an η^3-allyl palladium carbonate or an η^3-allyl palladium carboxylate, followed by subsequent decarboxylation. In agreement with this proposed mechanism, treatment of sodium 2-oxocyclohexanecarboxylate with a stoichiometric amount of $PdCl_2(PPh_3)_2$ and an excess of sodium acetate at room temperature affords cyclohex-2-enone (Scheme 10). A catalytic process is possible by including copper(II) chloride as the oxidant.[47]



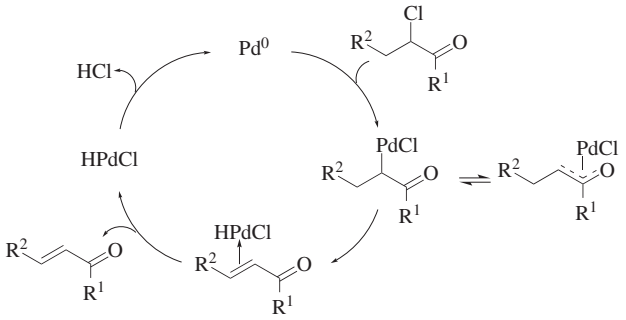
Scheme 9



Scheme 10

α-Chloro Ketones as Substrates

The synthesis of enones from α-chloro ketones proceeds by oxidative insertion of palladium(0) into the C–Cl bond to afford a chloropalladium enolate, which then likely follows the catalytic cycle shown in Scheme 11.[48]

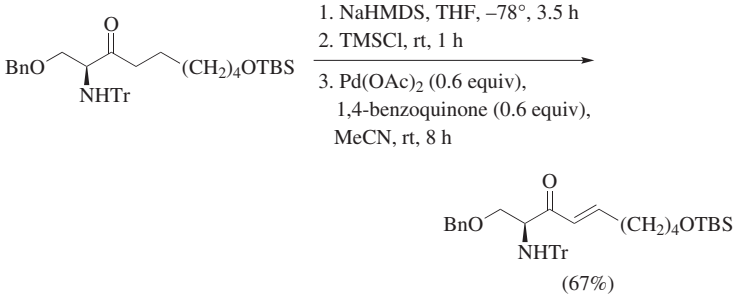


Scheme 11

SCOPE AND LIMITATIONS

Silyl Enol Ethers or Silyl Ketene Acetals as Substrates

Palladium(II) and 1,4-Benzoquinone or Copper Salt (Methods A and B). The seminal report by Ito, Hirato, and Saegusa describes the synthesis of α,β-unsaturated ketones and aldehydes from trimethylsilyl enol ethers using either a stoichiometric amount of palladium(II) acetate (Method A^S) or 0.5 equivalents each of palladium(II) acetate and 1,4-benzoquinone (Method A^C) at room temperature in acetonitrile.[12] Both procedures are well documented. Trimethylsilyl enol ethers are obtained from the corresponding saturated carbonyl compounds (Scheme 12)[49] and are often used without purification owing to their hydrolytic instability. More stable silyl enol ethers such as triethylsilyl (TES),[50–59] TBS,[27,53,60–67,68] or TIPS ethers[59,69–72] can be employed as well, though these products are also typically used without purification.

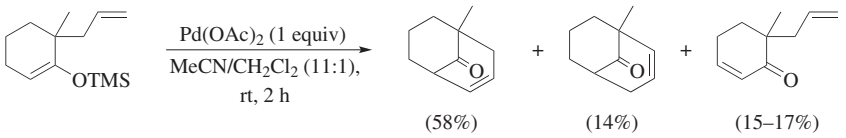


Scheme 12

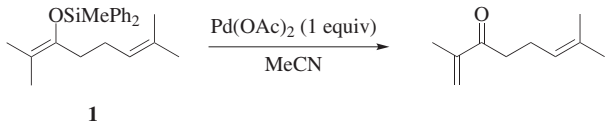
Saegusa's original conditions are effective for the synthesis of α,β-unsaturated lactones, dienones, and heterocyclic 2,3-en-1-ones. Some reactions are, however,

carried out with stoichiometric or excess amounts of both palladium(II) acetate and 1,4-benzoquinone.[64,65,73] Saegusa Reactions are compatible with halides[74] and ethers, but acid-catalyzed hydrolysis of the trimethylsilyl enol ethers may compete with the desired reaction, resulting in isolation of the original saturated ketones.[75]

Another possible side reaction is cyclization onto a tethered alkene (Scheme 13).[76,77] This pathway likely involves the coordination of the tethered alkene to the palladium enolate[78,79] or addition of the silyl enol ether to the palladium-complexed pendant alkene.[80,81] This cyclization reaction is sensitive to crowding around the C=C bond, as shown in the reaction of silyl enol ether **1**, which affords only the enone (Scheme 14).[82] By comparison, silyl enol ether **2** affords a mixture of cyclohexenones **3**–**5** (Scheme 15).[82] This cycloalkenylation procedure has been utilized in the synthesis of a variety of natural products.[80,83–90]



Scheme 13



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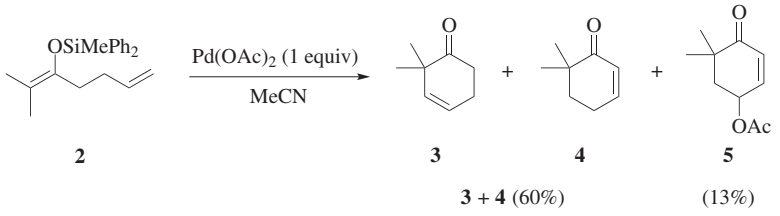
Scheme 14

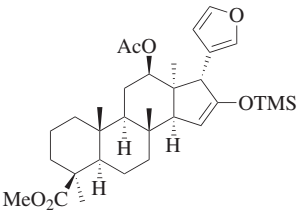


2 **3** **4** **5**

3 + **4** (60%) (13%)

Scheme 15

When subjected to the original Saegusa conditions, a number of substrates afford none of the expected α,β-unsaturated carbonyl compounds or form them only in low yields. These problematic substrates are summarized in Figure 1. The nature of the silyl group or the troublesome step (silylation or palladation) is not always specified, and consequently, the problematic substrates may be depicted as either the silyl enol ether or the carbonyl compound. In some cases, strong complexation of the catalyst to basic groups such as an isoquinoline moiety precludes the Saegusa Reaction.[91]



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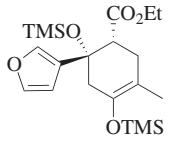

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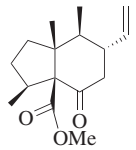

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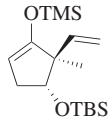

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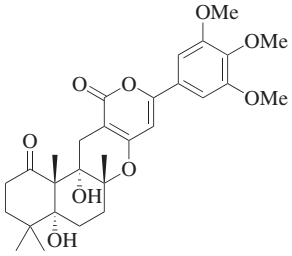

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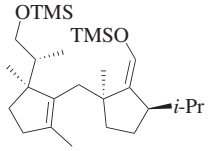

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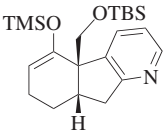

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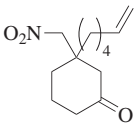

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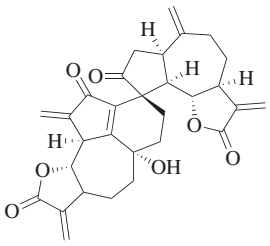

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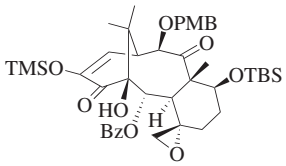

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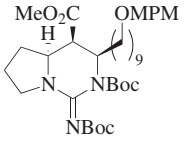
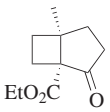
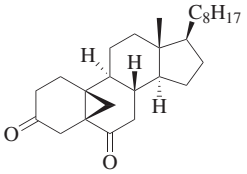


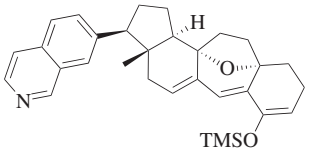
Refs 102, 103[b]



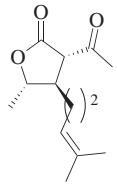
Ref 104[a]



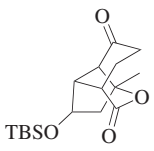
Ref 105



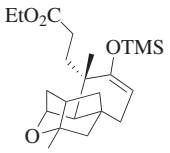
Ref 91



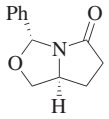
Ref 106



Ref 107

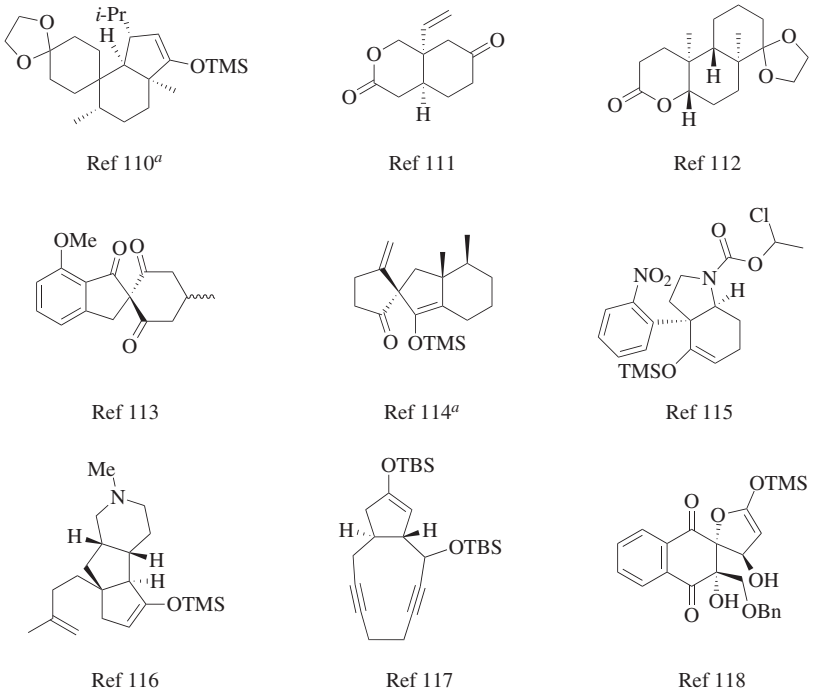


Ref 108[a]



Ref 109

Figure 1. (cont.)



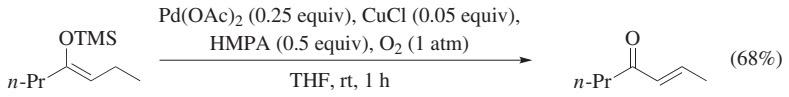
[a] A low yield of the enone product was obtained.
[b] The silylation reaction was unsuccessful.

Figure 1. Substrates leading to inefficient reactions under Saegusa's conditions.

Several modifications of the Saegusa procedure have been reported, such as using stoichiometric amounts of $Pd(OCOCF_3)_2$ in MeCN,[119] CH_2Cl_2/MeCN,[120] or DMF;[117] using stoichiometric amounts of $Pd(OAc)_2$ in DMSO,[100,121–126] DMSO/MeCN,[100,127] or THF;[128] and using 1–5 equivalents of $Pd(OAc)_2$ with 0.5–5 equivalents of 1,4-benzoquinone in MeCN[64,65,73,129–137] or CH_2Cl_2.[138] The $Pd(OAc)_2$/DMSO procedure appears to furnish the highest yields with small-scale reactions.[124]

In a footnote, Saegusa and coworkers mention that 6-methyl-2-cyclohexenone is produced quantitatively at room temperature by treating an oxygenated acetonitrile solution of 6-methyl-1-trimethylsilyloxy-1-cyclohexene with catalytic amounts of both palladium(II) acetate and copper(II) acetate.[78] Under an oxygen atmosphere, superstoichiometric quantities of both palladium(II) acetate and copper(II) acetate at 50° in acetonitrile provide the desired product,[55] as do catalytic amounts of palladium(II) acetate. Alternative reaction conditions include the use of palladium(II) acetate and copper(I) chloride in the presence of HMPA (0.5 equivalents) in THF at room temperature (Method B, Scheme 16).[139] The α-hydroxy ketone

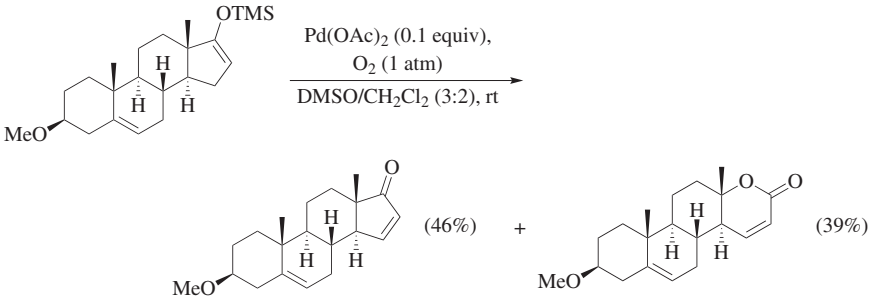
can be formed as the major product if traces of water are present in the reaction mixture.[139]



Scheme 16

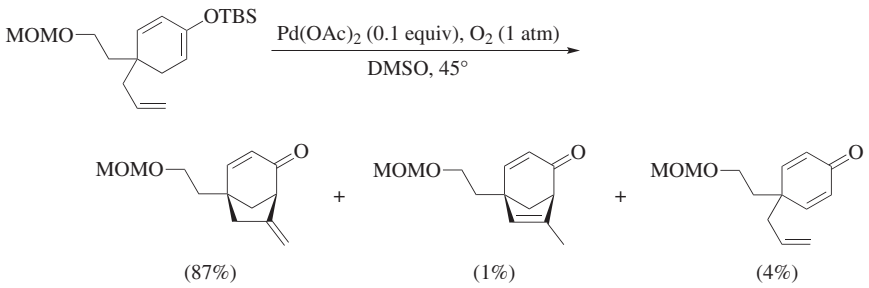
Palladium Acetate, DMSO, and Oxygen (Method C). The use of anhydrous DMSO as the solvent under an oxygen atmosphere at room temperature is particularly effective for the Saegusa Reaction,[27] likely due to the ability of DMSO to coordinate to palladium species.[26,28–31,140–144] Under these conditions, traces of water or an increase of the reaction temperature to 80° leads to the concomitant formation of large amounts of the saturated ketone. Switching the solvent from DMSO to acetonitrile results in the formation of no enone product.[27]

A variety of silyl groups may be used in this procedure: trimethyl-, triethyl-, triisopropyl-, and *tert*-butyldimethylsilyl enol ethers are all viable substrates. However, substitution on the enol itself is problematic, and trisubstituted enoxysilanes afford low yields. The method is effective for the preparation of α,β-unsaturated ketones and aldehydes, but extension to α,β-unsaturated esters is only moderately successful.[27] For less reactive substrates, heating in DMSO under oxygen with catalytic[27] or superstoichiometric[145,146] amounts of palladium(II) acetate can be successful, but desilylation of the starting material can become a significant side reaction.[27] This desilylation appears to depend on the batch of palladium(II) acetate used and on the scale of the reaction.[147] Another possible side reaction is the formation of unsaturated lactones by a Baeyer–Villiger-type oxidation in the reaction of cyclic silyl enol ethers (Scheme 17).[54]



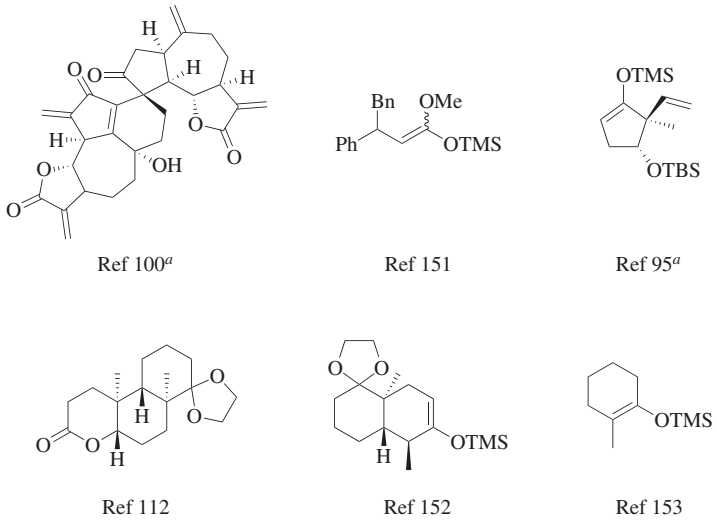
Scheme 17

Silyl enol ethers bearing tethered alkenes cyclize to form bridged bicyclic products using palladium(II) acetate and oxygen in DMSO (Scheme 18).[77,89,90,148–150]



Scheme 18

Figure 2 depicts substrates which do not undergo clean dehydrogenation under the aforementioned conditions.



[a] A low yield of the enone product was obtained.

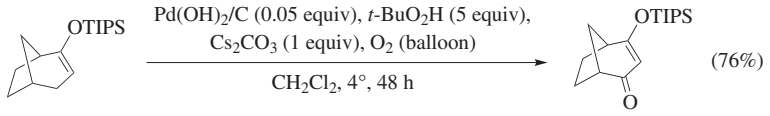
Figure 2. Substrates leading to inefficient $Pd(OAc)_2/O_2$/DMSO reactions.

Palladium(0)/SiO_2 and Oxygen (Method D). The trimethylsilyl enol ethers of cyclopentanone and cyclohexanone are converted to the corresponding cycloalk-2-en-1-ones by employing a heterogeneous catalyst—palladium(0)/SiO_2—under an oxygen atmosphere at 60° in NMP.[34] To date, this procedure has been used only for these two substrates.

Palladium(II) Acetate, Oxone, and Oxygen (Method E). Oxone has been employed as the stoichiometric oxidant for the palladium(II) acetate catalyzed oxidative dehydrogenation of trimethylsilyl enol ethers. The reaction takes place under an atmosphere of oxygen in acetonitrile that contains disodium hydrogen

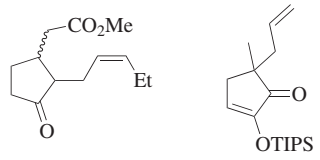
phosphate. Enones and enals are formed in good yields,[33] and this protocol is compatible with the presence of a cyclic acetal, or an OTBS group.

Palladium(II) Hydroxide, *tert*-Butyl Hydroperoxide, Oxygen, and a Base (Method F). Triisopropylsilyl enol ethers of cycloalkanones may be converted to the corresponding enones by using 20 mol % of palladium(II) hydroxide on carbon (Pearlman's catalyst), either disodium hydrogen phosphate or triethylamine, and an excess of *tert*-butyl hydroperoxide in CH_2Cl_2 at room temperature under oxygen.[36] Interestingly, β-silyloxy-α,β-enones are obtained when cesium carbonate is used as the base (Scheme 19).



Scheme 19

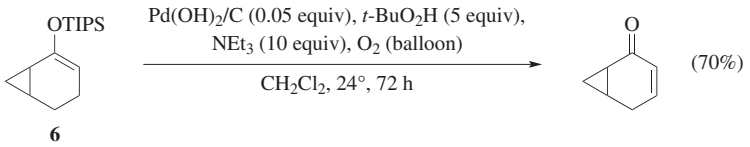
These reaction conditions cannot be used with trimethylsilyl enol ethers or with the substrates depicted in Figure 3. An allylic peroxide intermediate is thought to be involved (Scheme 6),[36] and the presence of radicals may limit the reaction scope. However, the survival of the cyclopropyl unit of substrate **6** under the experimental conditions (Scheme 20) is "an indication that the reaction of the allylic radical with molecular oxygen or *t*-BuOO• is fast relative to cleavage of the three-membered ring".[36,37,154–156]



Ref 157 Ref 158[a]

[a] A low yield of the enone product was obtained, and/or substantial side reactions were observed.

Figure 3. Substrates leading to inefficient reactions under $Pd(OH)_2$/*t*-BuOOH conditions.

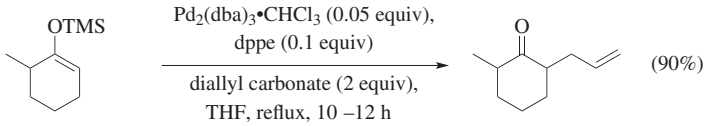


6

Scheme 20

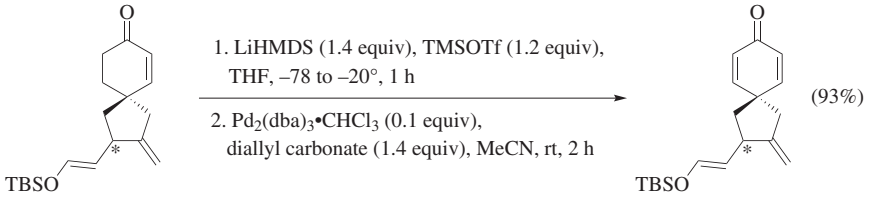
Palladium(0) Complexes and Diallyl Carbonate (Method G). When palladium(0) reacts with an allyl carbonate, the resulting palladium(II) species can

participate in the Saegusa Reaction with a trimethylsilyl enol ether formed from a ketone, aldehyde, ester, or lactone. This method relies on the allyl carbonate to generate the reactive η^3-allyl palladium(II) complex (Scheme 9), usually in either acetonitrile or benzonitrile. However, the optimal experimental conditions depend on the type of substrates. For the synthesis of enones and enals, $Pd(OAc)_2$/dppe (1:1) and diallyl carbonate appear to be best, whereas dppe-free $Pd(OAc)_2$ with allyl methyl carbonate is superior for preparing α,β-unsaturated esters and lactones. Typical conditions involve 0.01–0.1 equivalents of the catalyst and 1.4–2 equivalents of an allyl carbonate in a solvent at reflux.[39,159–161] The importance of the solvent is clearly seen in reactions carried out with $Pd_2(dba)_3$•$CHCl_3$/dppe: selective formation of the α-allyl ketones or aldehydes (the Tsuji–Trost reaction) is observed in THF (Scheme 21), whereas the Saegusa Reaction is observed in acetonitrile.[162] The use of a silica-supported palladium catalyst favors the *C*-allylation reaction pathway in a variety of solvents, including acetonitrile.[163,164]

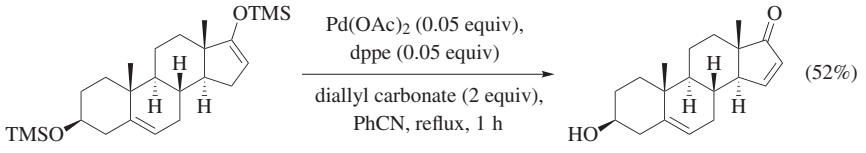


Scheme 21

Some silyl protecting groups are removed under the reaction conditions. The TBS enol ether in substrate **7** is unaffected by the use of diallyl carbonate and $Pd_2(dba)_3$•$CHCl_3$ in acetonitrile at room temperature[165–170] (Scheme 22).[170] However, the TMS protecting group in substrate **8** is cleaved with $Pd(OAc)_2$/dppe in benzonitrile at reflux (Scheme 23).[159]



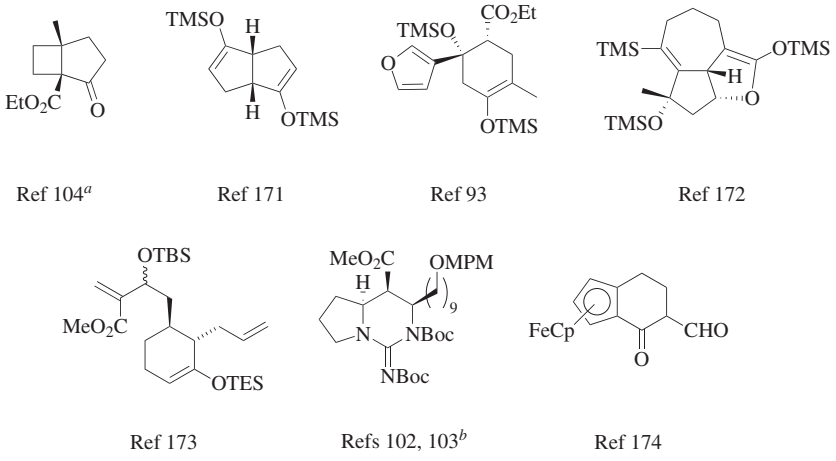
Scheme 22



8

Scheme 23

Unsuccessful examples of the Saegusa Reaction under the aforementioned conditions are shown in Figure 4.



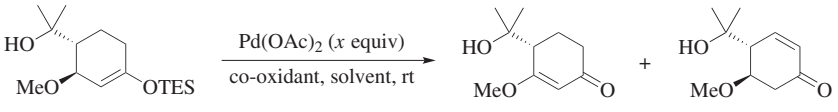
Ref 104[a] Ref 171 Ref 93 Ref 172

Ref 173 Refs 102, 103[b] Ref 174

[a] A low yield of the enone product was obtained.
[b] The silylation reaction was unsuccessful.

Figure 4. Substrates leading to inefficient reactions under Pd(0)/allyl carbonate conditions.

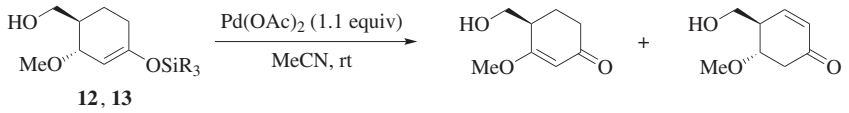
Atypical Dehydrogenation Reactions. In the course of the synthesis of (–)-platyphyllide, the expected product **10** is obtained from TES enol ether **9** with Method A^S, whereas a mixture of constitutional isomers **10** and **11** is produced with Method C (Scheme 24).[52] The unexpected isomer forms only in the presence of the free hydroxyl group on the side chain and is favored by a bulky silyl ether, as exemplified by the different reactivities of silyl enol ethers **12**, **13**, **14**, and **15** (Schemes 25 and 26).[59] A substituent at the 3-position of the cyclohex-1-en-1-yloxysilyl unit appears to be indispensable to the formation of the isomeric enone, which becomes the sole product when the 3-position is blocked (Scheme 27).[59] The participation of the hydroxyl group in the palladium-mediated isomerization of the silyl enol ether appears to promote the atypical constitutional site selectivity.[59]



9 **10** **11**

				Yield (%)	
x	Co-oxidant	Solvent	Time (h)	**10**	**11**
1	—	MeCN	3	90	—
0.1	O_2 (1 atm)	DMSO	8	62	22

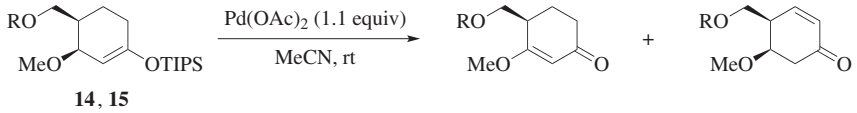
Scheme 24



12, **13**

			Yield (%)	
	R	Time (h)	Vinylogous ester	α,β-Unsaturated ketone
12	Et	6	73	2
13	*i*-Pr	18	25	45

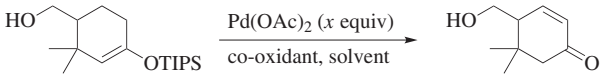
Scheme 25



14, **15**

			Yield (%)	
	R	Time (h)	Vinylogous ester	α,β-Unsaturated ketone
14	H	18	10	48
15	Me	26	19	0

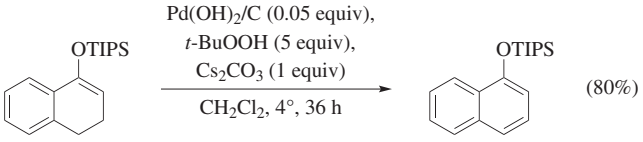
Scheme 26



x	Co-oxidant	Solvent	Temp (°)	Time (h)	
1.1	—	MeCN	rt	23	(51%)
0.2	O_2 (1 atm)	DMSO	80	—	(39%)

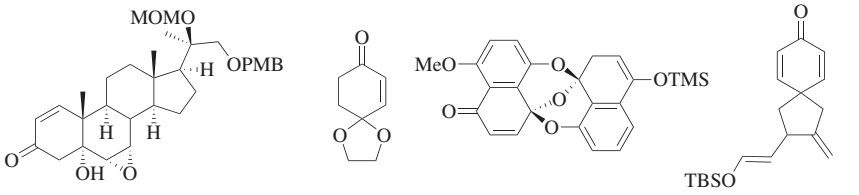
Scheme 27

When the TIPS enol ether of α-dihydronaphthol is subjected to Method F, aromatization occurs without cleavage of the silyl protecting group (Scheme 28).[36,37]

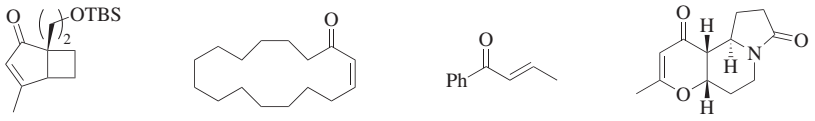


Scheme 28

Comparison of the Aforementioned Procedures. A comparison of the palladium-catalyzed oxidative dehydrogenation methods of several silyl enol ethers is summarized in Figure 5.

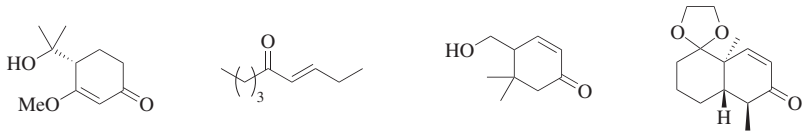


A^S (54%) > A^C (poor yield) Ref 69 | A^S (92%) > G (82%) Ref 175 | A^S (91%) > C (0%) Refs 176, 177 | G (>93%) > A^S (>68%) Refs 170, 178

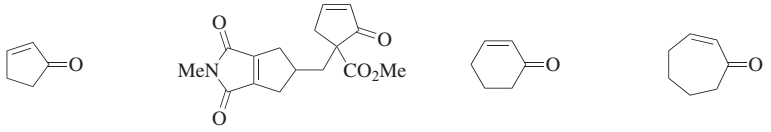


A^S (88%) > C Ref 123 | A^S (87%) > A^C (70%) Ref 179 | C (74%) > G (66%) Refs 27, 39, 159 | G (>70%) > A^S, C Ref 169

A^C (41%) > G (0%) Ref 171 | G (>90%) > A^S (79%) Refs 165, 166 | A^C (94%) > G (78%) Refs 12, 39, 159 | A^C ~ C (75–77%) Ref 54



A^S (90%) > C (63%) Ref 52 | A^C (97%) > C (67%) Refs 12, 27 | A^S (51%) > C (39%) Ref 59 | A^S (>82%) > C (0%) Ref 152



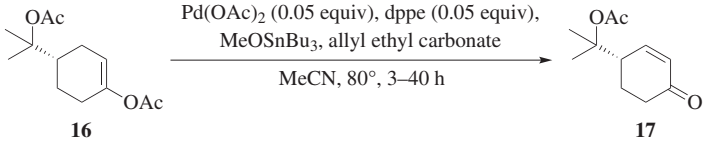
A^C ~ D (98%) > B ~ G (80%) Refs 12, 34, 139, 160 | A^S (87%) > A^C (53%) > C (25%) Ref 180 | A^C ~ E ~ G (93%) > B (89%) > C (58%) Refs 12, 27, 33, 39, 139 | A^C (91%) > F (74%) Refs 12, 36, 37

Method A^C: $Pd(OAc)_2$ (cat.), benzoquinone, MeCN.
Method A^S: $Pd(OAc)_2$ (1 equiv or more), with or without benzoquinone, MeCN.
Method B: $PdCl_2(MeCN)_2$ or $Pd(OAc)_2$ (cat.), CuCl (0.05 equiv), HMPA (0.5 equiv), O_2, THF.
Method C: $Pd(OAc)_2$ (cat.), O_2, DMSO.
Method D: Pd(0)/SiO_2 (cat.), O_2, *N*-methyl-2-pyrrolidone.
Method E: $Pd(OAc)_2$ (cat.), Oxone (1 equiv), Na_2HPO_4 (1 equiv), O_2, MeCN.
Method F: $Pd(OH)_2$ (cat.), *t*-BuOOH (2.5 equiv), Na_2HPO_4 or NEt_3 (0.1–10 equiv), O_2, CH_2Cl_2.
Method G: $Pd(0)L_n$ (cat.), allyl carbonate (2 equiv), MeCN or PhCN.

Figure 5. α,β-Enones obtained from silyl enol ethers using Methods A–G.

Enol Acetates as Substrates

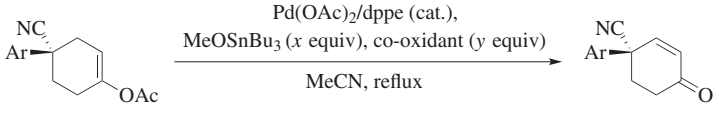
The initial report on the formation of α,β-unsaturated cycloalkenones from enol acetates involves allyl carbonate in refluxing acetonitrile with catalytic amounts of tributyltin methoxide and either $Pd(OAc)_2$ or $Pd(OAc)_2$/dppe.[181] Since this report, the reaction has been found to be highly dependent on the purity of the reagents,[182] and the most effective palladium catalyst appears to be substrate-dependent.[39] The transformation of (*S*)-enol acetate **16** under the aforementioned conditions produces (*S*)-enone **17** without loss of enantiomeric purity (analyzed by specific rotation),[183–185] but reinvestigation by chiral stationary phase HPLC analysis has since indicated partial racemization (Scheme 29).[186] An increase in racemization at a longer reaction time is attributed to the formation of an (η^3-allyl)PdH species derived from product **17**.[186] The formation of the enones from (*S*)-enol acetates **18** and **19** proceeds without racemization (Scheme 30),[187] as evidenced by chiral stationary phase HPLC analysis.[182] This preservation of enantiopurity is consistent with the racemization mechanism described, since substitution at the 4-position precludes the formation of an (η^3-allyl)PdH complex.



16 **17**

Time (h)		er
3	(38%)	90.5:9.5
10	(51%)	86:14
40	(—)	81:19

Scheme 29



18, **19**

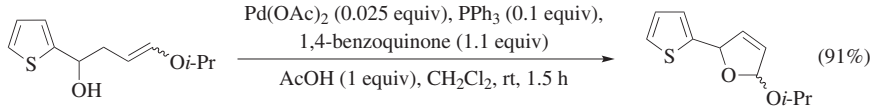
	Ar	*x*	Co-oxidant	*y*	Time (h)	Yield (%)
18	Ph	—	diallyl carbonate	—	—	65
19	3,4-$Cl_2C_6H_3$	0.3	allyl methyl carbonate	1.6	18	73

Scheme 30

Although this method is ineffective for the synthesis of enals,[39] it can be used for the synthesis of dienones and cycloalkenones and is compatible with cyano, chloroaryl, and ether groups.

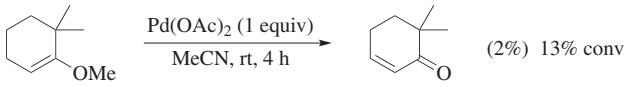
Alkyl Enol Ethers as Substrates

α,β-Unsaturated aldehydes can be prepared from alkyl enol ethers, and a typical procedure employs palladium(II) acetate (0.5 equivalents), copper(II) acetate monohydrate (1 equivalent), and sodium bicarbonate (0.5 equivalents) in acetonitrile.[41] By changing the solvent to water/acetic acid or acetic acid/dichloromethane, the catalyst loading can be lowered to 0.01–0.05 equivalents of palladium(II) acetate. This reaction takes place between room temperature and 40° and uses 1,4-benzoquinone as the oxidant.[42] Because these reactions involve a Wacker-type addition, alkyl enol ethers containing pendant OH groups afford 2,5-dihydrofurans instead of α,β-unsaturated aldehydes (Scheme 31).[42] Common functional groups such as alkenes, silyl ethers, acetates, benzyl groups, vinylsilanes, and dioxolanes are compatible with these reaction conditions.



Scheme 31

This method is effective for the synthesis of α,β-unsaturated aldehydes, but there are no literature examples for the synthesis of α,β-unsaturated ketones from alkyl enol ethers. However, traces of cyclohexenone **20** were formed from the reaction of 1-methoxy-6,6-dimethylcyclohex-1-ene with a stoichiometric amount of palladium(II) acetate in acetonitrile (Scheme 32).[80]

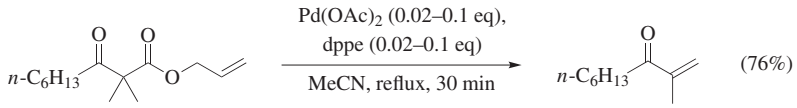


20

Scheme 32

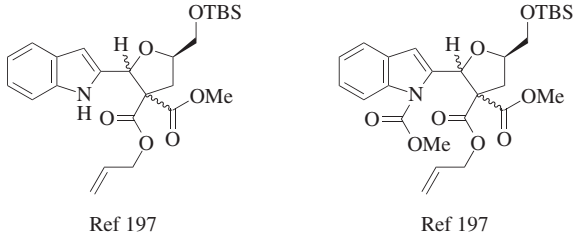
Allyl Enol Carbonates, Allyl β-Keto Carboxylates, or Allyl Malonates as Substrates

α,β-Unsaturated ketones can be prepared from allyl β-keto carboxylates or allyl enol carbonates by treatment with $Pd(OAc)_2$/dppe in refluxing acetonitrile (Scheme 33).[46] This approach is very sensitive to the nature of the catalyst and experimental conditions. For example, at room temperature or with solvents such as acetone or *tert*-butanol, the main product is either the saturated ketone or the α-allyl ketone,[46,188] the latter compound being selectively obtained from the $Pd(PPh_3)_4$ catalyzed reaction of allyl β-keto carboxylates in DMF.[47]



Scheme 33

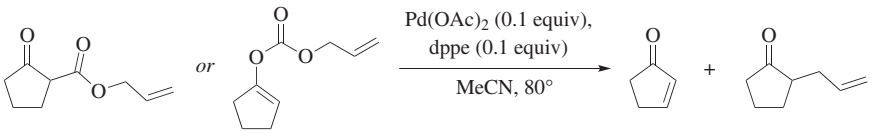
With respect to catalyst, palladium(II) acetate or $Pd_2(dba)_3$ (with or without PPh_3) is sometimes preferred to $Pd(OAc)_2$/dppe,[16,160,189–194] depending on the substrate.[188] This method has been used to prepare isoflavones[195] and α,β-unsaturated esters,[196–198] but has rarely been used to make α,β-unsaturated aldehydes[16,188] owing to decarboxylative allylation.[199] The procedure is compatible with the presence of phenol and cyano groups, as well as alkyl, benzyl, aryl, and silyl ethers, but is ineffective for substrates having an indole or a carbamate-protected indolyl group (Figure 6).[197]



Ref 197 Ref 197

Figure 6. Allyl malonates leading to inefficient reactions.

The substitution pattern of the substrate affects its reactivity. In general, allyl β-keto carboxylates generate 2-substituted cyclopent-2-enones in yields up to 90%.[16,46,160,193,194] However, the synthesis of unsubstituted cyclopent-2-enone is problematic; neither allyl carboxylate **21** nor allyl carbonate **22** furnishes the desired enone product in a useful yield. Instead, the major product is 2-allylcyclopentanone, which results from decarboxylative allylation (Scheme 34).[188,200]



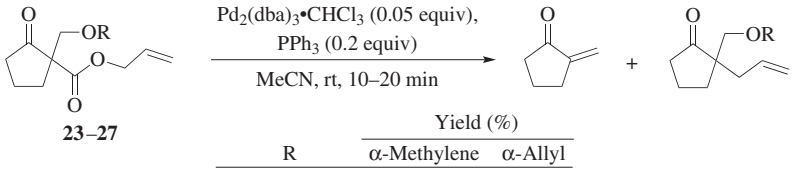
21 **22**

	Yield (%)	
	Enone	Ketone
21	0	81
22	13	57

Scheme 34

As depicted in Scheme 9, a Pd–H species is involved in the dehydrogenation reaction. When carbon–palladium(II) intermediates have both a hydrogen and an acetate

in the β-position, competition can occur between β-H and β-OAc elimination.[201] Favoring the latter pathway provides an effective synthesis of α-methylene ketones, esters, lactones, and lactams from allyl acetoxymethyl carboxylates such as substrate **23** (Scheme 35). The same reaction is observed from substrates **24** and **25** which bear a carbonate or a benzoate instead of an acetate group.[202,203] On the other hand, substrates **26** and **27**, which bear a methoxy or a hydroxyl group, respectively, afford the α-allyl carbonyl compounds as the major products.[202]



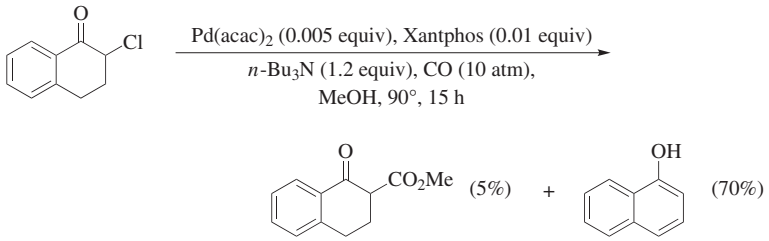
23–27

		Yield (%)	
	R	α-Methylene	α-Allyl
23	Ac	93	—
24	MeO_2C	94	—
25	PhC(O)	59	—
26	Me	4	94
27	H	4	72

Scheme 35

α-Chloro Ketones as Substrates

α-Chloro ketones undergo palladium-catalyzed dehydrohalogenation to form the corresponding enones.[48,204] Attempts to effect a methoxycarbonylation of 2-chloro-1-tetralone afford 70% of 1-naphthol and only 5% of the β-keto ester (Scheme 36).[48]



Scheme 36

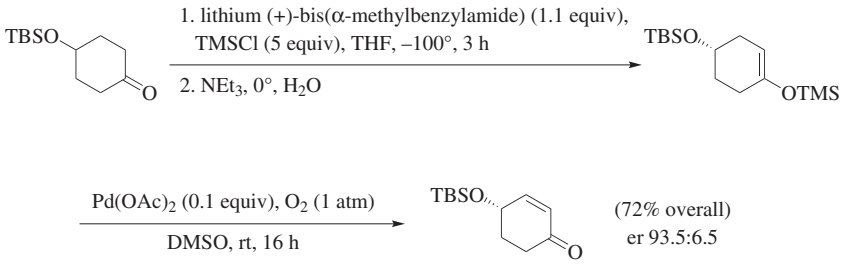
This method for preparing enones by palladium-catalyzed dehydrohalogenation of α-halo ketones has not seen synthetic applications. Simpler reaction conditions than those documented[48,204] may be effective but remain uninvestigated.

APPLICATIONS TO SYNTHESIS

A number of examples in the Tabular Survey describe the synthesis of key intermediates that are used for subsequent elaboration. Only selected applications of Saegusa-type reactions are detailed below.

Desymmetrization/Palladium-Mediated Dehydrosilylation Reaction Sequence

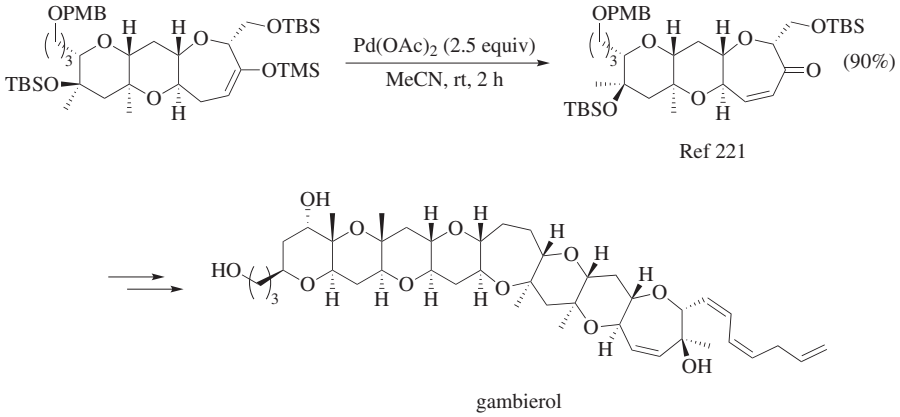
Enantioselective deprotonation of prochiral cyclic ketones[205–209] provides convenient access to non-racemic, 4-substituted cyclohex-2-en-1-ones (Scheme 37).[210–216] This method involves quenching with chlorotrimethylsilane[217] followed by palladium-catalyzed dehydrosilylation.



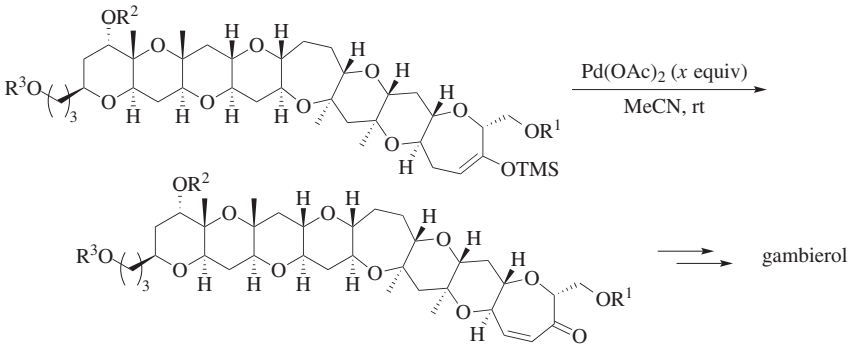
Scheme 37

Enones as Intermediates in Natural Product Synthesis

Enones are useful intermediates in the total synthesis of natural products, wherein they are often prepared by the Saegusa Reaction. Representative examples include the syntheses of gambierol (Schemes 38 and 39),[218–227] (±)-preussomerins F, K and L (Scheme 40),[176,177] zoanthamine,[50,228] zoanthenol,[229] norzoanthamine (Scheme 41),[50,228,230,231] gochnatiolides,[232] methyl (±)-jasmonate (Scheme 42),[233] (–)-nahuoic acid $C_i(B_{ii})$ (Scheme 43),[234] and maoecrystal P (Scheme 44).[235]

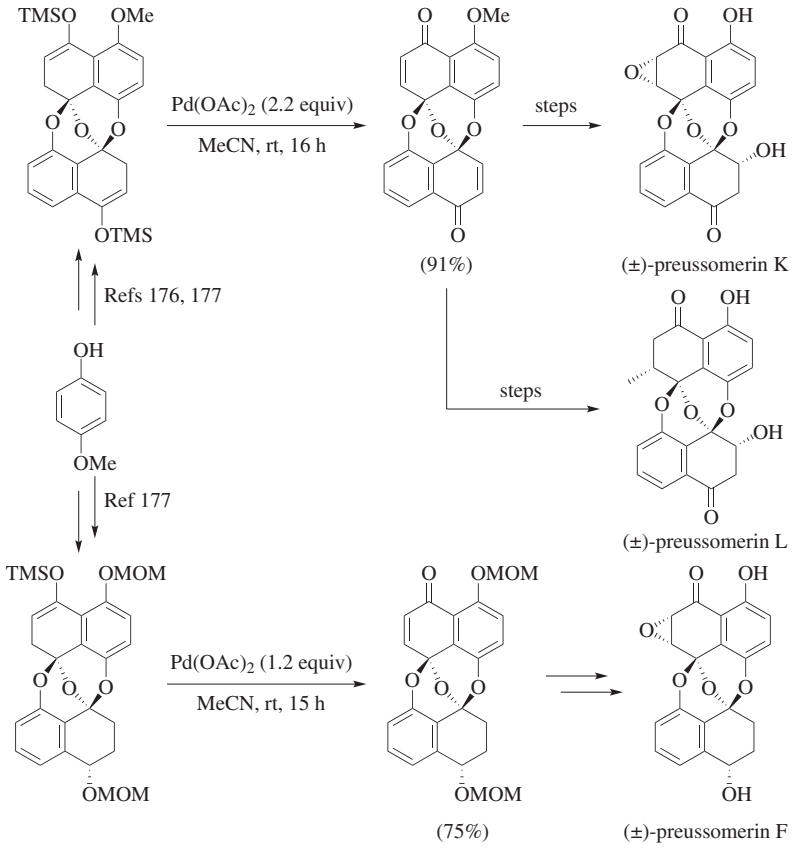


Scheme 38

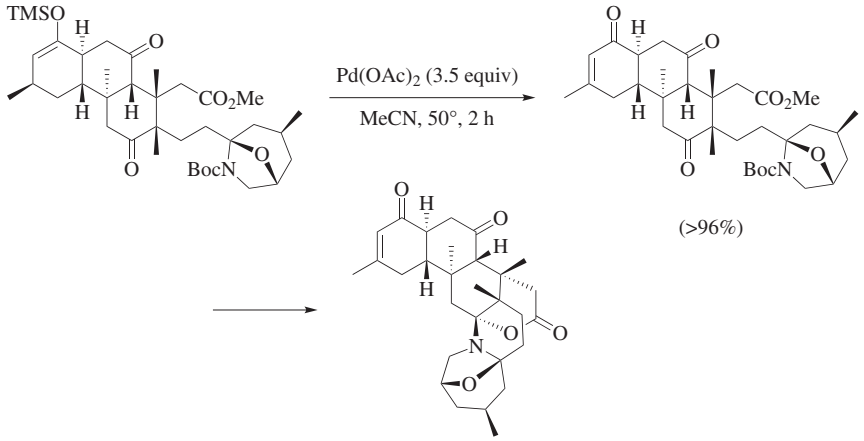


R^1	R^2	R^3	*x*	Time (min)		Refs.
TBDPS	Bn	Bn	5	75	(98%)	219, 218, 220
TBS	TIPS	Piv	3	60	(92%)	222, 223
TBS	Bn	Bn	5.2	75	(>94%)	224, 225

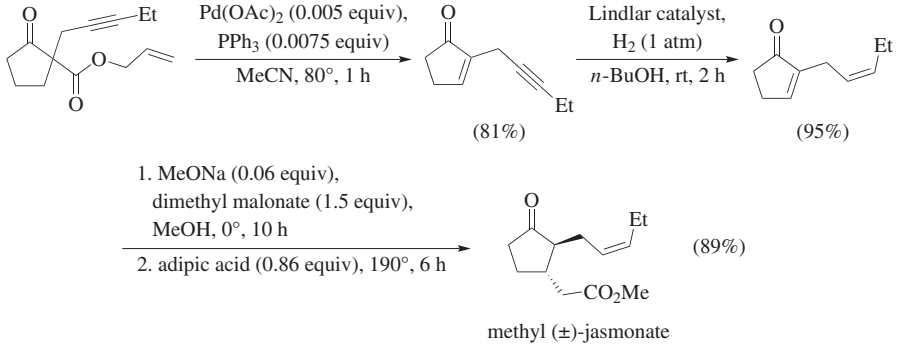
Scheme 39



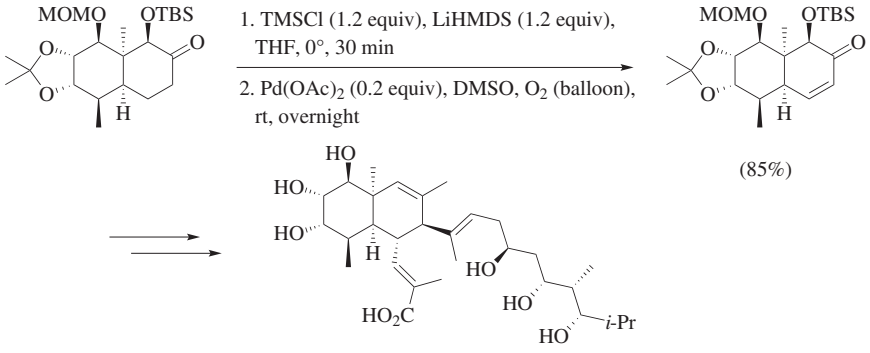
Scheme 40



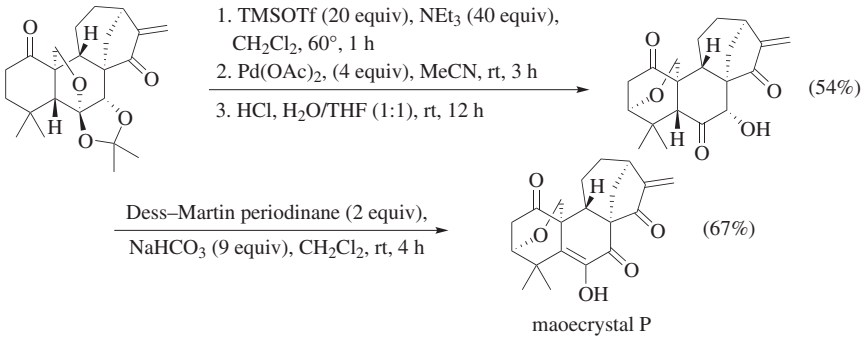
Scheme 41



Scheme 42



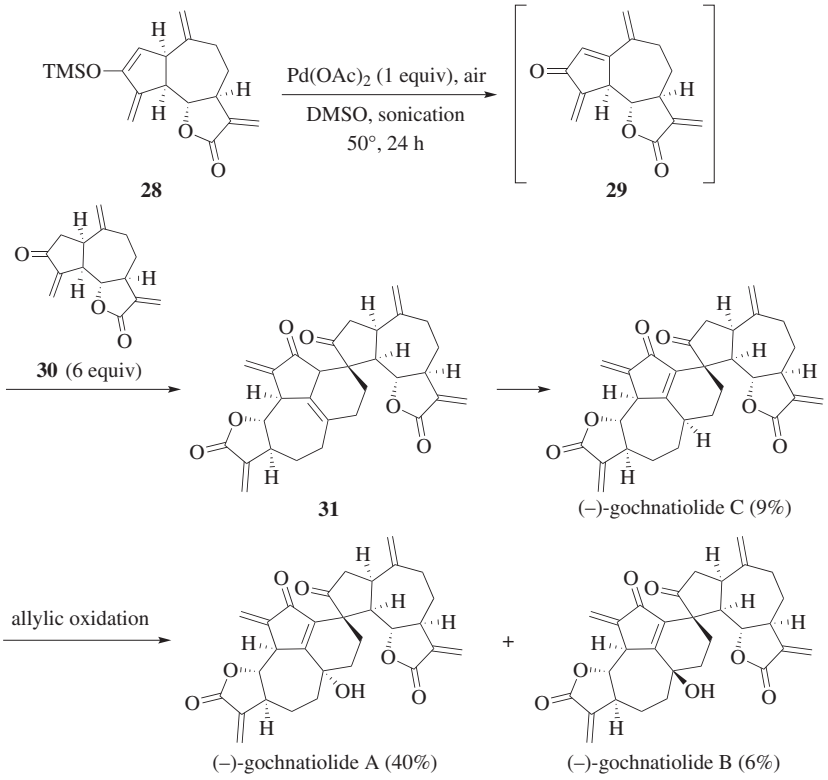
Scheme 43



Scheme 44

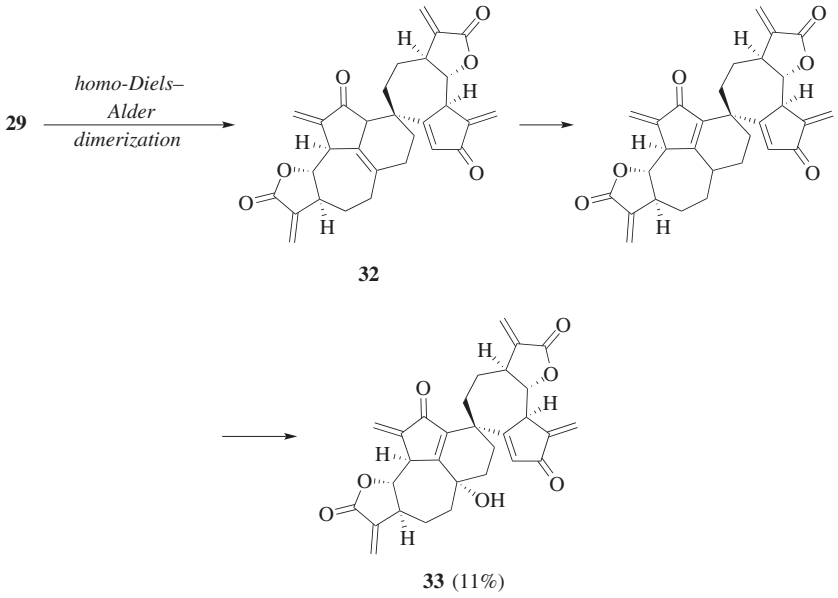
Tandem Reactions Involving Enones

Saegusa Reaction products have been used as intermediates in various tandem reactions. For example, sonication of a DMSO solution of silyl enol ether **28** in the presence of palladium(II) acetate under an atmosphere of air generates dienone **29**, which undergoes a cross-Diels–Alder reaction with enone **30** to produce intermediate **31** (Scheme 45).[232] Isomerization of compound **31** yields gochnatiolide C, and allylic



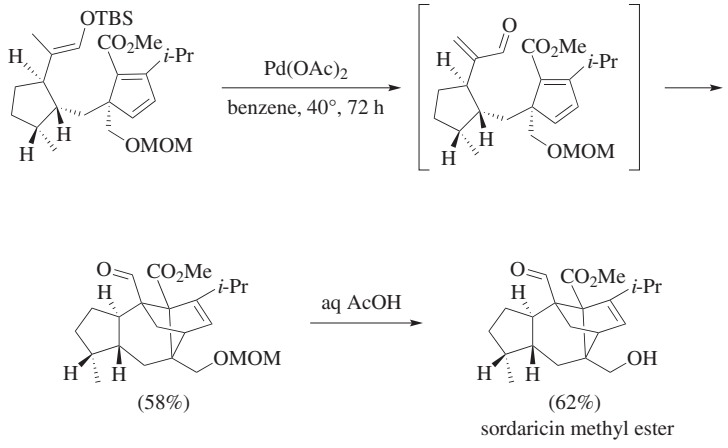
Scheme 45

oxidation of the latter compound affords gochnatiolides A and B. Also isolated is compound **33**, which arises from a homo-Diels–Alder reaction of dienone **29** to form intermediate **32**, followed by isomerization and allylic oxidation (Scheme 46).



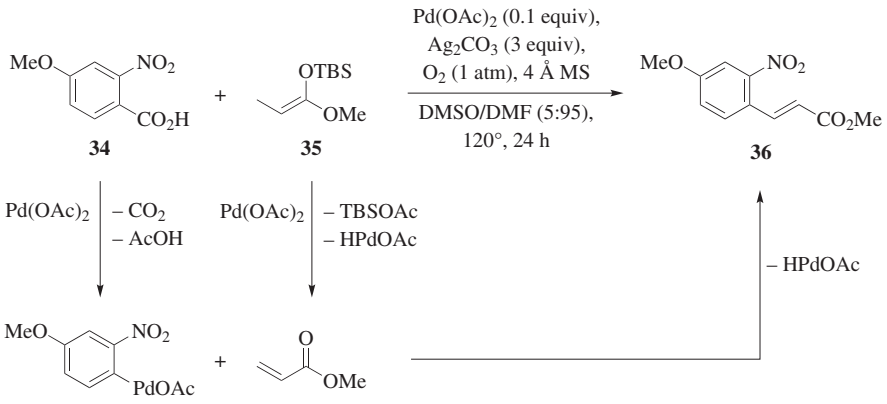
Scheme 46

Scheme 47 depicts a spontaneous intramolecular Diels–Alder reaction of a Saegusa product en route to the methyl ester of sordaricin.[67]



Scheme 47

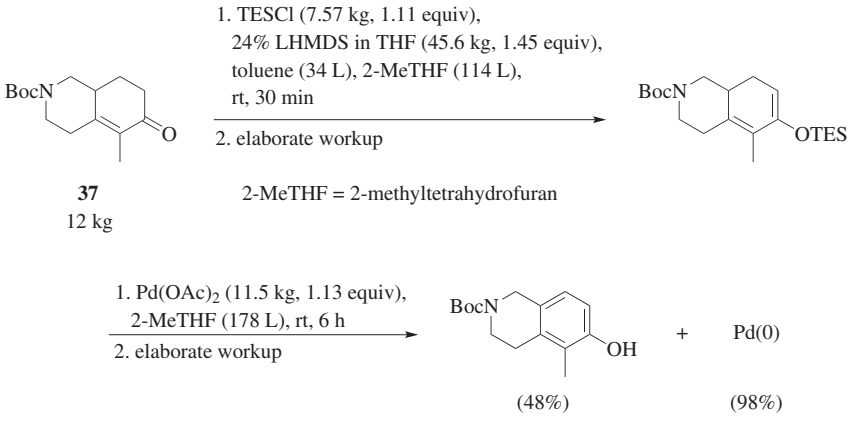
The synthesis of 3-arylacrylate **36** involves decarboxylative palladation of acid **34** and oxidative dehydrogenation of enol silane **35**, followed by a Heck-type coupling (Scheme 48).[236] Notably, all three steps of this tandem reaction are catalyzed by the same palladium species, palladium(II) acetate.



Scheme 48

Saegusa Reaction on an Industrial Scale

Because the Saegusa Reaction is a reliable method for enone synthesis, it has found application in industrial syntheses. The synthesis of a receptor agonist involves a phenol intermediate that can be accessed from enone **37** by palladium-mediated, oxidative dehydrogenation (Scheme 49).[15,128] Up to 11.5 kg of palladium(II) acetate is used in this stoichiometric dehydrogenation reaction, resulting in kilogram quantities of the desired intermediate. Elaborate workup procedures are used to recover the palladium metal; in one example, 10.3 kg of palladium metal was recovered from a reaction that employed 10.5 kg of palladium(II) metal.

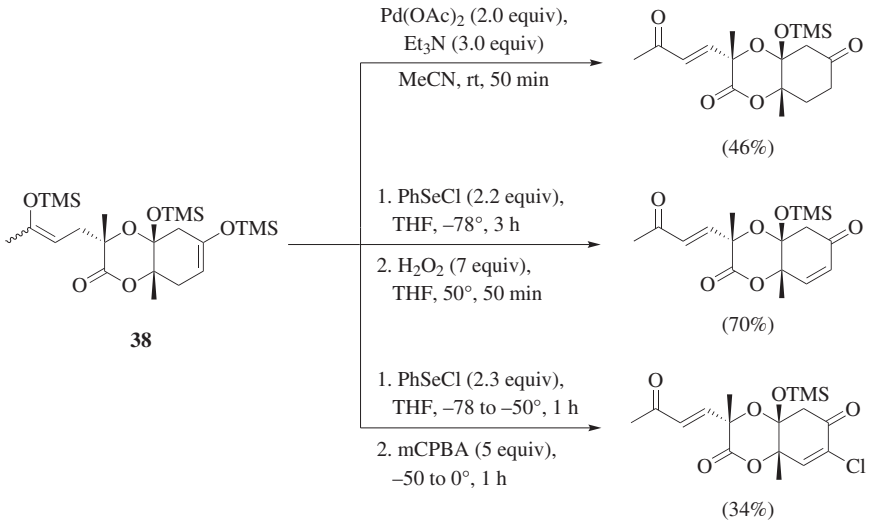


Scheme 49

COMPARISON WITH OTHER METHODS

Because of the well-known utility of α,β-unsaturated carbonyl compounds in increasing molecular complexity in organic synthesis, their preparation has been the subject of a large number of studies and many different approaches are available. In this section, the Saegusa Reaction is compared with alternative methods for the dehydrogenation of carbonyl compounds and related substances to the corresponding α,β-unsaturated carbonyl compounds. Included in this discussion are bromination–dehydrobromination,[237−241] thiolation–oxidation–elimination,[242] and selenation–oxidation–elimination[243−248] reaction sequences. In addition, palladium,[7,8,249−251] iodine,[252−257] *N-tert*-butyl benzenesulfinimidoyl chloride,[258,259] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[260] chemistry are discussed as well, as is dye-sensitized photooxygenation.[261] Examples of products that are best prepared by methods other than the Saegusa Reaction are summarized in Table A, whereas Table B depicts substrates for which the Saegusa Reaction was most efficient. Table C depicts the examples of the α,β-unsaturated carbonyl compounds that have been obtained in similar yields by the Saegusa Reaction and by another method. The relationships between the method, substrate, and yield are not obvious within these datasets, and therefore, identifying the best reaction sequence for a given substrate remains a largely empirical process.

The dehydrogenation of bis(trimethylsilyl) enol ether **38** is an interesting case, because multiple reaction pathways are possible (Scheme 50).[75] Chemoselective dehydrogenation of substrate **38** is observed in the presence of two equivalents of palladium(II) acetate (Method A^S). On the other hand, both enol ethers react with phenylselenyl chloride, and the products that are isolated depend on the nature of the oxidant, which can also promote a Pummerer-type reaction prior to the desired dehydrogenation reaction.



Scheme 50

Table A. α,β-Unsaturated Carbonyl Compounds Prepared More Efficiently by Methods Other Than Pd-Mediated Oxidative Dehydrogenation of Silyl Enol Ethers.

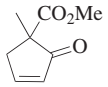
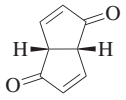
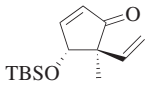
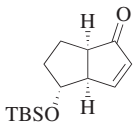
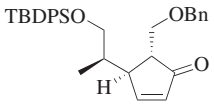
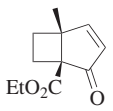
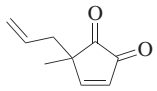
α,β-Unsaturated Carbonyl Product	Pd-Mediated Oxidative Dehydrogenation Conditions	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	C	CS: 2-iodoxybenzoic acid/DMSO	262
	C	SS: phenylselenation, oxidative elimination	153
	$A^?$	CS: bromination, ketalisation, dehydrobromination, deprotection	171
	$A^?$, C	SS: bromination, dehydrobromination	95
	$A^?$	CS: sulfenylation, dehydrosulfenylation	51
	A^S	CS: phenylselenation, oxidative elimination	263
	$A^?$, G	CS: bromination, dehydrobromination	104
	F	CS: $Pd(OAc)_2$	158

Table A. (cont.)

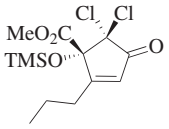
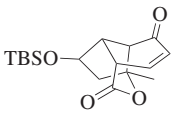
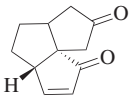
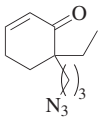
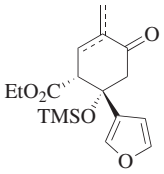
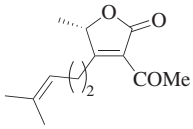
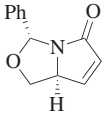
α,β-Unsaturated Carbonyl Product	Pd-Mediated Oxidative Dehydrogenation Conditions	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	A?	CS: SeO_2	264
	A?	CS: bromination, dehydrobromination, phenylselenation, oxidative elimination	107
	A^S	CS: benzeneseleninic anhydride	265
	C	CS: 2-iodoxybenzoic acid/DMSO	266
	A?, G	SS: phenylselenation, oxidative elimination	93
	A?	CS: NaH, PhSe(O)Cl, warming	106
	A?	CS: LDA, *N-t*-butyl benzenesulfinimidoyl chloride	109

Table A. (cont.)

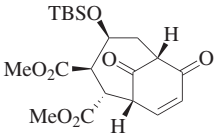
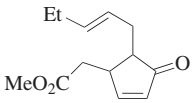
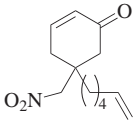
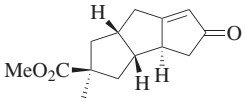
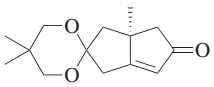
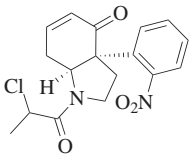
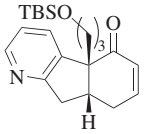
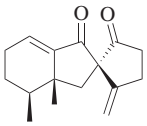
α,β-Unsaturated Carbonyl Product	Pd-Mediated Oxidative Dehydrogenation Conditions	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	A?	CS: 2-iodoxybenzoic acid/DMSO	267, 268
	F	CS: 2-iodoxybenzoic acid/DMSO, CF_3CO_2H	157
	A?	CS: 2-iodoxybenzoic acid/NMO/DMSO	99
	A^S	CS: 2-iodoxybenzoic acid/DMSO, TsOH	134
	A^S	CS: benzeneseleninic anhydride	265
	A?	SS: phenylselenation, oxidative elimination	115
	A^S	SS: 2-iodoxybenzoic acid/NMO/DMSO	98
	A?	CS: phenylselenation, oxidative elimination	114

Table A. (cont.)

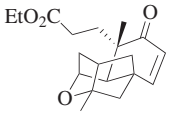
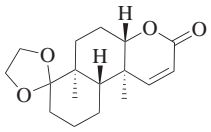
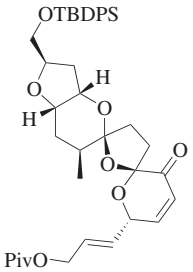
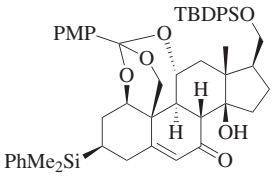
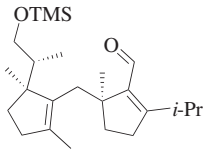
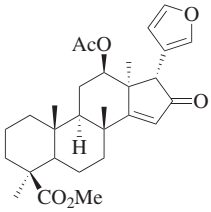
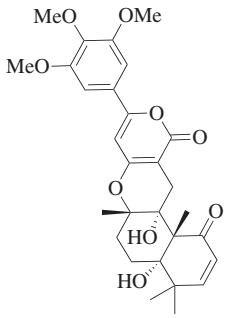
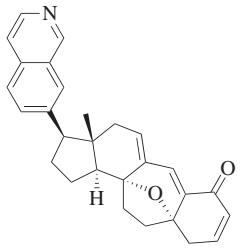
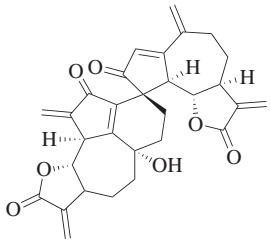
α,β-Unsaturated Carbonyl Product	Pd-Mediated Oxidative Dehydrogenation Conditions	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	A?	CS: phenylselenation, oxidative elimination	108
	A?, C	CS: LDA, *N*-*t*-butyl benzenesulfinimidoyl chloride	112
	A^S	SS: phenylselenation, oxidative elimination	269
	A?	SS: DDQ, 2,6-di-*t*-butyl-4 -methylpyridine	66
	A^S	SS: singlet oxygen, PPh_3	97
	A?	CS: epoxidation, TsOH	92

Table A. (cont.)

α,β-Unsaturated Carbonyl Product	Pd-Mediated Oxidative Dehydrogenation Conditions	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	$A^{?}$	CS: phenylselenation, oxidative elimination	96
	$A^{?}$	CS: 2-iodoxybenzoic acid/ 4-methoxypyridine *N*-oxide/DMSO	91
	$A^{?}$, C	CS: $Pd(OAc)_2$	100

Method A^{S}: $Pd(OAc)_2$ (1 equiv or more), with or without benzoquinone, MeCN.
Method $A^{?}$: $Pd(OAc)_2$ (unspecified amount), benzoquinone, MeCN.
Method C: $Pd(OAc)_2$ (cat.), O_2, DMSO.
Method F: $Pd(OH)_2$ (cat.), *t*-BuOOH (2.5 equiv), Na_2HPO_4 or NEt_3 (0.1–10 equiv), O_2, CH_2Cl_2.
Method G: $Pd(0)L_n$ (cat.), allyl carbonate (2 equiv), MeCN or PhCN.

Table B. α,β-Unsaturated Carbonyl Compounds Prepared More Efficiently by Pd-Mediated Oxidative Dehydrogenation of Silyl Enol Ethers Than by Other Methods.

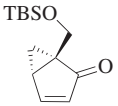
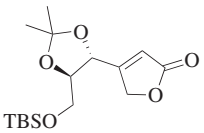
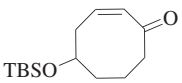
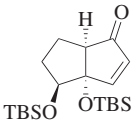
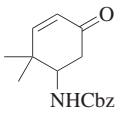
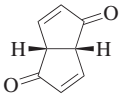
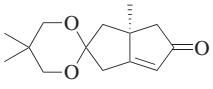
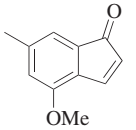
α,β-Unsaturated Carbonyl Product	Effective Procedure	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	C	CS: phenylselenation, oxidative elimination	270
	A[C]	CS: phenylselenation, oxidative elimination	271
	A[S]	CS: phenylselenation, oxidative elimination	272
	A[S]	SS: 2-iodoxybenzoic acid/ 4-methoxypyridine *N*-oxide/DMSO CS: 2-iodoxybenzoic acid/DMSO	273
	A[S]	CS: bromination, dehydrobromination and sulfenylation, dehydrosulfenylation	274
	A[C]	CS: phenylselenation, oxidative elimination, 2-iodoxybenzoic acid/DMSO, 2-iodoxybenzoic acid/ 4-methoxypyridine *N*-oxide/DMSO, 2-iodoxybenzoic acid/NMO/DMSO, and HIO_3/DMSO	171
	A[S]	CS: benzeneseleninic anhydride	265
	A[C]	CS: bromination, ketalisation, dehydrobromination, deprotection	275

Table B. (cont.)

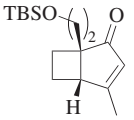
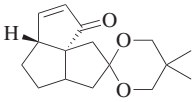
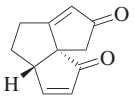
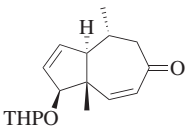
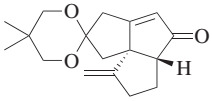
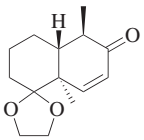
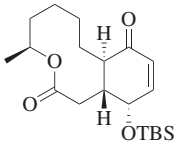
α,β-Unsaturated Carbonyl Product	Effective Procedure	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	A^S	CS: bromination, dehydrobromination and phenylselenenylation, oxidative elimination and 2-iodoxybenzoic acid/DMSO	123
	A^S	CS: benzeneseleninic anhydride	265
	A^S	CS: benzeneseleninic anhydride	265
	A^S	CS: sulfenylation, dehydrosulfenylation	276
	A^S	CS: benzeneseleninic anhydride	265
	A^S	CS: 2-iodoxybenzoic acid/DMSO	152
	A^S	CS: phenylselenation, oxidative elimination and 2-iodoxybenzoic acid/DMSO	277

Table B. (cont.)

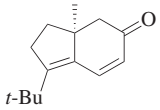
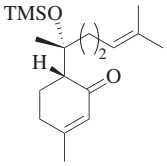
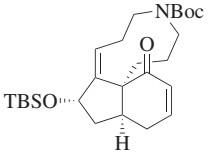
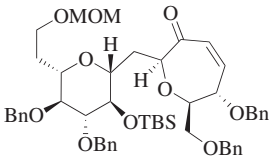
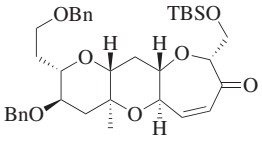
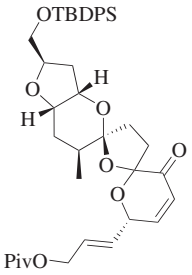
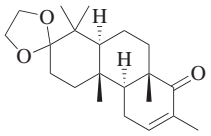
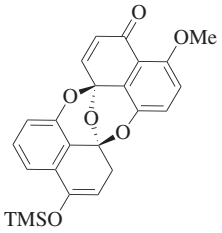
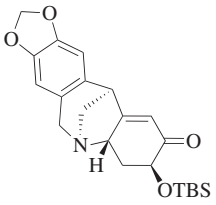
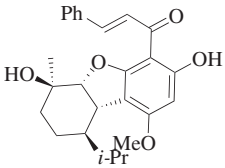
α,β-Unsaturated Carbonyl Product	Effective Procedure	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	A^S	SS: 2-iodoxybenzoic acid	278
	C	SS: 2-iodoxybenzoic acid/ 4-methoxypyridine *N*-oxide/DMSO CS: 2-iodoxybenzoic acid/DMSO	279
	A^S	CS: iodoxybenzoic acid/NMO/DMSO and 2-iodoxybenzoic acid/DMSO	280
	A^S	CS: phenylselenation, oxidative elimination	281
	A^S	SS: phenylselenation, oxidative elimination CS: LDA, *N*-*t*-butyl benzenesulfinimidoyl chloride and 2-iodoxybenzoic acid/DMSO	225
	A^S	CS: phenylselenation, oxidative elimination and 2-iodoxybenzoic acid/DMSO	269

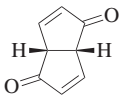
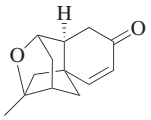
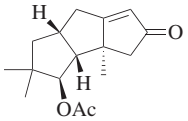
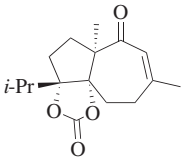
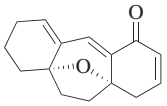
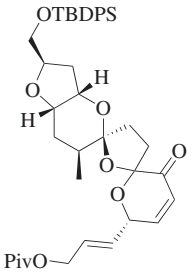
Table B. (cont.)

α,β-Unsaturated Carbonyl Product	Effective Procedure	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	C[a]	CS: 2-iodoxybenzoic acid/DMSO	145
	A^S	CS: 2-iodoxybenzoic acid/DMSO and benzeneseleninic anhydride and 2-iodoxybenzoic acid/ 4-methoxypyridine *N*-oxide/DMSO	176, 177
	A^S	SS: DDQ/2,6-di-*t*-butyl-4-methylpyridine	282
	A^S	CS: 2-iodoxybenzoic acid/DMSO	283, 284

Method A^C: $Pd(OAc)_2$ (cat.), benzoquinone, MeCN.
Method A^S: $Pd(OAc)_2$ (1 equiv or more), with or without benzoquinone, MeCN.
Method C: $Pd(OAc)_2$ (cat.), O_2, DMSO.

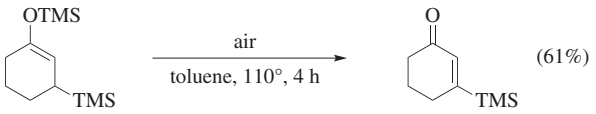
[a] 1.5 equivalents of $Pd(OAc)_2$ were used.

Table C. α,β-Unsaturated Enones Prepared in Comparable Yields Using Seagusa's Procedures and Other Methods.

α,β-Unsaturated Carbonyl Product	Seagusa's procedure	Other Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Refs.
	A^C	CS: 2-iodoxybenzoic acid/DMSO or HIO_3/DMSO	171
	A^S	SS: 2-iodoxybenzoic acid/ 4-methoxypyridine *N*-oxide/DMSO	285
	A^S	CS: 2-iodoxybenzoic acid/DMSO, TsOH	137
	A^S	SS: 2-iodoxybenzoic acid/DMSO	286
	A^C	SS: 2-iodoxybenzoic acid/ 4-methoxypyridine *N*-oxide/DMSO	91
	A^S	CS: LDA, *N*-*t*-butyl benzenesulfinimidoyl chloride or phenylselenation, oxidative elimination	269

Method A^C: $Pd(OAc)_2$ (cat.), benzoquinone, MeCN.
Method A^S: $Pd(OAc)_2$ (1 equiv or more), with or without benzoquinone, MeCN.
Method C: $Pd(OAc)_2$ (cat.), O_2, DMSO.

All of the methods discussed herein involve a metal (either catalytic or stoichiometric), but there is one example of a metal-free dehydrogenation of a silyl enol ether. 3-(Trimethylsilyl)cyclohex-2-enone is formed by aerobic oxidation of 1-(trimethylsilyloxy)-3-(trimethylsilyl)cyclohex-1-ene in the absence of a metal (Scheme 51).[287]



Scheme 51

EXPERIMENTAL CONDITIONS

The potential hazards in Saegusa oxidations include the use of oxygen and organotin reagents. Oxygen enrichment may result in combustion or lead to explosions under certain conditions. Caution is required when using tin, as it may induce acute and chronic health effects.

The efficiencies of the aforementioned palladium-mediated syntheses of α,β-unsaturated carbonyl compounds may be significantly affected by solvent, catalyst, temperature, and purity of the reagents, as well as the scale of the reactions. Typical findings are summarized below.

Silyl Enol Ethers as Substrates

When diallyl carbonate is used to regenerate the catalyst, $Pd_2(dba)_3 \bullet CHCl_3$ produces higher yields than $Pd(OAc)_2$ (with or without dppe) at room temperature and at reflux.[166] In the case of Method C, side reactions may occur to varying degrees depending on the batch of $Pd(OAc)_2$ and on the scale.[147,288]

Enol Acetates as Substrates

Product yields are very sensitive to the purity of the reagents when $Pd(OAc)_2$/dppe and allyl methyl carbonate are employed.[182] In some cases, the use of dppe lowers the yields.[39,160]

Allyl Enol Carbonates as Substrates

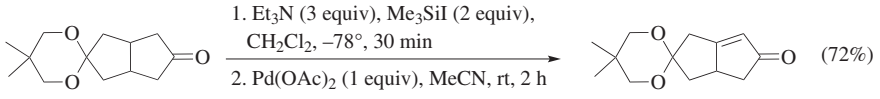
α,β-Unsaturated ketones are obtained in better yields using $Pd(OAc)_2$/dppe at 80° than with $Pd(OAc)_2/PPh_3$ at 80°. The decarboxylation/allylation pathway predominates at room temperature or with $Pd_2(dba)_3$/dppe or $Pd(PPh_3)_4$/dppe.[188]

Both $Pd(OAc)_2$ and $Pd_2(dba)_3$ in MeCN are effective in the absence of phosphine ligands.[160]

Allyl β-Keto Carboxylates as Substrates

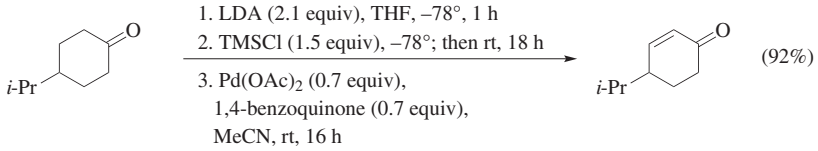
The use of $Pd(OAc)_2$/dppe is slightly more efficient in MeCN than in DMF, whereas the use of acetone or *t*-BuOH as solvent provides mainly the decarboxylation/allylation product.[46] Decarboxylative allylation also predominates when PPh_3 is employed instead of dppe.[46,289] With $Pd_2(dba)_3$ as the catalyst, the reaction may stop prematurely in DMF.[197]

EXPERIMENTAL PROCEDURES



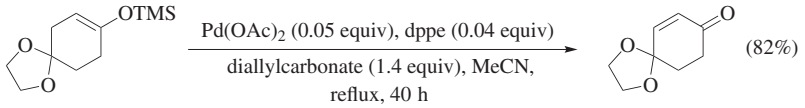
5,5-Dimethyl-3a′,4′-dihydro-1′*H*-spiro[[1,3]dioxane-2,2′-pentalen]-5′(3′*H*)-one [Stoichiometric Dehydrogenation of a Ketone via a Silyl Enol Ether].[290] To a stirred solution of the cyclopentanone (1.80 g, 8.0 mmol, 1 equiv) in dry CH_2Cl_2 (100 mL) at –78° under an argon atmosphere were added Et_3N (3.44 mL, 24 mmol, 3 equiv) and Me_3SiI (2.35 mL, 16 mmol, 2 equiv). After the mixture had been stirred at –78° for 30 min, saturated aqueous $NaHCO_3$ (10 mL) was added, and the mixture was allowed to warm to rt. The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 10 mL). The organic extracts were combined and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the silyl enol ether (2.19 g, 92%) as a colorless oil. The silyl enol ether was used without further purification.

To a solution of $Pd(OAc)_2$ (1.59 g, 7.1 mmol, 1.0 equiv) in dry MeCN (90 mL) at rt was added a solution of the unpurified silyl enol ether (2.09 g, 7.1 mmol, 1 equiv) in dry MeCN (10 mL). After the mixture had been stirred at rt for 2 h, it was filtered through a short column of Florisil. The column was washed with Et_2O, and the combined filtrates were concentrated under reduced pressure. Colum chromatography on silica gel (4 cm × 25 cm; petroleum ether/EtOAc, 2:1) of the residue gave the product (1.29 g, 72%) as a white solid: mp 84–86° (after recrystallization from hexane); IR (KBr) 2959, 1704, 1635, 1103 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.94 (s, 3H), 1.01 (s, 3H), 1.40 (dd, J = 6.2, 6.2 Hz, 1H), 2.08 (dd, J = 9.0, 1.7 Hz, 1H), 2.60 (dd, J = 9.0, 3.0 Hz, 1H), 2.65 (dd, J = 6.2, 4.0 Hz, 1H), 2.87 (d, J = 9.0 Hz, 1H), 2.99 (d, J = 9.0 Hz, 1H), 3.12 (m, 1H), 3.47 (dd, J = 5.0 Hz, 2H), 3.52 (dd, J = 5.0 Hz, 2H), 5.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3, 22.4, 30.1, 38.1, 42.0, 42.1, 43.4, 71.6, 72.5, 109.0, 125.8, 185.6, 209.6; HRMS (*m/z*): $[M]^+$ calcd for $C_{13}H_{18}O_3$, 222.1256; found, 222.1255. Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16. Found: C, 70.36; H, 8.30.



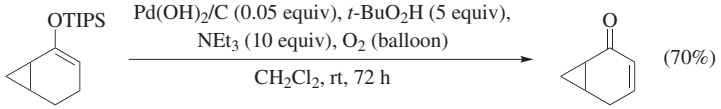
4-Isopropylcyclohex-2-enone [Dehydrogenation of a Ketone in the Presence of Benzoquinone via a Silyl Enol Ether].[291] A 2.3 M solution of *n*-BuLi (1.93 mL, 4.49 mmol, 2.1 equiv) was added to a solution of *i*-Pr_2NH (0.660 mL, 4.71 mmol, 2.2 equiv) in THF (8 mL) at −78°. The mixture was warmed to 0° over 30 min and then cooled to −78°. A solution of 4-isopropylcyclohexanone (0.300 g, 2.14 mmol, 1 equiv) in THF (2 mL) was added dropwise, and the reaction mixture was stirred at −78° for 1 h. TMSCl (0.410 mL, 3.21 mmol, 1.5 equiv) was added dropwise, and the resulting mixture was stirred at rt for 18 h before being quenched with saturated aqueous $NaHCO_3$ solution (8 mL). The reaction mixture was diluted with Et_2O (8 mL), and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (30 mL), dried over Na_2SO_4, and concentrated in vacuo to yield 4-isopropylcyclohex-1-enyloxytrimethylsilane (0.590 g, 2.79 mmol) as a yellow oil that was used without further purification.

A solution of 4-isopropylcyclohex-1-enyloxytrimethylsilane (0.590 g, 2.79 mmol, 1 equiv) in MeCN (3 mL) was added dropwise to a solution of $Pd(OAc)_2$ (0.440 g, 1.95 mmol, 0.7 equiv) and 1,4-benzoquinone (0.210 g, 1.95 mmol, 0.7 equiv) in MeCN (8 mL) at rt. The reaction mixture was stirred at rt for 16 h, and then was filtered through a pad of Celite. The pad of Celite was washed with Et_2O (30 mL), and the filtrates were concentrated in vacuo. This material was purified by silica gel column chromatography (petroleum ether/EtOAc, 9:1) to yield the product (0.270 g, 1.96 mmol, 92% over two steps) as a pale-yellow oil: IR (liquid film) 2960, 2872, 1676, 1419, 1389, 1187, 1145 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.97 (app t, J = 7.1 Hz, 6H), 1.72–1.87 (m, 2H), 1.97–2.05 (m, 1H), 2.27–2.39 (m, 2H), 2.51 (dt, J = 16.7, 4.1 Hz, 1H), 6.15 (dd, J = 10.4, 2.5 Hz, 1H), 6.90 (dt, J = 10.4, 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.4, 19.6, 25.2, 31.5, 37.4, 42.5, 129.6, 154.4, 200.1; EIMS (*m/z*): $[M + H]^+$ 139 (49), 94 (100), 81 (48), 64 (81), 52 (60), 40 (45); HRMS (*m/z*): $[M]^+$ calcd for $C_9H_{14}O$, 138.1039; found, 138.1039.

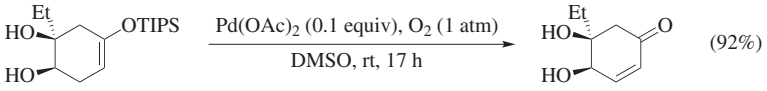


1,4-Dioxaspiro[4.5]dec-6-en-8-one [Catalytic Dehydrogenation of a Silyl Enol Ether in the Presence of an Allyl Carbonate].[175] A solution of $Pd(OAc)_2$ (36.0 mg, 0.16 mmol, 0.05 equiv) and dppe (58.0 mg, 0.14 mmol, 0.04 equiv) in MeCN (50 mL) was heated to reflux, and then diallyl carbonate (0.64 g, 4.51 mmol,

1.4 equiv) and the silyl enol ether (0.74 g, 3.24 mmol, 1 equiv) were added. The mixture was heated at reflux for 40 h. The solvent was then evaporated under reduced pressure to furnish a residue, which was purified by filtration through a column of silica gel (Et_2O/light petroleum, 1:1). The filtrate was evaporated under reduced pressure to provide the product (0.41 g, 82%) as a pale-yellow oil: IR (film) 1683 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.20 (t, J = 6.5, 2H), 2.63 (t, J = 6.5, 2H), 4.05 (m, 4H), 6.00 (d, J = 10.2, 1H), 6.61 (d, J = 10.2, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.0, 35.4, 65.2, 104.1, 130.6, 146.6, 198.8; HRMS (*m/z*): $[M + H]^+$ calcd for $C_8H_{11}O_3$, 155.0708; found, 155.0710. Anal. Calcd for $C_8H_{10}O_3$: C, 62.30; H, 6.50. Found: C, 62.31; H, 6.35.

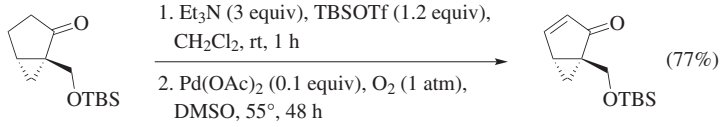


Bicyclo[4.1.0]hept-3-en-2-one [Catalytic Dehydrogenation of a Silyl Enol Ether in the Presence of *tert*-Butyl Hydroperoxide and Oxygen].[36,37] Under an atmosphere of air, a 50-mL, round-bottomed flask equipped with a magnetic stir bar was charged with $Pd(OH)_2$/C (20% Pd) (17 mg, 0.032 mmol, 0.05 equiv), NEt_3 (0.86 mL, 6.4 mmol, 10 equiv), CH_2Cl_2 (2 mL), and the silyl enol ether (69 mg, 0.64 mmol, 1 equiv). The flask was purged with pure oxygen gas and was kept under an oxygen atmosphere with a balloon. To this mixture was added *tert*-butyl hydroperoxide (40 μL, 0.40 mmol, 5 equiv) [sic] in 4 portions every 2 h with vigorous stirring. The resulting mixture was stirred at rt for 72 h, at which point TLC analysis indicated that the reaction was complete. The mixture was then filtered through a short pad of silica gel, and the pad was washed with CH_2Cl_2. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/Et_2O, 1:1) to provide the product as a clear oil (48 mg, 70%): IR (neat) 2923, 1704, 1664, 1362, 1258, 864 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.28–1.34 (m, 2H), 1.72–1.78 (m, 1H), 1.86–1.90 (m, 1H), 2.64–2.77 (m, 2H), 5.88–5.90 (m, 1H), 6.47–6.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.3, 21.9, 25.4, 51.1, 127.0, 143.3, 197.7; HRMS (70 eV) (*m/z*): $[M + H]^+$ calcd for C_7H_9O, 109.0653; found, 109.0658.



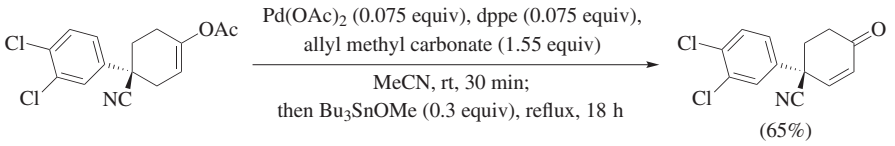
(4*R*,5*S*)-5-Ethyl-4,5-dihydroxycyclohex-2-enone [Catalytic Dehydrogenation of a Silyl Enol Ether in the Presence of Oxygen].[71] A 500-mL, round-bottomed flask was charged sequentially with a Teflon-coated stir bar, the starting diol (9.60 g, 30.6 mmol, 1 equiv), and DMSO (15.3 mL). $Pd(OAc)_2$ (685 mg, 3.06 mmol, 0.1 equiv) was then added. The reaction flask was purged

with oxygen by three evacuation–refill cycles, using a balloon of oxygen to fill the flask. The resulting mixture was stirred under a balloon of oxygen for 10 h at rt. The reaction flask was then purged again three times with oxygen, and stirring was continued for an additional 7 h at rt under a balloon of oxygen. The product mixture was purified by column chromatography on silica gel (hexanes/acetone, 55:45) to afford the product as a viscous, colorless oil (4.41 g, 92%): TLC R_f 0.20 (ethyl acetate/hexanes, 7:3, SiO_2); IR (film) 3407, 1675, 1463, 1385 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.97 (t, J = 8.0 Hz, 3H), 1.72 (app q, J = 7.5 Hz, 2H), 2.26 (s, 1H), 2.48 (d, J = 16.5 Hz, 1H), 2.64 (dd, J = 16.5, 0.5 Hz, 1H), 2.76 (d, J = 8.5 Hz, 1H), 4.38 (dt, J = 9.0, 2.5 Hz, 1H), 6.04 (ddd, J = 11.0, 2.0, 1.0 Hz, 1H), 6.74 (dd, J = 10.0, 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz), δ 7.9, 31.2, 46.1, 70.1, 76.8, 128.9, 149.8, 198.3; HRMS–CI (*m/z*): $[M + H]^+$ calcd for $C_8H_{13}O_3$, 157.0859; found, 157.0855.

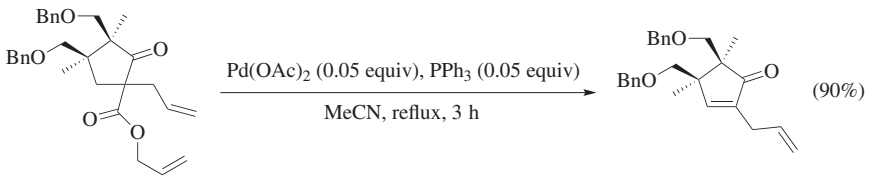


(1*R*,5*R*)-1-[(((1,1-Dimethylethyl)dimethylsilyloxy)methyl)]bicyclo[3.1.0]hex-3-en-2-one [Catalytic Dehydrogenation of a Ketone in the Presence of Oxygen via a Silyl Enol Ether].[270] To a solution of the ketone (0.647 g, 2.69 mmol, 1 equiv) in CH_2Cl_2 (13.5 mL) was added TBSOTf (0.742 mL, 3.23 mmol, 1.2 equiv). Triethylamine (1.12 mL, 8.07 mmol, 3 equiv) was added dropwise. The reaction mixture was stirred at rt for 1 h and then was diluted with a saturated aqueous $NaHCO_3$ solution. The organic layer was removed, and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was passed through a short column of silica gel (pretreated with 3% triethylamine in hexanes). The silyl enol ether was eluted with 1% triethylamine in hexanes. Concentration of the fractions in vacuo yielded a colorless liquid that was dissolved in DMSO (26.9 mL).

To the solution of the silyl enol ether in DMSO was added $Pd(OAc)_2$ (60.4 mg, 0.269 mmol, 0.1 equiv). The reaction flask was purged with oxygen before attaching a balloon filled with oxygen. The reaction mixture was heated to 55° and stirred at that temperature for 48 h. The reaction mixture was allowed to cool to rt and was extracted with hexanes. The combined extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate, 97:3 to 92:8) to provide the product as a colorless oil (0.495 g, 77% over two steps): ^1H NMR (C_6D_6, 400 MHz) δ 0.02 (s, 6H), 0.82–0.93 (m, 10H), 1.11 (app dd, J = 6.9, 3.3 Hz, 1H), 2.02 (ddd, J = 6.8, 2.9, 2.9, 1H), 3.68 (d, J = 10.5 Hz, 1H), 4.22 (d, J = 10.5 Hz, 1H), 5.42 (d, J = 5.7 Hz, 1H), 6.90 (dd, J = 5.7, 2.8 Hz, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ –5.34, –5.27, 18.5, 26.1, 26.3, 36.1, 37.6, 60.0, 128.8, 162.0, 204.5; HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{13}H_{22}O_2NaSi$, 261.1287; found, 261.1300.

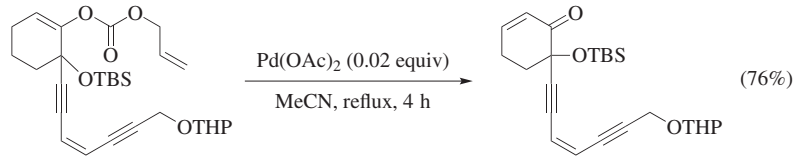


4-Cyano-4-(3,4-dichlorophenyl)cyclohex-2-enone [Catalytic Dehydrogenation of an Enol Acetate in the Presence of an Allyl Carbonate].[182] To a solution of 4-cyano-4-(3′,4′-dichlorophenyl)cyclohex-1-enyl acetate (150 mg, 0.4 mmol, 1 equiv) in dry MeCN (5 mL) were added $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 0.075 equiv), dppe (12 mg, 0.03 mmol, 0.075 equiv), and allyl methyl carbonate (0.07 mL, 0.62 mmol, 1.55 equiv). The mixture was stirred for 30 min at rt, and then tributyltin methoxide (0.03 mL, 0.12 mmol, 0.3 equiv) was added. The reaction mixture was heated at reflux for 18 h, cooled to rt, and filtered through a pad of Celite. After CH_2Cl_2 (15 mL) was added, the organic layer was washed with a saturated aqueous NH_4Cl solution (3 × 15 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane; then hexane/Et_2O, 1:1) to yield the product (77.4 mg, 65%) as a colorless oil: TLC R_f 0.62 (hexane/EtOAc, 1:1); IR (film) 2239, 1693 cm^{-1}; ^1H ($CDCl_3$, 300 MHz) δ 2.13–2.86 (m, 4H), 6.33 (d, J = 9.9 Hz, 1H), 6.80 (d, J = 9.9 Hz, 1H), 7.24–7.54 (m, 3H); ^{13}C ($CDCl_3$, 75 MHz) δ 34.65, 37.63, 42.25, 118.41, 125.48, 128.31, 131.52, 132.49, 133.73, 134.03, 137.91, 143.61, 195.22; EIMS (*m/z*): $[M]^+$ 265 (44), 237 (82), 202 (23), 267 (32), 239 (57), 174 (100); HRMS–ESI (*m/z*): $[M]^+$ calcd for $C_{13}H_9Cl_2NO$, 265.0061; found 265.0065.

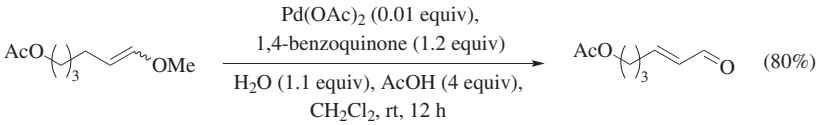


(4*R*,5*S*)-2-Allyl-4,5-bis((benzyloxy)methyl)-4,5-dimethylcyclopent-2-enone [Catalytic Decarboxylative Dehydrogenation of an Allyl β-Keto Carboxylate].[194] A solution of (3*S*,4*R*)-allyl 1-allyl-3,4-bis((benzyloxy)methyl)-3,4-dimethyl-2-oxocyclopentanecarboxylate (5.0 g, 10.5 mmol, 1 equiv) in MeCN (20 mL) was added slowly to a solution of $Pd(OAc)_2$ (117 mg, 0.525 mmol, 0.05 equiv) and PPh_3 (37 mg, 0.525 mmol, 0.05 equiv) in MeCN at 90° under Ar. The reaction mixture was then stirred at 90° for 3 h before being allowed to cool to rt. Filtration of the reaction mixture through a plug of silica, removal of solvent, and column chromatography on silica gel (hexanes/EtOAc, 20:1) furnished the product (3.6 g, 90%) as a colorless oil: IR (film) 3064, 3030, 2979, 2858, 1705, 1454, 1360, 1093, 914, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.13 (s, 3H), 1.15 (s, 3H), 2.91 (ddd, J = 6.6, 2.7, 1.3 Hz, 1H), 3.48 (d, J = 9.0 Hz, 1H), 3.50 (d, J = 9.0 Hz, 1H), 3.56 (d, J = 9.4 Hz, 1H),

3.59 (d, $J = 9.4$ Hz, 1H), 4.33 (s, 2H), 4.33 (d, $J = 11.9$ Hz, 1H), 4.38 (d, $J = 11.9$ Hz, 1H), 5.01–5.10 (m, 2H), 5.83 (tdd, $J = 16.8$, 10.1, 6.6 Hz, 1H), 6.97 (t, $J = 1.4$ Hz, 1H), 7.17–7.31 (m, 10H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 19.8, 20.1, 29.1, 49.5, 54.3, 72.8, 73.1, 73.5, 74.7, 116.4, 127.2, 127.3, 127.4, 128.1, 128.2, 134.5, 138.2, 138.3, 140.6, 161.5, 210.9; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{36}H_{31}O_3$, 391.2268; found, 391.2273.

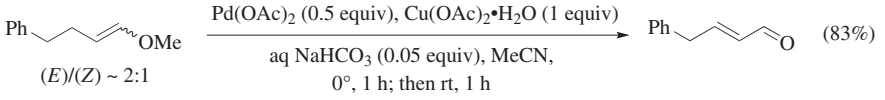


6-[(*Z*)-7-[(Tetrahydropyranyl)oxy]hept-1,5-diyn-3-ene]-6-[(*tert*-butyldimethylsilyl)oxy]cyclohex-2-en-1-one [Catalytic Decarboxylative Dehydrogenation of an Allyl Enol Carbonate].[191] To a solution of the carbonate (41.7 g, 83.3 mmol, 1 equiv) in anhydrous MeCN (420 mL) heated at reflux under argon was added $Pd(OAc)_2$ (375 mg, 1.67 mmol, 0.02 equiv). The reaction mixture was heated at 80° for 4 h until TLC (hexanes/Et_2O, 4:1) showed that the reaction was complete. Celite 545 (15 g) was added, and the mixture was allowed to cool over 30 min with vigorous stirring. The solution was filtered through a pad of Celite, and the solvent was evaporated in vacuo. The residue was immediately purified by column chromatography on silica gel (hexanes/Et_2O, 4:1) to provide the product as a colorless oil (26.2 g, 76%): IR (film) 2928, 2854, 1706, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.18 (s, 3H), 0.20 (s, 3H), 0.86 (s, 9H), 1.50–1.83 (m, 6H), 2.17–2.41 (m, 2H), 2.35–2.47 (m, 1H), 2.50–2.66 (m, 1H), 3.46–3.55 (m, 1H), 3.78–3.84 (m, 1H), 4.32–4.46 (m, 2H), 4.78 (bt, 1H), 5.77–5.88 (m, 2H), 5.95 (bd, 1H), 6.84–6.89 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –3.2, –3.1, 18.3, 19.0, 25.1, 25.3, 25.8, 30.2, 38.8, 54.7, 62.0, 73.2, 82.9, 84.4, 93.2, 94.4, 96.9, 118.9, 120.2, 126.9, 149.8, 193.6; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{35}O_4Si$, 415.2315; found, 415.2305.



(*E*)-6-Oxohex-4-en-1-yl Acetate [Catalytic Dehydrogenation of an Alkyl Enol Ether in the Presence of Benzoquinone].[42] To a 4-mL borosilicate glass vial containing 6-methoxyhex-5-en-1-yl acetate (172 mg, 1.00 mmol, 1 equiv), 1,4-benzoquinone (130 mg, 1.2 mmol, 1.2 equiv), water (20.0 μL, 1.11 mmol, 1.1 equiv), and AcOH (240 μL, 4.19 mmol, 4 equiv) was added $Pd(OAc)_2$ (2.4 mg, 0.02 mmol, 0.01 equiv), followed by CH_2Cl_2 (1 mL). The reaction mixture was

stirred at rt until completion (12 h), as indicated by GC analysis. The reaction mixture was then diluted with CH_2Cl_2 (50 mL) and washed with water (50 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 9:1) to provide the product (125 mg, 80%) as a clear, colorless oil: FTIR (film) 2955, 1734, 1686, 1367, 1242, 1045 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.87 (quint, J = 6.4 Hz, 2H), 2.06 (s, 1H), 2.41–2.47 (m, 2H), 4.12 (t, J = 6.4 Hz, 2H), 6.87 (dt, J = 15.6, 6.8 Hz, 1H), 9.52 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.8, 26.8, 29.1, 63.2, 133.3, 156.9, 170.9, 193.7; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_8H_{12}NaO_3$, 179.0679; found, 179.0671.



(*E*)-4-Phenyl-2-butenal [Catalytic Dehydrogenation of an Alkyl Enol Ether in the Presence of Cu(II)].[41] To a stirred suspension of $Pd(OAc)_2$ (30 mg, 0.134 mmol, 0.5 equiv) in MeCN (0.6 mL) at rt were added 5% aqueous $NaHCO_3$ (0.05 mL, 0.05 equiv) and $Cu(OAc)_2 \bullet H_2O$ (54 mg, 0.268 mmol, 1.0 equiv). After the mixture was cooled to 0°, a solution of (4-methoxybut-3-en-1-yl)benzene (43 mg, 0.268 mmol, 1 equiv) in MeCN (0.35 mL) was added. The resulting mixture was stirred vigorously at 0° for 1 h and then at rt for 1 h. The mixture was poured into saturated aqueous NH_4Cl solution, and the aqueous layer was extracted with $CHCl_3$. The organic extract was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc, 7:1) to provide the product (45 mg, 83%): UV (EtOH) λ_{max} 217 nm; IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (270 MHz) δ 3.65 (dd, J = 6.4, 1.7 Hz, 2H), 6.11 (ddt, J = 15.8, 7.7, 1.7 Hz, 1H), 6.97 (dt, J = 15.8, 6.4 Hz, 1H), 9.53 (d, J = 7.7 Hz, 1H); EIMS (*m/z*): $[M]^+$ 146 (84), 117 (100), 115 (61), 91 (51); HRMS (*m/z*): $[M]^+$ calcd for $C_{10}H_{10}O$, 146.0730; found, 146.0730.

TABULAR SURVEY

The Tabular Survey covers the literature through August 2016. The tables are organized according to the type of substrates and the resulting products. In all tables and subtables, the substrates are listed in order of increasing carbon count. The carbon count is based on all carbon atoms of the starting materials, but small groups on heteroatoms, protecting groups, and the ester groups of β-keto esters are excluded.

Full experimental conditions are typically available for the Saegusa Reaction steps only. When overall yields of the successive steps are shown in the tables, they reflect the available data from the literature. Silyl enol ethers are often used without purification.

Table 1 presents oxidative dehydrogenation reactions leading to enones, cross-conjugated dienones, and phenols. Tables 2 and 3 concern the synthesis

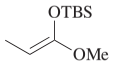
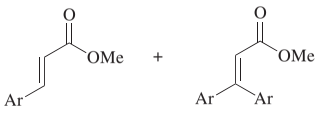
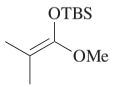
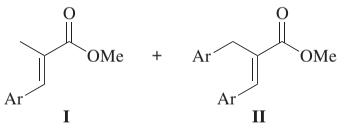
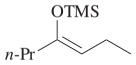
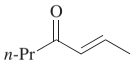
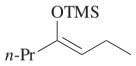
of α,β-unsaturated aldehydes and esters, respectively. Table 4 shows oxidative dehydrogenations leading to unsaturated lactones and lactams. Table 5 contains the synthesis of α,β,γ,δ-unsaturated ketones, esters, and amides.

Some dehydrogenation reactions, which were used to prepare key intermediates starting from the silyl enol ethers, were reported without experimental details and yields, and consequently are not included in the Tables. These compounds include 2-methoxy-14,15-dehydro-estrone,[292] 2-cyclooctenone,[293,294] and 8,9-dihydro-5*H*-benzo[7]annulen-5-one[294] prepared by Methods A;[292−294] 6-phenylcyclohex-2-en-1-one[295] by Method G;[159] and (*R*)-4-((*tert*-butyldimethylsilyl)oxy)-cyclohex-2-enone,[296] 4-*tert*-butylcyclohexenone,[297] and 3-nonen-5-one[297] using Method C.[27]

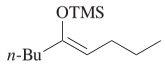
In addition to those listed in "*The Journal of Organic Chemistry* Standard Abbreviations and Acronyms", the following abbreviations are used in the Tabular Survey:

BOM	benzyloxymethyl
C_4H_3S	thienyl
CSA	camphorsulfonic acid
dba	dibenzylideneacetone
dppe	1,2-bis(diphenylphosphino)ethane
HMDS	hexamethyldisilazane
MPM	4-methoxybenzyl
MS	molecular sieves
PMP	4-methoxyphenyl
TBDPS	*tert*-butyldiphenylsilyl
TES	triethylsilyl
TPAP	tetra-*n*-propylammonium perruthenate
Xantphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene

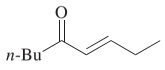
TABLE 1A. ACYCLIC α,β-UNSATURATED KETONES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3  2 eq	$Pd(OAc)_2$ (0.1 eq), Ph_3N (0.2 eq), 2,4,6-trimethoxybenzoic acid, DMF/DMSO (95:5), MS 3 Å, O_2 (1 atm), 120°, 24 h	 **I** + **II** (65), **I/II** = 43:57 Ar = 2,4,6-$(MeO)_3C_6H_2$	236
C_4  2 eq	$Pd(OAc)_2$ (0.1 eq), Ph_3N (0.2 eq), 2,6-dimethoxybenzoic acid, DMF/DMSO (95:5), MS 3 Å, O_2 (1 atm), 120°, 24 h	 **I** + **II** (84), **I/II** = 38:62 Ar = 2,6-$(MeO)_2C_6H_3$	236
C_7  (*Z*)/(*E*) > 20:1	$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq), Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), rt, 18 h	 (74), (*E*)/(*Z*) > 20:1	33
	$Pd(OAc)_2$ (0.25 eq), CuCl (0.05 eq), HMPA (0.5 eq), THF, O_2 (1 atm), rt, 1 h	 **I** **I** + **II** (72), **I/II** = 95:5 **II**	139

C_9

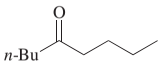


$Pd(OAc)_2$ (*x* eq), oxidant, solvent, rt



I

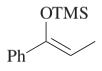
+



II

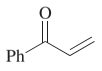
12, 27

x	Oxidant	Solvent	Time (h)	**I**	**II**
0.1	O_2 (1 atm)	DMSO	12	(2)	(2)
0.5	1,4-benzoquinone (0.5 eq)	MeCN	3	(97)	(—)



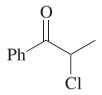
(*Z*)/(*E*) > 20:1

$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq), Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), 45°, 18 h

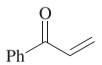


(56)

33

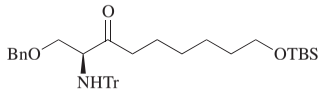


$Pd(OAc)_2$ (0.1 eq), tris(2-furyl)phosphine (0.4 eq), *n*-Bu_3N (1.5 eq), allyl alcohol (15 eq), PhMe, CO (20 atm), 130°, 2 h

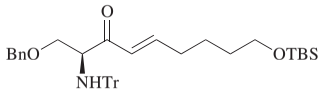


(—)

204



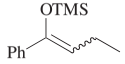
1. NaHMDS, THF, –78°, 3.5 h
2. TMSCl, rt, 1 h
3. $Pd(OAc)_2$ (0.6 eq), 1,4-benzoquinone (0.6 eq), MeCN, rt, 8 h



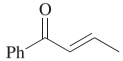
(67)

49

C_{10}



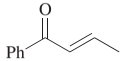
$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), diallyl carbonate (2 eq), MeCN, reflux, 1–3 h



(66)

159, 39

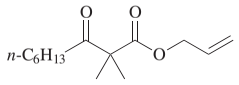
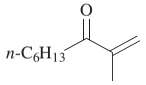
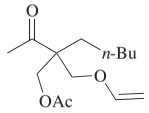
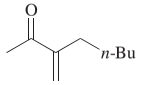
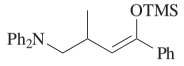
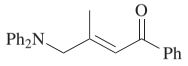
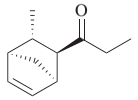
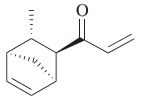
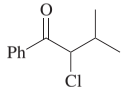
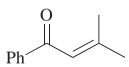
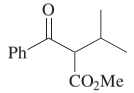
$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 72 h



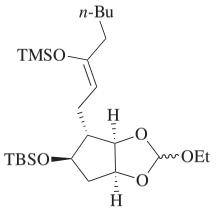
(74)

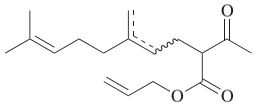
27

TABLE 1A. ACYCLIC α,β-UNSATURATED KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	$Pd(OAc)_2$ (0.02–0.1 eq), dppe (0.02–0.1 eq), MeCN, reflux, 0.5 h	 (76)	46
	$Pd_2(dba)_3$•$CHCl_3$ (0.05 eq), PPh_3 (0.2 eq), MeCN, rt, 10–20 min	 (88)	202
C_{11}			
	$Pd(OAc)_2$ (1.5 eq), MeCN, rt, 12 h	 (56)	298
	1. LHMDS, TMSCl, THF, –78° to rt, 1 h 2. $Pd(OAc)_2$ (1.1 eq), rt, 12 h	 (80)	299
	$Pd(acac)_2$ (0.005 eq), Xantphos (0.01 eq), *n*-Bu_3N (1.2 eq), MeOH, CO (10 atm), 90°, 15 h	 (81) +  (19)	48

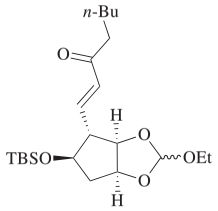
C_{13}





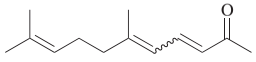
I

$Pd(OAc)_2$, MeCN, rt

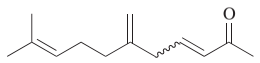


(>58) 300

$Pd(OAc)_2$ (0.1 eq),
1,6-dicyanohexane, rt, 1 h



II 189

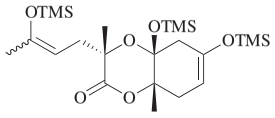
+ 

+ **I**

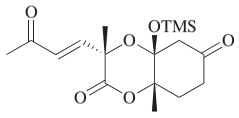
III

I + **II** + **III** (91), **II**/**III**/**I** = 46:44:8

C_{14}

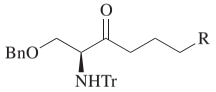


$Pd(OAc)_2$ (2 eq),
MeCN, rt, 50 min

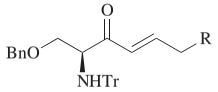


(46) 75

C_{14-18}



1. NaHMDS, THF, –78°, 3.5 h
2. TMSCl, rt, 1 h
3. $Pd(OAc)_2$ (0.6 eq),
1,4-benzoquinone (0.6 eq),
MeCN, rt, 8 h



49

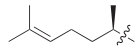
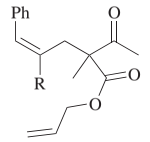
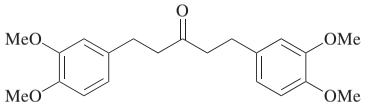
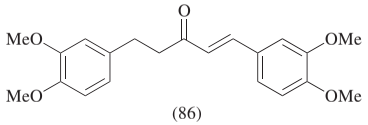
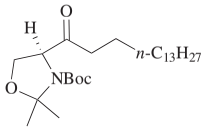
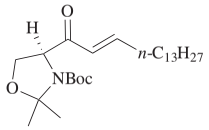
R	
	(70)
4-$MeOC_6H_4(CH_2)_2$	(70)
n-$C_{12}H_{25}$	(90)

TABLE 1A. ACYCLIC α,β-UNSATURATED KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{14–15}$ 	$Pd(OAc)_2$ (0.1 eq), PPh_3 (0.1 eq), MeCN, reflux, 1 h	 **I** + **II**	196
C_{17} 	1. Pyridine, TMSOTf, CH_2Cl_2 2. $Pd(OAc)_2$, MeCN	 (86)	301
C_{18} 	1. NaHMDS, TMSCl, –78° 2. $Pd(OAc)_2$, MeCN	 (90)	302

R	I	II
MeO_2C	(83)	(8)
EtO_2C	(72)	(—)
NC	(73)	(—)
MeCO	(72)	(10)

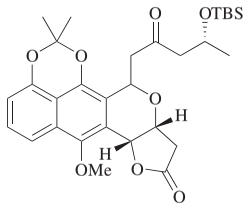
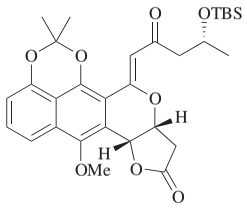
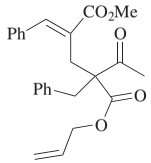
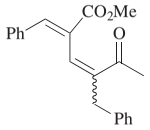
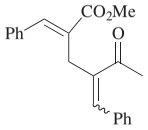
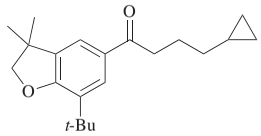
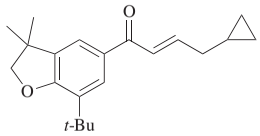
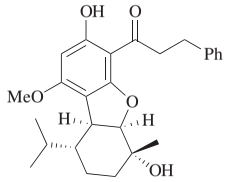
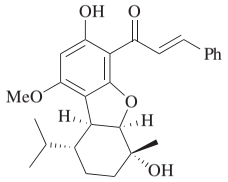
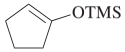
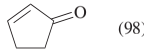
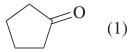
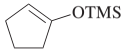
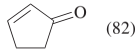
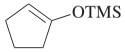
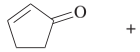
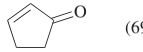
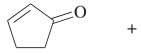
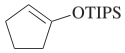
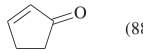
C_{20}		1. TESCl, DBU, CH_2Cl_2, rt, 15 h 2. $Pd(OAc)_2$ (0.2 eq), DMSO, O_2 (1 atm), 50°, 15 h		(45)	303
		$Pd(OAc)_2$ (0.05 eq), PPh_3 (0.05 eq), MeCN, reflux, 1 h	 +  **I** **I + II** (80), **I/II** = 57:43 **II**		196
C_{21}		1. LDA, TMSCl, THF, –78° to rt, 1 h 2. $Pd(OAc)_2$ (1 eq), 1,4-benzoquinone (1 eq), MeCN, rt, 18 h		(56)	132
C_{25}		1. TMSOTf, NEt_3, CH_2Cl_2, 0° to rt, 70 min 2. $Pd(OAc)_2$ (1 eq), MeCN/THF, rt, 2 h		(77)	283

TABLE 1B. CYCLIC 2,3-EN-1-ONES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 2 h	 (98) +  (1)	12
 **I**	Pd (3.9 wt %)/SiO_2, NMP, O_2 (1 atm), 60°, 24 h	 (82) +  (2) + **I** (15)	34
	$Pd(OAc)_2$ (0.1 eq), allyl methyl carbonate (2 eq), MeCN	 +  **I** **II**	39, 160
		Temp / Time (h) / **I** / **II**: 80° / — / (81) / (12); reflux / 2–6 / (81) / (—)	
	$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), diallyl carbonate (2 eq), PhCN, reflux, 1–3 h	 (69)	159, 39
	$Pd(OAc)_2$ (0.5 eq), CuCl (0.1 eq), HMPA (0.5 eq), THF, O_2 (1 atm), rt, 1 h	 +  **I** **II** **I** + **II** (79), **I/II** = 99:1	139
	$Pd(OH)_2/C$ (0.05 eq), Na_2HPO_4 (1 eq), *t*-BuO_2H (5 eq), CH_2Cl_2, rt, 42 h	 (88)	36

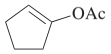
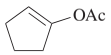
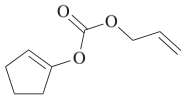
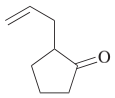
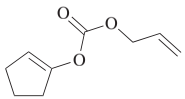
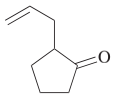
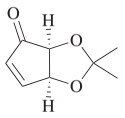
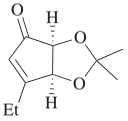
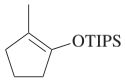
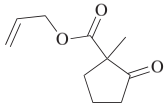
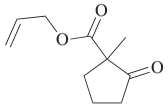
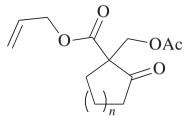
 **I**	Pd (4.2 wt %)/SiO_2, NMP, O_2 (9 atm), 60°, 24 h	 (64) + **I** (10)	40
	1. $Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), allyl methyl carbonate (2 eq), MeCN, rt, 10 min 2. $MeOSnBu_3$ (0.2 eq), reflux, 5–10 h	 (59)	181, 39
	$Pd(OAc)_2$ (0.1 eq), $MeOSnBu_3$ (0.2 eq), allyl methyl carbonate (2 eq), MeCN, reflux, 5–10 h	 (100)	160, 39
	$Pd(OAc)_2$ (0.1 eq), dppe (0.1 eq), MeCN, 80°, 1 h	 (57) +  (13)	188
 **I**	$Pd(OAc)_2$ (0.02 eq), PPh_3 (0.08 eq), MeCN, reflux, 1.5 h	 +  +  + **I** (2)	16
		II (71) **III** (—) **IV** (—)	
		II/III/IV = 96:3.5:0.5	
	$Pd(OAc)_2$ (0.1 eq), tris(2-furyl)phosphine (0.4 eq), *n*-Bu_3N (1.5 eq), allyl alcohol (15 eq), PhMe, CO (20 atm), 130°, 2 h	 (—)	204

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	1. EtMgBr, CuI, HMPA, TESCl, THF, –78 to –40° 2. $Pd(OAc)_2$ (cat.), DMSO, O_2 (1 atm), 50°, 9 h	 (89)	58
C_6 	$Pd(OH)_2/C$ (0.05 eq), Na_2HPO_4 (1 eq), *t*-BuO_2H (5 eq), CH_2Cl_2, rt, 48 h	 (72)	36
	$Pd(OAc)_2$ (0.1 eq), MeCN, 80°	 (85)	160
	$Pd(OAc)_2$ (0.1 eq), MeCN, reflux, 35 min	 (75) +  (tr)	304
 **I**	$Pd_2(dba)_3$•$CHCl_3$ (0.025 eq), PPh_3 (0.0125 eq), MeCN, reflux, 1 h	 +  + **I** (2) **II** (84) **III** (—) **II/III** = 96:4	16

C_{6-13}

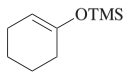


$Pd_2(dba)_3{\bullet}CHCl_3$ (0.05 eq),
PPh_3 (0.2 eq),
MeCN, rt, 10–20 min

n	
1	(67)
2	(63)
8	(83)

202

C_6



$Pd(OAc)_2$ (0.5 eq),
1,4-benzoquinone (0.5 eq),
MeCN, rt, 3 h

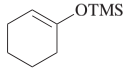
(95) +  (3)

12

$Pd(OAc)_2$ (0.1 eq),
DMSO, O_2 (1 atm), rt, 12 h

(58)

27

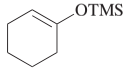


I

Pd (3.1 wt %)/SiO_2,
DMF, O_2 (1 atm), 60°, 24 h

(69) +  (26) + **I** (6)

35



$PdCl_2(MeCN)_2$ (0.05 eq),
CuCl (0.05 eq),
HMPA (0.05 eq),
THF, O_2 (1 atm), rt, 1 h

(89)

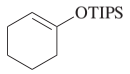
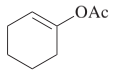
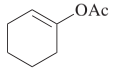
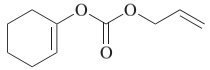
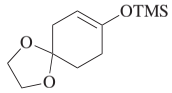
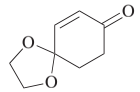
139

$Pd(OAc)_2$ (x eq), dppe (x eq),
diallyl carbonate (y eq),
MeCN, reflux

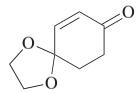
x	y	Time (h)	
0.01	1.4	30	(95)
0.05	2	1–3	(87)

39, 159, 39

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	$Pd(OH)_2/C$ (0.05 eq), Na_2HPO_4 (1 eq), *t*-BuO_2H (5 eq), CH_2Cl_2, rt, 42 h	 (73)	36
 **I**	Pd (4.2 wt %)/SiO_2, NMP, O_2 (9 atm), 60°, 24 h	 (37) + **I** (46)	40
	1. $Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), allyl methyl carbonate (2 eq), MeCN, rt, 10 min 2. $MeOSnBu_3$ (0.2 eq), reflux, 5–10 h	 (97)	181, 39
	$Pd(OAc)_2$ (0.1 eq), dppe (0.1 eq), MeCN, 80°, 1 h	 (92)	188
	Catalyst (*x* eq), solvent		

Catalyst	*x*	Solvent	Temp	Time (h)		
$Pd(OAc)_2$	1.05	MeCN	rt	24	(92)	175, 306
$Pd(OCOCF_3)_2$	—	—	0°	—	(98)	117, 305

$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq), Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), rt, 18 h	 (66)	33

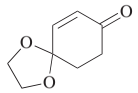
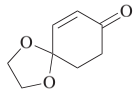
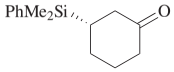
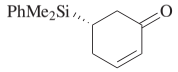
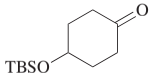
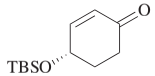
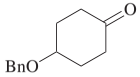
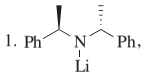
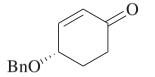
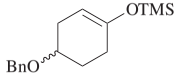
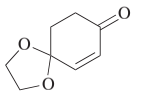
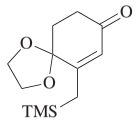
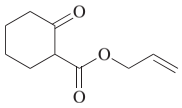
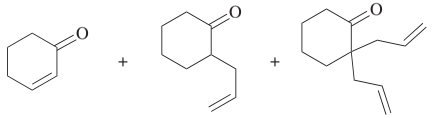
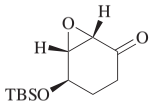
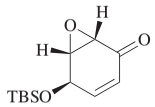
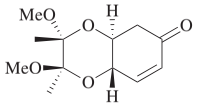
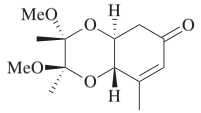
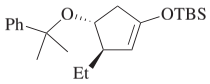
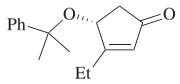
	$Pd(OAc)_2$ (cat.), DMSO, O_2 (1 atm)		(—)	307
	$Pd(OAc)_2$ (0.05 eq), dppe (0.04 eq), diallyl carbonate (1.4 eq), MeCN, reflux, 40 h		(82)	175, 306
	1. LHMDS, $TMSCl$, NEt_3, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 11 h 3. $Pd(OAc)_2$ (0.01 eq), O_2 (1 atm), rt, 3 h		(85)	308
	1. Lithium (+)-bis(α-methylbenzylamide), TMSCl, THF, –100°, 3 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 16 h		(72) er 88.5:11.5–92.5:7.5, (*S*)	210
	1.  TMSCl, –78°, 10 min 2. $Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 10 h	 + 	(48) er 90:10, (*S*) (40)	213

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	1. $TMSCH_2MgCl$, CuI, HMPA, NEt_3, TMSCl, THF, –78 to –60° to rt 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 4 h	 (73)	72
	$Pd(OAc)_2$ (0.02–0.1 eq), dppe (0.02–0.1 eq), MeCN, reflux, 20 min	 (15) + (16) + (22)	46
	1. LHMDS, TMSCl, THF, –78 to –25° 2. $Pd_2(dba)_3$•$CHCl_3$ (0.14 eq), diallyl carbonate (0.94 eq), MeCN, rt, 24 h	 (78)	168
	1. MeLi, CuCN, TMSCl, THF, –78°, 1 h 2. $Pd(OAc)_2$ (0.2 eq), DMSO, O_2 (1 atm), rt, 20 h	 (92)	309
C_7			
	$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm)	 (90)	60

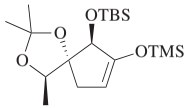
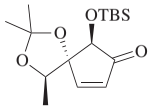
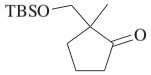
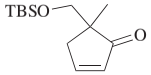
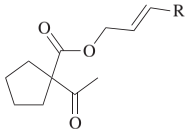
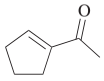
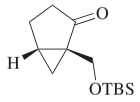
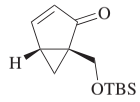
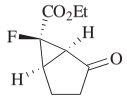
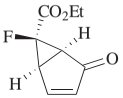
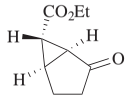
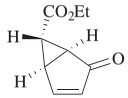
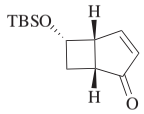
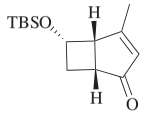
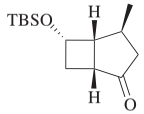
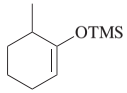
	$Pd(OAc)_2$ (1 eq), MeCN, rt		(57)	310
	1. LDA, TMSCl, NEt_3 2. $Pd(OAc)_2$ (0.1 eq), 1,4-benzoquinone		(60)	311
	1. LDA, TMSCl, THF, –78° 2. $Pd(OAc)_2$, MeCN, reflux		(80)	312
	1. LDA, TMSCl, THF 2. $Pd(OAc)_2$, DMSO, O_2, rt, 12 h		(12–51)	262
$C_{7–15}$ 	1. NEt_3, TMSOTf, CH_2Cl_2, 0° to rt, 0.5 h 2. $Pd(OAc)_2$ (0.05 eq), DMSO, O_2 (1 atm), rt, 24 h		R Me (87) $TBDPSOCH_2$ (88) Bn (90) n-C_9H_{19} (91)	313, 314, 315
C_7 	$Pd(OAc)_2$ (0.02–0.1 eq), dppe (0.02–0.1 eq), dioxane, reflux		R Time (h) H 0.25 (57) Ph 0.5 (82)	46

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. NEt_3, TBSOTf, CH_2Cl_2, rt, 1 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 55°, 48 h	 (77)	270
	1. LHMDS, TMSCl, THF, –75° to rt, 1.5 h 2. $Pd(OAc)_2$ (1.1 eq), MeCN, rt, 16 h	 (89)	316, 317
	1. LHMDS, TMSCl, THF, –75° to rt, 1 h; or NEt_3, TMSI, 0° to rt, 12 h 2. $Pd(OAc)_2$ (1.1 eq), MeCN, rt, 12–16 h	 (86–92)	316, 318
	1. MeLi, CuI, Et_2O, –78°, 1 h 2. TMSCl, NEt_3, 0°, 16 h 3. $Pd(OAc)_2$ (0.5 eq), DMSO, O_2 (1 atm), 32–40°, 3–30 h	 (60–90) +  (10–40)	147, 288
	$Pd(OAc)_2$ (0.1 eq), $Cu(OAc)_2$ (0.2 eq), MeCN, O_2 (1 atm), rt, 24 h	 (100)	78
	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 5 h	 (85) +  (8)	12

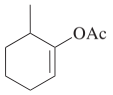
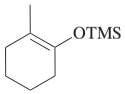
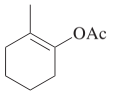
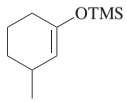
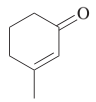
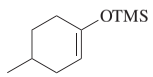
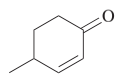
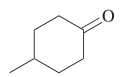
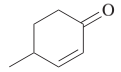
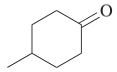
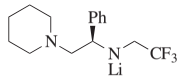
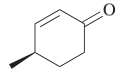
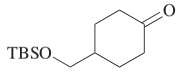
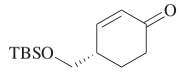
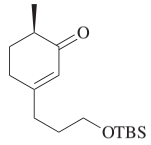
	$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), diallyl carbonate (2 eq), MeCN, reflux, 1–3 h		(87)			159, 39
	1. $Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), allyl methyl carbonate (2 eq), MeCN, rt, 10 min 2. $MeOSnBu_3$ (0.2 eq), reflux, 5–10 h		(87)			181, 39
	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 30 h		(94)	+	 (5)	12
	$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), diallyl carbonate (2 eq), MeCN, reflux, 1–3 h		(81)			39
	$Pd(OAc)_2$ (0.05 eq), $MeOSnBu_3$ (0.2 eq), allyl methyl carbonate (2 eq), MeCN, reflux, 5–10 h		(90)			160, 39
	1. $Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), allyl methyl carbonate (2 eq), MeCN, rt, 10 min 2. $MeOSnBu_3$ (0.2 eq), reflux, 5–10 h		(9)			181, 39

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt	 (91)	12
	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 5 h	 (91) +  (8)	12
	$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm)	 Temp / Time (h): rt / 6 / (72); 40° / 24 / (36)	153 319
	1.  , TMSCl 2. $Pd(OAc)_2$	 (27) er 97.0:3.0, (*R*)	214
	1. Lithium (+)-bis(α-methylbenzyl)amide, TMSCl, THF, –95°, 3 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 16 h	 (69) er >99.5:0.5	210
	1. $TBSO(CH_2)_3MgBr$, CuCN•2LiCl, TMSCl, THF, –45° to rt 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 72 h	 (85) er 97.5:2.5, (*R*)	320

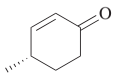
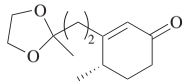
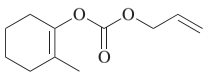
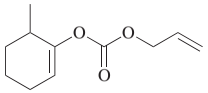
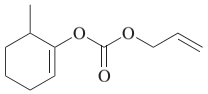
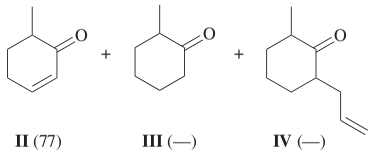
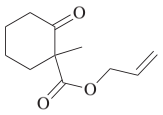
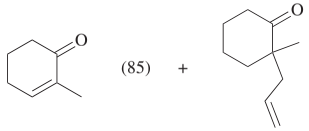
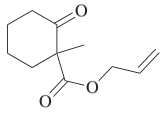
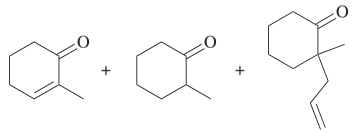
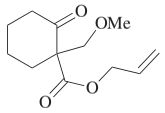
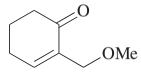
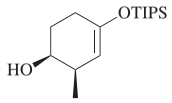
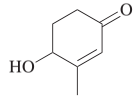
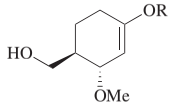
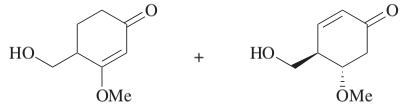
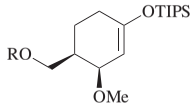
	1.  TMSCl, NEt_3, THF, –20 to –78°, 15 h 2. $Pd(OAc)_2$ (0.2 eq), DMSO, O_2 (1 atm), rt, 24 h	 (50)	321
	$Pd(OAc)_2$ (0.1 eq), dppe (0.1 eq), MeCN, 80°, 1 h	 (98) +  (1)	46, 188, 160
	$Pd(OAc)_2$ (0.1 eq), dppe (0.1 eq), MeCN, 80°, 1 h	 (81)	188
 **I**	$Pd(OAc)_2$ (0.0125 eq), PPh_3 (0.0116 eq), MeCN, reflux, 2 h	 **II** (77) **III** (—) **IV** (—) **II/III/IV** = 93:6:1 + **I** (1)	16
	$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), MeCN, reflux, 0.5 h	 (85) + (5)	46

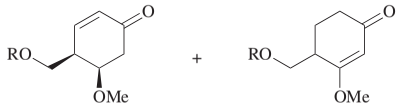
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
 **I**	$Pd(OAc)_2$ (0.02 eq), dppe (0.01 eq), MeCN, reflux, 4 h	 **II** (72) **III** (—) **IV** (—) **II/III/IV** = 88:8:4 + **I** (1)	16
	$Pd(OAc)_2$ (0.02–0.1 eq), dppe (0.02–0.1 eq), MeCN, reflux, 0.5 h	 (46)	46
	$Pd(OAc)_2$ (1.1 eq), MeCN, rt, 24 h	 (8)	59
	$Pd(OAc)_2$ (1.1 eq), MeCN, rt	 **I** + **II**	59

R	Time (h)	**I**	**II**
TES	6	(73)	(2)
TIPS	18	(25)	(45)



$Pd(OAc)_2$ (1.1 eq), MeCN, rt

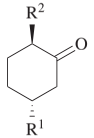


I **II**

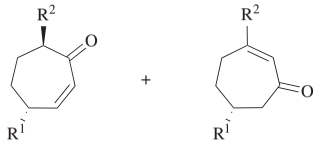
59

R	Time (h)	**I**	**II**
H	18	(48)	(10)
Me	26	(0)	(19)

C_{7-14}



1. $TMSCHN_2$, $AlMe_3$, CH_2Cl_2, –78° to rt, 12 h
2. $Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 24 h



I **II**

322

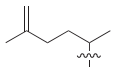
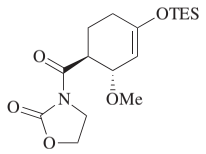
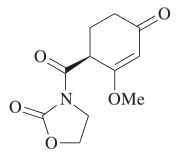
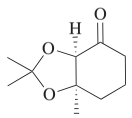
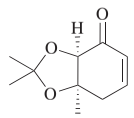
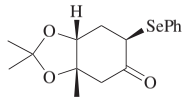
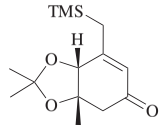
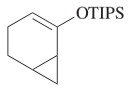
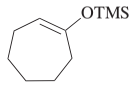
R^1	R^2	**I + II**	**I/II**
H	Me	(90)	2.1:1
Me	*i*-Pr	(91)	1.1:1
Me		(80)	1.2:1
Me	BnO 	(69)	1:2.3

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	$Pd(OAc)_2$ (1 eq), MeCN, rt, 3 h	 (77)	52
 **I**	1. NEt_3, TMSOTf, benzene, rt, 4 h 2. $Pd(OAc)_2$ (1.3 eq), MeCN, rt, 24 h	 (71) + **I** (9)	323
	1. H_2O_2, pyridine, CH_2Cl_2, rt 2. $TMSCH_2MgCl$, CuI, TMSCl 3. $Pd(OAc)_2$	 (73)	72
	$Pd(OH)_2/C$ (0.05 eq), NEt_3 (10 eq), *t*-BuO_2H (5 eq), CH_2Cl_2, rt, 72 h	 (70)	36
	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 2 h	 (91) +  (8)	12
	$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 12 h	 (82)	27

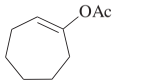
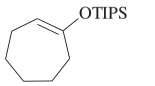
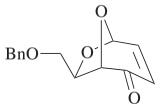
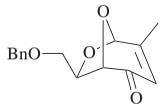
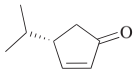
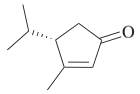
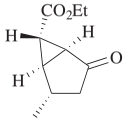
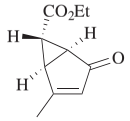
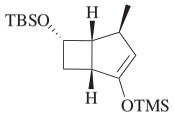
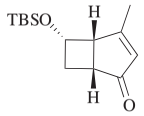
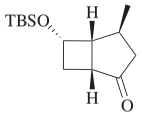
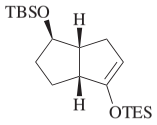
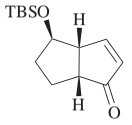
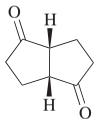
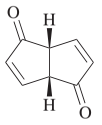
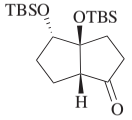
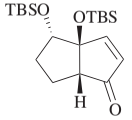
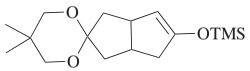
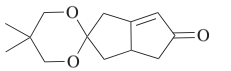
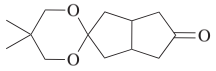
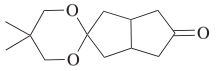
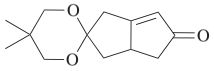
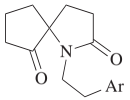
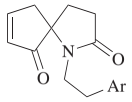
		1. $Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), allyl methyl carbonate (2 eq), MeCN, rt, 10 min 2. $MeOSnBu_3$ (0.2 eq), reflux, 5–10 h		(70)	181, 39
		$Pd(OH)_2/C$ (0.05 eq), Na_2HPO_4 (1 eq), *t*-BuO_2H (5 eq), CH_2Cl_2, rt, 44 h		(74)	36
		1. MeLi, $CuBr•SMe_2$, Et_2O, –78°, 0.5 h 2. TMSCl, –78° to rt, 1.5 h 3. $Pd(OAc)_2$ (0.2 eq), DMSO, O_2 (1 atm), rt, 43 h		(96)	324
C_8		1. Me_2CuLi, TMSCl, Et_2O, –40° to rt, 16 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 9 h		(70)	325
		1. NEt_3, TMSI, 5°, 10 h 2. $Pd(OAc)_2$ (1.1 eq), MeCN, 5° to rt, 12 h		(88)	318
		$Pd(OAc)_2$ (0.5 eq), DMSO, O_2 (1 atm), 32°, 3 h		(81) + 	(19) 147

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

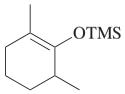
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	$Pd(OAc)_2$	 (42)	51
	1. NEt_3, TMSOTf 2. $Pd(OAc)_2$, 1,4-benzoquinone	 (41)	171
	1. LDA, TMSCl, THF, –78° to rt, 3 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 12 h	 (80)	273, 326
	$Pd(OAc)_2$ (1 eq), MeCN, rt, 2 h	 (72) +  (4)	290
	1. NEt_3, TMSI, CH_2Cl_2, –78°, 0.5 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 2 h	 (72)	265, 290



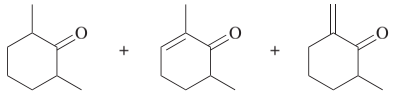
1. NEt_3, TMSOTf, CH_2Cl_2, 0° to rt, 18 h
2. $Pd(OAc)_2$ (1.1–1.63 eq), MeCN, rt, 18 h



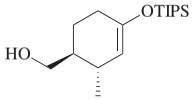
Ar		
Ph	(81)	327
2-naphthyl	(78)	



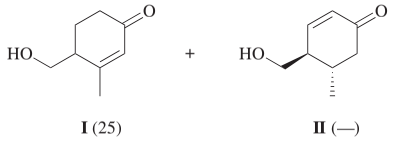
$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 80°, 12 h



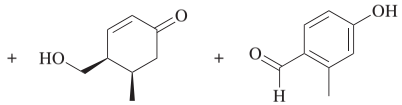
I + **II** + **III** (90), **I/II/III** = 50:46:4 — 27



$Pd(OAc)_2$ (1.1 eq), MeCN, rt, 23 h



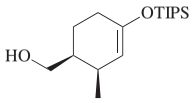
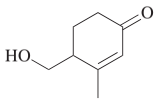
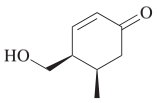
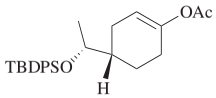
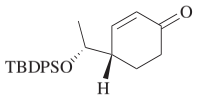
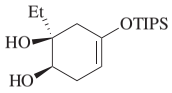
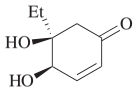
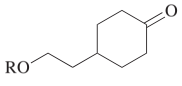
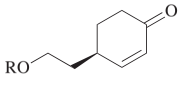
I (25) **II** (—)



III (—) **IV** (17) — 59

II + **III** (23), **II/III** = 5:1

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	$Pd(OAc)_2$ (*x* eq), solvent, O_2 (*y* atm)	 +  **I** **II** *x* Solvent *y* Temp Time (h) **I** **II** 0.2 DMSO 1 80° — (37) (34) 1.1 MeCN — rt 36 (12) (41)	59
	$Pd(OAc)_2$ (0.1 eq), dppe (0.1 eq), $MeOSnBu_3$ (0.3 eq), allyl methyl carbonate (2 eq), MeCN, 80°, 3 h	 (91)	328
	$Pd(OAc)_2$ (*x* eq), DMSO, O_2 (*y* atm)	 *x* *y* Temp Time (h) 0.1 1 rt 17 (92) — — — — (92)	71, 72
	1. Bis[(*R*)-1-phenylethyl]amine, *n*-BuLi, TMSCl, THF, –78°, 1.5 h 2. $Pd(OAc)_2$ (0.05 eq), O_2 (1 atm), rt, 18 h	 R (63) er TBS (63) 91.0:9.0 Ac (39) — 4-ClC_6H_4CO (92) 94.0:6.0 TBDPS (88) 92.0:8.0 Piv (89) — Bn (79) 92.0:8.0 Tr (83) 91.0:9.0	329

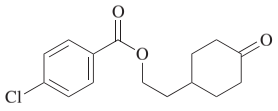
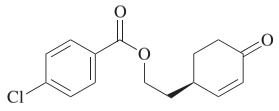
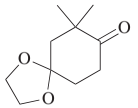
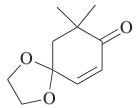
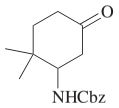
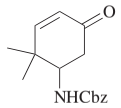
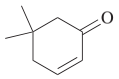
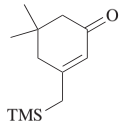
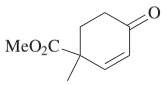
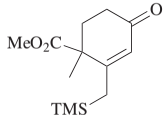
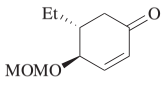
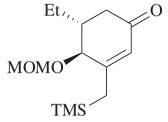
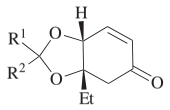
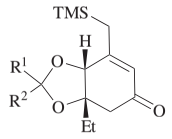
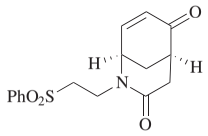
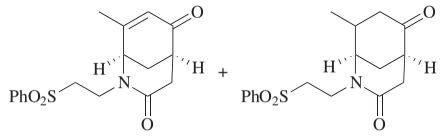
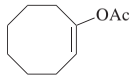
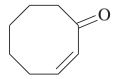
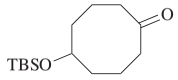
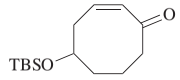
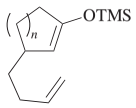
	1. Bis[(*R*)-1-phenylethyl]amine, *n*-BuLi, THF, –78°, 0.5 h 2. TMSCl, –78°, 2 h 3. $Pd(OAc)_2$ (0.05 eq), DMSO, O_2 (1 atm), rt, 18 h		(92) er 94.0:6.0, (*R*)	330
	1. LHMDS, TMSCl 2. $Pd(OAc)_2$ (1.2 eq), 23°, 2 d		(98)	331
	1. LHMDS, NEt_3, TMSCl, THF, –78° to rt 2. $Pd(OAc)_2$ (1.19 eq), $CaCO_3$ (1.08 eq), MeCN, reflux, 2 h		(70)	274
	1. $TMSCH_2MgCl$, CuI, HMPA, NEt_3, TMSCl, THF, –30 to –78° to rt 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 12 h		(61)	72
	1. $TMSCH_2MgCl$, CuI, HMPA, NEt_3, TMSCl, THF, –50 to –60° to rt 2. $Pd(OAc)_2$ (0.89 eq), MeCN, rt, 4 h		(41)	72
	1. $TMSCH_2MgCl$, CuI, HMPA, NEt_3, TMSCl, THF, –30 to –70° to rt 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 12 h		(69)	72

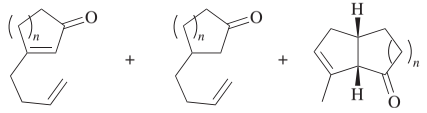
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. $TMSCH_2MgCl$, CuI, HMPA, NEt_3, TMSCl, THF, –30 to –78° to rt 2. $Pd(OAc)_2$ (1.1–1.2 eq), MeCN, rt, 12–13 h		71, 72
		R^1 = H, R^2 = mesityl (79–82) R^1 = Me, R^2 = Me (86)	
	1. MeMgBr, CuI, HMPA, NEt_3, TMSCl, –78° to rt 2. $Pd(OAc)_2$ (1.13 eq), MeCN, O_2 (1 atm), rt, 40 h		11
		(47) + (11)	
	$Pd(OAc)_2$ (0.05 eq), $MeOSnBu_3$ (0.2 eq), allyl methyl carbonate (2 eq), MeCN, reflux, 5–10 h	 (73–80)	160, 39
	1. LHMDS, TMSCl, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 1 h	 (95)	272

C_{9-10}



$Pd(OAc)_2$ (0.1 eq),
DMSO, O_2 (1 atm), 45°, 20 h

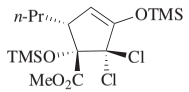


I **II** **III**

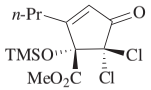
n	**I**	**II**	**III**
1	(44)	(29)	(11)
2	(42)	(31)	(5)

332

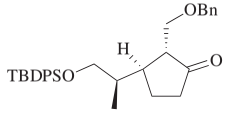
C_9



$Pd(OAc)_2$, MeCN

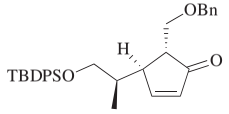


(25) 264



I

1. LDA, TMSCl, THF, –78°, 0.5 h
2. $Pd(OAc)_2$ (1 eq), MeCN, 0° to rt, 2.5 h
3. HCl, MeOH, 0°

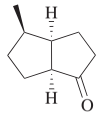


(51) + **I** (24) 263

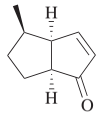
I

1. NEt_3, TMSOTf, CH_2Cl_2, 0°, 0.5 h
2. $Pd(OAc)_2$ (0.1 eq),
methyl allyl carbonate (1.35 eq),
MeCN, 80°, 1.5 h

(83) + **I** (9) 333

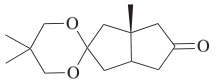
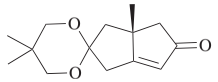
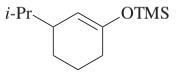
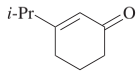
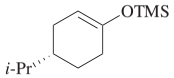
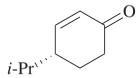
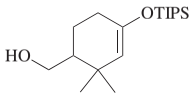
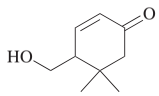


1. LHMDS, TMSCl
2. $Pd(OAc)_2$, MeCN

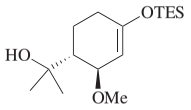


(80) 334

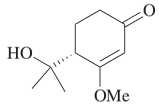
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
 **I**	1. NEt_3, TMSI, CH_2Cl_2, –78°, 0.5 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 2 h	 (42) + **I** (9)	265
	$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq), Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), rt, 18 h	 (82)	33
	$Pd(OAc)_2$, MeCN	 (79)	211
	$Pd(OAc)_2$ (*x* eq), solvent, O_2 (*y* atm)		59

x	Solvent	*y*	Temp	Time (h)	
0.2	DMSO	1	80°	—	(39)
1.1	MeCN	—	rt	23	(51)

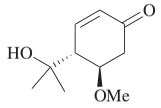


$Pd(OAc)_2$ (*x* eq),
solvent, O_2 (*y* atm), rt



I

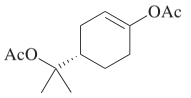
+



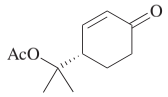
II

52

x	Solvent	*y*	Time (h)	**I**	**II**
0.1	DMSO	1	8	(63)	(22)
1	MeCN	—	3	(90)	(—)

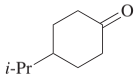


$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq),
$MeOSnBu_3$ (0.2 eq),
allyl ethyl carbonate (2 eq),
MeCN, 80°, 5 h

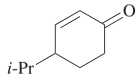


(85)

185



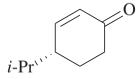
1. LDA, TMSCl, –78° to rt, 18 h
2. $Pd(OAc)_2$ (0.7 eq),
1,4-benzoquinone (0.7 eq),
MeCN, rt, 16 h



(92)

291

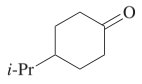
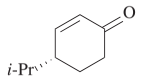
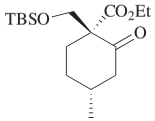
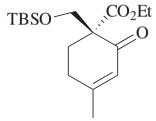
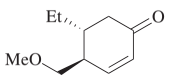
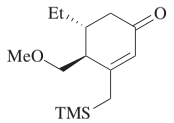
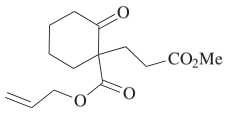
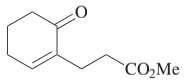
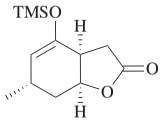
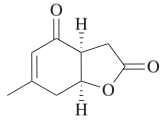
1. *n*-BuLi, [(*R*)-1-phenylethyl]-
2,2,2-trifluoroethylamine,
TMSCl, THF, –100°, 0.25 h
2. $Pd(OAc)_2$ (0.1 eq),
DMSO, O_2 (1 atm), rt, 18 h



(87) er 91.5:8.5, (*R*)

215

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	1.  , TMSCl 2. $Pd(OAc)_2$, MeCN	 (—) er 82.5:17.5, (*R*)	212
	1. LHMDS, TMSCl, THF, –78° to rt, 1 h 2. $Pd(OAc)_2$ (0.2 eq), DMSO, O_2 (1 atm), 55°, 72 h	 (87)	335, 336
	1. $TMSCH_2MgCl$, CuI, HMPA, NEt_3, TMSCl, THF, –30 to –70° to rt 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 12 h	 (69)	72
	$Pd(OAc)_2$ (0.02–0.1 eq), dppe (0.02–0.1 eq), MeCN, reflux, 1 h	 (82)	46
	$Pd(OAc)_2$ (2 eq), MeCN, rt, 72 h	 (58)	337

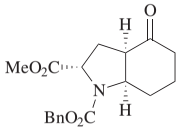
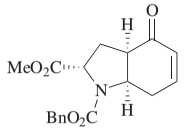
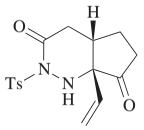
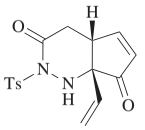
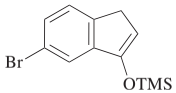
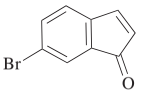
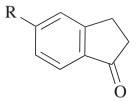
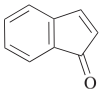
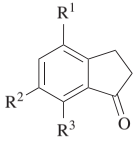
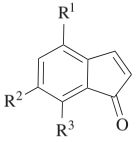
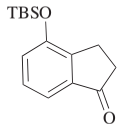
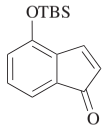
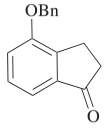
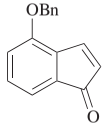
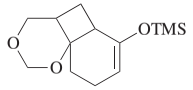
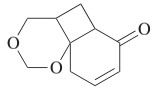
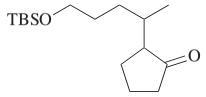
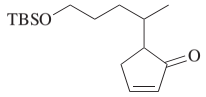
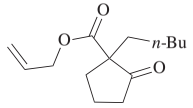
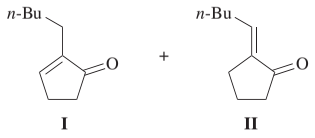
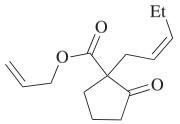
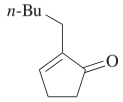
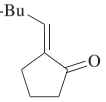
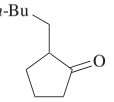
	1. TMSOTf, *i*-Pr_2NEt, CH_2Cl_2, 2–4 h 2. $Pd(OAc)_2$ (1 eq), MeCN, 24 h		(43)	338
	1. HMDS, TMSI, CH_2Cl_2, 0° to rt, 1.25 h 2. $Pd(OAc)_2$ (1 eq), DMSO, rt, 4 h		(78)	121
	$Pd(OAc)_2$ (1.2 eq), CH_2Cl_2, rt, 1 h		(29)	138
	1. NEt_3, TMSOTf, 0° to rt, 10 min 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 1 h		R: H (72); Br (79)	339
	1. NEt_3, TMSOTf, 0° to rt, 10 min 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 1 h		R^1 / R^2 / R^3: H, MeO, H (68); MeO, H, H (82); MeO, H, MeO (67)	339

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

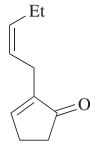
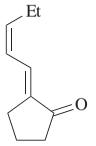
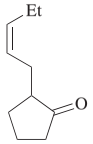
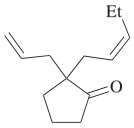
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	1. LHMDS, TMSCl, THF, –78°, 1 h 2. $Pd(OAc)_2$ (1.2 eq), rt, 1 h	 (79)	340, 341
	1. NEt_3, TMSCl, DMF, 60°, 16 h 2. $Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 2 h	 (64)	342, 343
	$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 72 h	 (86)	27
C_{10}  dr 1:1	1. LDA, TMSCl, NEt_3, –78° to rt, 1 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 40°, 12 h	 (83)	344, 345
	$Pd(OAc)_2$ (0.02–0.1 eq), dppe (0.02–0.1 eq), MeCN, reflux, 40 min	 **I** + **II** (81), **I**/**II** = 4:1	46

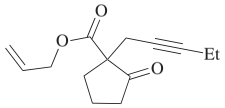


$Pd(OAc)_2$ (0.05 eq),
dppe (0.05 eq),
MeCN, reflux


(65)
+

(16)
+

(5)
233

$Pd(OAc)_2$ (0.05 eq),
dppe (0.05 eq),
MeCN, reflux


(55)
+

(27)
233
+

(7)
+

(1)



$Pd(OAc)_2$ (0.05 eq),
dppe (0.05 eq),
MeCN, reflux

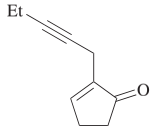
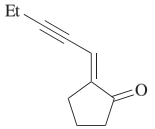
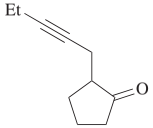
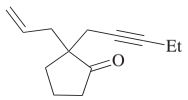
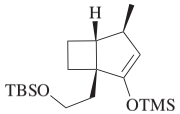
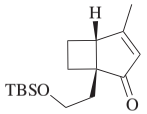
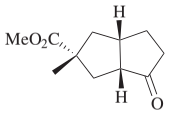
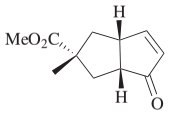
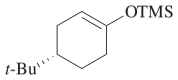
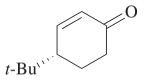
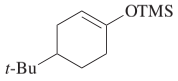
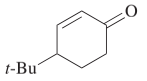
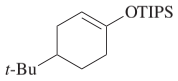
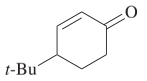
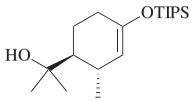
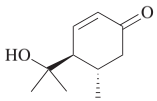
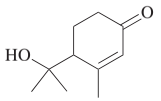
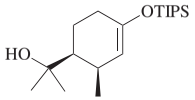
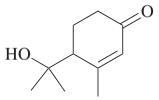

(85)
+

(5)
233
+

(4)
+

(1)

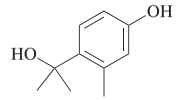
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	$Pd(OAc)_2$ (1 eq), DMSO, rt, 48 h	 (88)	123
	1. LHMDS, TMSCl, THF, –78°, 0.5 h 2. $Pd(OAc)_2$, MeCN, rt, 2 h	 (86)	346
	$Pd(OAc)_2$, MeCN	 (87)	211
	$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq), Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), rt, 18 h	 (65)	33
	$Pd(OH)_2$/C (0.05 eq), Na_2HPO_4 (1 eq), *t*-BuO_2H (5 eq), CH_2Cl_2, rt, 48 h	 (86)	36
	$Pd(OAc)_2$ (1.1 eq), MeCN, rt, 22 h	 (39) +  (13)	59

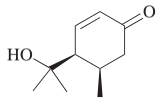


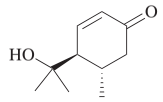
$Pd(OAc)_2$ (1.1 eq), MeCN, rt, 23 h



I (26) + 

II (7)

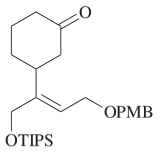
+ 

III (—) + 

IV (—)

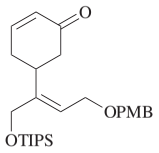
III + **IV** (4), **III/IV** = 1:0.7

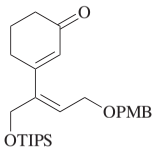
59



I

1. LTMP, TMSCl, THF, –78°, 2 h
2. Catalyst (*x* eq), diallyl carbonate (*y* eq), MeCN

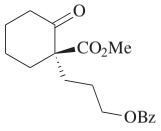


II + 

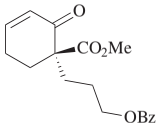
III

165, 166

Catalyst	*x*	*y*	Time (h)	**II** + **III**	**II/III**	**I**
$Pd(OAc)_2$	1.2	0	—	(79)	>6:1	(8)
$Pd_2(dba)_3$•$CHCl_3$	0.07	1.4	12	(90)	>6:1	(1)



1. NEt_3, TMSOTf, CH_2Cl_2
2. $Pd(OAc)_2$ (cat.), DMSO, O_2 (1 atm), 80°



(67)

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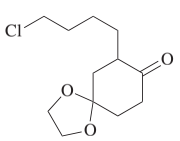
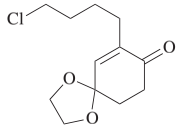
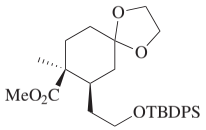
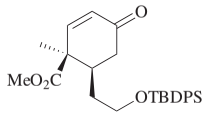
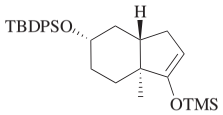
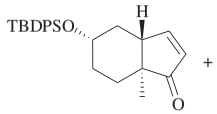
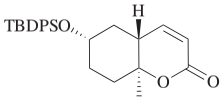
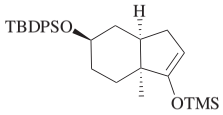
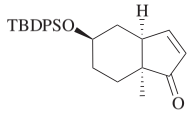
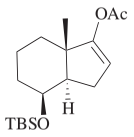
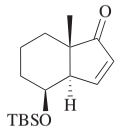
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	1. $FeCl_3$, MeMgBr, TMSCl, NEt_3, HMPA, Et_2O 2. $Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.6 eq), MeCN, rt, 24 h	 (68)	348
	1. $HClO_4$, H_2O, CH_2Cl_2, rt, 6 h 2. LHMDS, TMSCl, THF, –78° to rt, 1.5 h 3. $Pd(OAc)_2$ (0.15 eq), DMSO, O_2 (1 atm), overnight	 (72)	349
	$Pd(OAc)_2$ (0.1 eq), $DMSO/CH_2Cl_2$ (1:1), O_2 (1 atm), 0°	 (47) +  (19)	54
	$Pd(OAc)_2$ (0.1 eq), $DMSO/CH_2Cl_2$ (1:1), O_2 (1 atm), 0°	 (85)	54
 **I**	$Pd(OAc)_2$ (0.3 eq), $MeOSnBu_3$ (0.5 eq), allyl methyl carbonate (4 eq), MeCN, reflux, 2 h	 (52) + **I** (38)	350

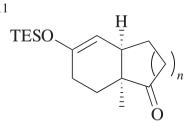
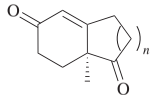
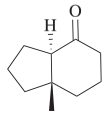
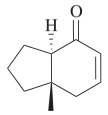
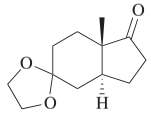
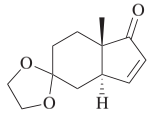
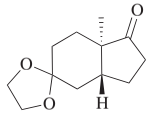
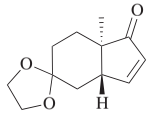
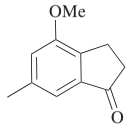
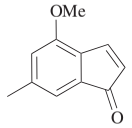
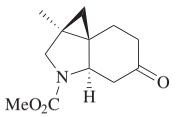
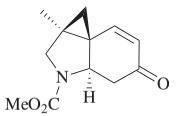
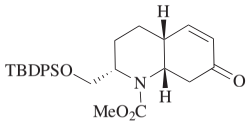
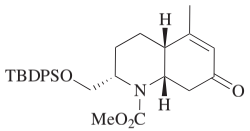
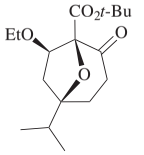
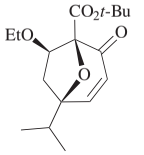
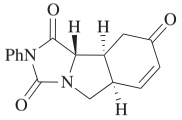
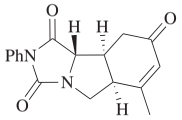
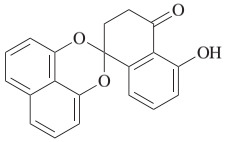
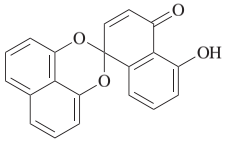
C_{10-11} 	$Pd(OAc)_2$ (1.1 eq), MeCN, rt		*n* 1 (75) 2 (78)	53
C_{10} 	1. LDA, TMSCl, THF, –78° to rt, 2.5 h 2. $Pd(OAc)_2$ (1.05 eq), MeCN, rt, 12 h		(89)	351
 **I**	1. TMSCl, LDA, NEt_3, THF/hexanes, –78°, 1 h 2. $Pd(OAc)_2$ (1.1 eq), $MeCN/CH_2Cl_2$ (1:3), 37°, 4 h		(69) + **I** (22)	352
	1. LDA, TMSCl, NEt_3, –78° to rt, 12 h 2. $Pd(OAc)_2$ (1.05 eq), CH_2Cl_2/MeCN, 35–40°, 8 h		(95)	353
	1. NEt_3, TMSOTf, benzene, 0° to rt, 10 min 2. $Pd(OAc)_2$ (1 eq), CH_2Cl_2/MeCN (2:5), rt, 1 h		(75)	275

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	1. LDA, TMSCl, THF, –78°, 1.5 h 2. $Pd(OAc)_2$ (1.3 eq), MeCN, rt, 10 h	 (67)	354
	1. Me_2CuLi, HMPA, TMSCl, THF, –78°, 1 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 40 h	 (80)	355
	1. NaHMDS, TMSCl, THF, –78 to 0° 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 50 h	 (96)	356
	1. Me_2CuLi, TMSCl, THF, 0°, 10 min 2. $Pd(OAc)_2$ (1.1 eq), MeCN, rt, 4 h; then $Pd(OAc)_2$ (0.3 eq), 1 h	 (76)	357
	1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0° 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 16 h	 (60–78)	358

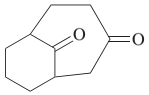
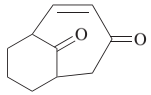
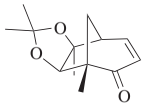
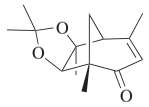
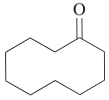
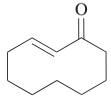
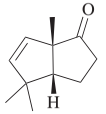
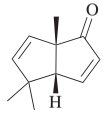
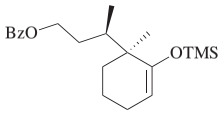
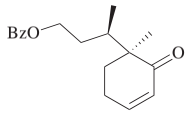
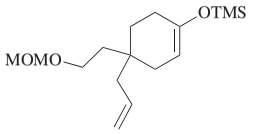
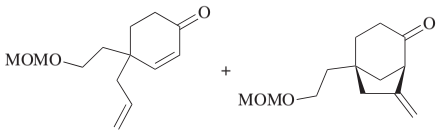
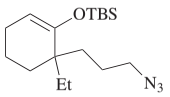
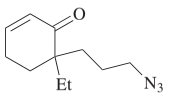
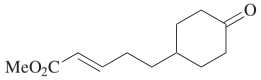
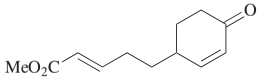
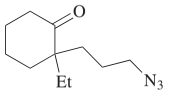
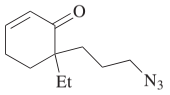
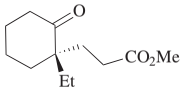
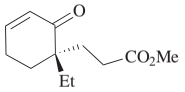
	1. LHMDS, TMSCl, –78 to 0°, 0.5 h 2. $Pd(OAc)_2$ (1.1 eq), MeCN, rt, 12 h		(66)	359
	1. MeLi, CuBr•SMe_2, Et_2O, –78°, 0.5 h 2. TMSCl, –78° to rt, 3.5 h 3. $Pd(OAc)_2$ (0.3 eq), DMSO, O_2 (1 atm), 50°, 48 h		(75)	360, 361
	1. LDA, TMSCl, THF, –78° to rt 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 24 h		(88)	362
C_{11}				
	1. TMSOTf, NEt_3, CH_2Cl_2, 0°, 1 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 24 h		(70)	363
	$Pd(OAc)_2$ (cat.), DMSO, O_2 (1 atm), 80°, 15 h		(91)	364

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 45°, 12 h	 (63) + (8)	89
	$Pd(OAc)_2$ (cat.), DMSO, O_2 (1 atm), 60°	 (70)	266
	1. NEt_3, TMSOTf, CH_2Cl_2, –78°, 3 h 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 4.5 h	 (91)	365
	1. TMSOTf, NEt_3, CH_2Cl_2, 0°, 0.5 h 2. $Pd(OAc)_2$ (0.4 eq), DMSO, O_2 (1 atm), 80°, 12 h	 (79)	266
	1. NEt_3, TMSCl, DMF, 100°, 72 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 40°, 72 h; then $Pd(OAc)_2$ (0.06 eq), 60°, 24 h	 (57)	366

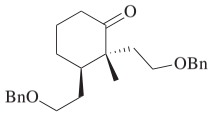
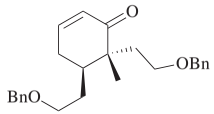
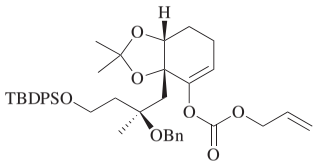
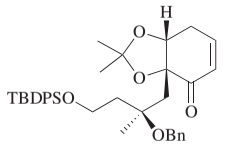
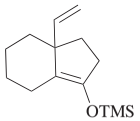
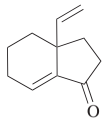
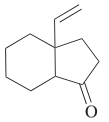
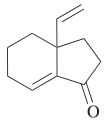
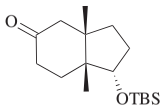
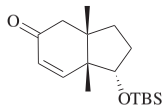
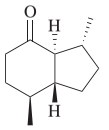
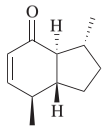
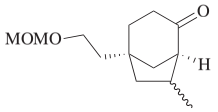
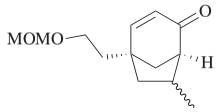
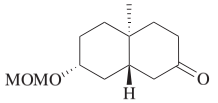
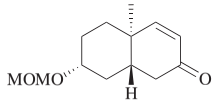
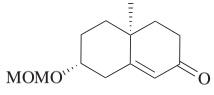
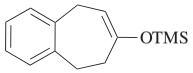
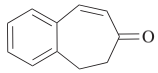
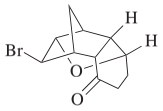
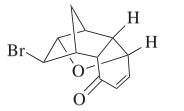
 **I**	1. NEt_3, TMSOTf, 0°, 0.75 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 80°, 16 h		(75) + **I** (21)	367
	$Pd(OAc)_2$, MeCN, 15 h		(82)	192
	$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq), Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), rt, 18 h		(78)	33
 dr 2:1	1. HMDS, TMSI, CH_2Cl_2, –20° to rt, 15 h 2. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 4.5 h		(68)	368
	1. NEt_3, TMSOTf, CH_2Cl_2, 0°, 1 h 2. $Pd(OAc)_2$ (0.15 eq), DMSO, O_2 (1 atm), 60°, 11 h		(92)	56

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	1. TMSOTf, NEt_3, CH_2Cl_2, –78°, 1.5 h 2. $Pd(OAc)_2$, O_2, DMSO, rt, 12 h	 (78)	369
	1. LDA, TMSCl, THF, –78° 2. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 48 h	 (75)	148
	1. LDA, HMPA, TMSCl, THF, –80°, 20 min 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 16 h	 (76) +  (16)	370
	$Pd(OAc)_2$ (*x* eq), oxidant, solvent, rt		371
	1. *i*-Pr_2NEt, $TMSOTf$, CH_2Cl_2, 0°, 2.5 h 2. $Pd(OAc)_2$, MeCN, rt, 26 h	 (80)	372

x	Oxidant	Solvent	Time (h)	
0.1	O_2 (1 atm)	DMSO	16	(50–85)
0.5	1,4-benzoquinone (0.5 eq)	MeCN	72	(45–75)

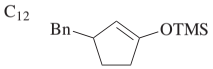
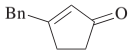
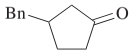
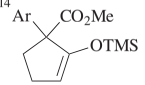
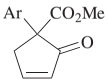
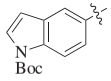
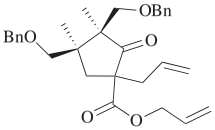
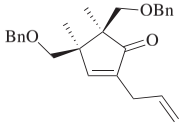
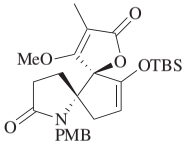
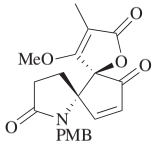
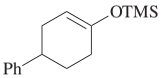
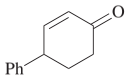
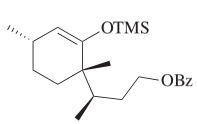
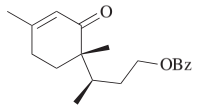
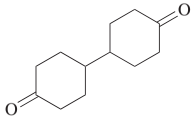
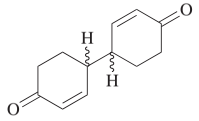
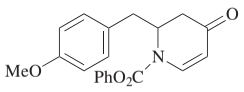
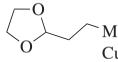
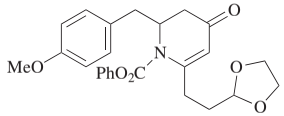
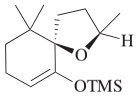
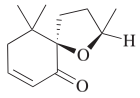
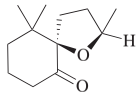
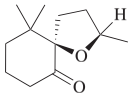
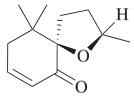
C_{12} 	$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 45°, 20 h	 (59) +  (26)		332
C_{12-14} 	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 2 h		Ar Ph (97) 2-MeC_6H_4 (61)  (60)	373, 374
C_{12} 	$Pd(OAc)_2$ (0.05 eq), PPh_3 (0.05 eq), MeCN, reflux, 3 h	 (90)		194
	$Pd(OAc)_2$ (0.85 eq), DMSO, O_2 (1 atm), 80°		Time (h) 45 (93) 55 (89)	61, 62
	$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq), Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), rt, 18 h	 (85)		33

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	$Pd(OAc)_2$ (0.4 eq), DMSO, O_2 (1 atm), 80°, 20 h	 (75)	375
	1. LDA TMSCl, THF, –78 to 0°, 1 h 2. $Pd(OAc)_2$ (2.2 eq), 1,4-benzoquinone (2.2 eq), MeCN, rt, 12 h	 (92)	73
	1.  MgBr, $CuBr•SMe_2$, TMSCl, NEt_3, THF, –78 to –45°, 26 h 2. $Pd(OAc)_2$ (0.15 eq), CuCl (1.4 eq), MeCN, O_2 (1 atm), 60°, 12 h	 (70)	376
	$Pd(OAc)_2$ (0.66 eq), MeCN, rt, 72 h	 (49) +  (41)	377
 **I**	1. LDA, TMSCl, THF, –78° to rt, 15 h 2. $Pd(OAc)_2$ (1.1 eq), MeCN, rt, 72 h	 (63) + **I** (27)	377

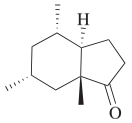
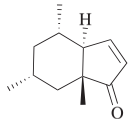
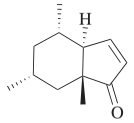
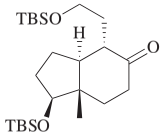
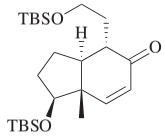
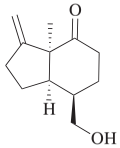
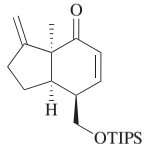
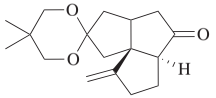
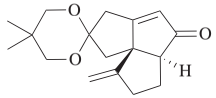
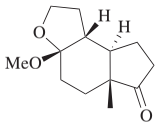
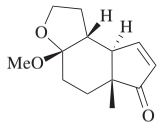
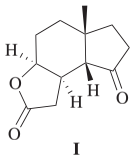
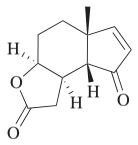
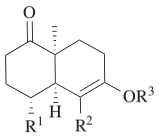
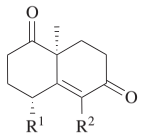
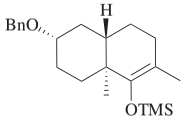
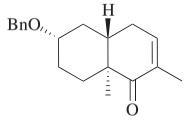
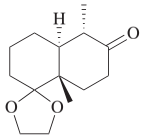
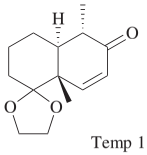
	1. LDA, THF, TMSCl, –78°, 3 h 2. $Pd(OAc)_2$ (0.1 eq), allyl carbonate, MeCN, reflux		(67)	378
	1. LDA, THF, TMSCl, –78° to rt, 1 h 2. $Pd(OAc)_2$, MeCN, 50°, 3 h		(77)	379
	1. $HN(TMS)_2$, NaI, TMSOTf, MeCN, 0° to rt, 6.5 h 2. $Pd(OAc)_2$ (2 eq), MeCN, rt, 12 h		(90)	380
	1. NEt_3, TIPSOTf, CH_2Cl_2, 0°, 10 min 2. NEt_3, TMSOTf, 0°, 10 min 3. $Pd(OAc)_2$ (1 eq), MeCN, rt, 10 h		(71)	381
	1. NEt_3, TMSI, CH_2Cl_2, –78°, 0.5 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 2 h		(73)	265

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

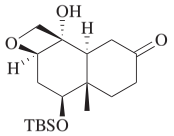
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	1. LDA, TMSCl, NEt_3, THF, –78° to rt 2. $Pd(OAc)_2$ (1.3 eq), $MeCN/CH_2Cl_2$ (1:3), 35–40°, 4.5 h	 (77)	382
 **I**	1. NEt_3, TMSOTf, CH_2Cl_2, 0° to rt, 4 h 2. $Pd(OAc)_2$ (4 eq), MeCN, rt, 14 h	 (76) + **I** (16)	383
	$Pd(OAc)_2$ (1.1 eq), MeCN, rt	 R^1 R^2 R^3 H Me TBS (82) Me H TES (68)	53
	$Pd(OAc)_2$ (cat.), DMSO, O_2 (1 atm)	 (70)	384



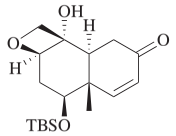
1. LDA, THF, TMSCl, temp 1, time 1
2. $Pd(OAc)_2$ (1.1 eq), MeCN, temp 2, 1 h



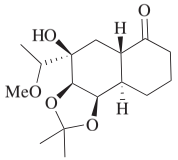
Temp 1 (°)	Time 1 (h)	Temp 2 (°)		
–78 to 0	—	reflux	(95)	385
–78	0.5	80	(82)	152



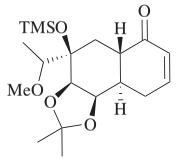
1. LDA, TMSCl, THF, –78° to rt
2. $Pd(OAc)_2$ (1.1 eq), MeCN, reflux, 5 h



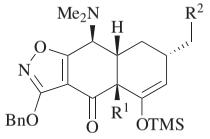
(77) 386



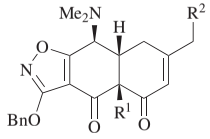
1. LDA, TMSCl, THF, –78° to rt
2. $Pd(OAc)_2$ (1.1 eq), MeCN, reflux, 1 h



(56) 387



$Pd(OAc)_2$ (*x* eq), DMSO



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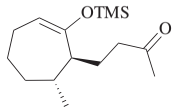
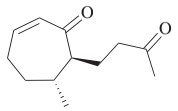
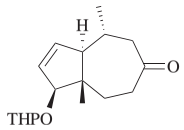
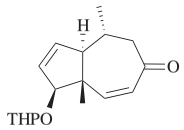
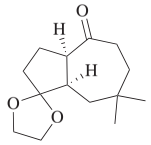
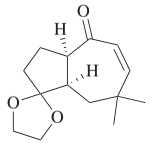
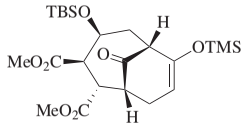
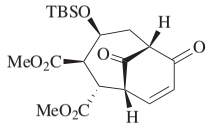
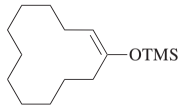
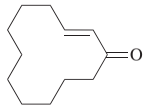
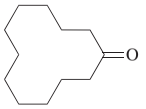
R^1	R^2	*x*	Temp (°)	Time (h)	
TBSO	H	1.15	80	16	(34–44)
TBSO	MOMO	1.05	50	14.5	(25–52)

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	$Pd(OAc)_2$ (0.5 eq), $Cu(OAc)_2$ (1 eq), MeCN, rt, 3 h	 (75)	388
	1. LHMDS, TMSCl, THF, –78° 2. $Pd(OAc)_2$, MeCN, rt	 (73)	276
	1. LDA, TBSOTf, THF, –78° 2. $Pd(OAc)_2$ (0.05 eq), DMSO, O_2 (1 atm), 40°	 (57)	63
	$Pd(OAc)_2$, MeCN	 (35)	267
	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 4 h	 (94) +  (4)	12

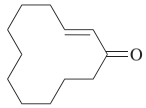
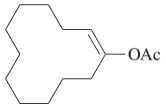
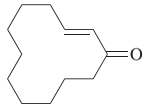
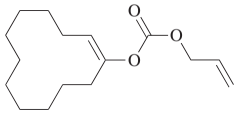
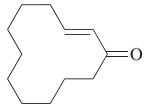
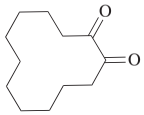
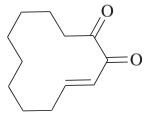
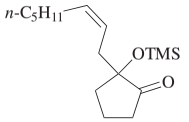
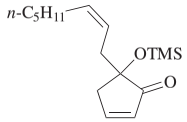
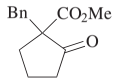
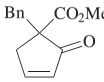
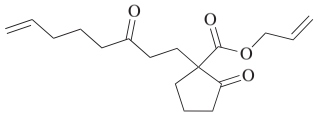
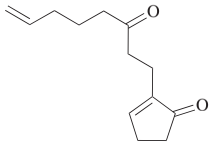
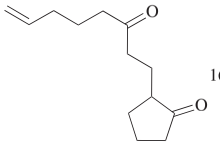
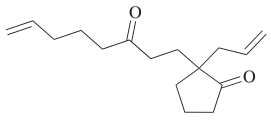
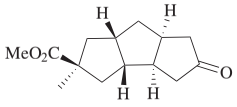
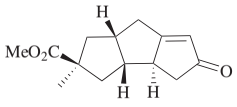
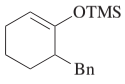
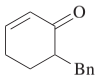
	$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), diallyl carbonate (2 eq), MeCN, reflux, 1–3 h		(78)	159, 39
	1. $Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), allyl methyl carbonate (2 eq), MeCN, rt, 10 min 2. $MeOSnBu_3$ (0.2 eq), reflux, 5–10 h		(85)	181, 39
	$Pd(OAc)_2$ (0.1 eq), dppe (0.1 eq), MeCN, 80°, 1 h		(76)	188
	1. NEt_3, TMSCl, DME, rt 2. $Pd(OAc)_2$ (1 eq), 1,4-benzoquinone (1 eq), MeCN, rt		(52)	130
C_{13} 	1. NEt_3, TMSOTf, CH_2Cl_2, rt 2. $Pd(OAc)_2$, MeCN, rt		(60–63)	389

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}  **I**	1. NEt_3, TMSOTf, CH_2Cl_2, 0° to rt, 0.5 h 2. $Pd(OAc)_2$ (0.05 eq), DMSO, O_2 (1 atm), rt, 24 h	 (82) + **I** (9)	390
 **I**	$Pd_2(dba)_3$•$CHCl_3$ (0.0125 eq), PPh_3 (0.025 eq), MeCN, reflux, 2 h	 +  16 **II** (79) **III** (—) +  + **I** (2) **IV** (—) **II/III/IV** = 89:7:4	
 **I**	1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0° to rt, 1 h 2. $Pd(OAc)_2$ (2 eq), 1,4-benzoquinone (1 eq), MeCN, rt, 18 h	 (59) + **I** (31)	134, 134a
	$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq), Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), rt, 18 h	 (65)	33

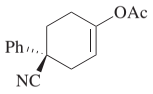
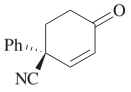
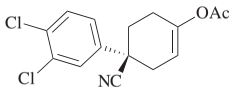
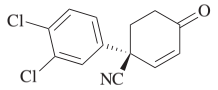
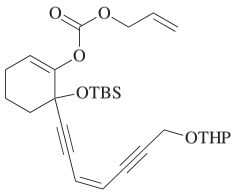
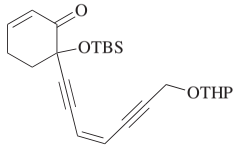
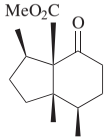
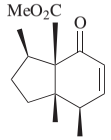
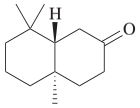
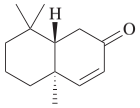
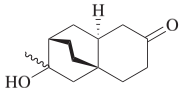
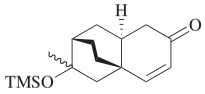
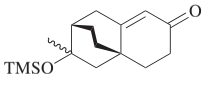
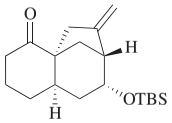
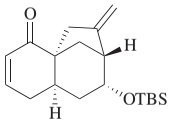
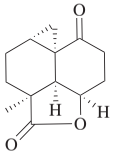
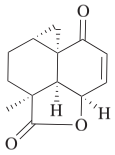
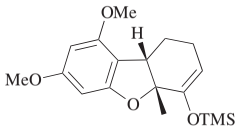
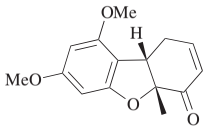
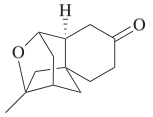
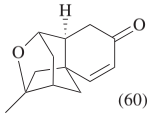
 er 97.5:2.5	$Pd(OAc)_2$, dppe, $MeOSnBu_3$, allyl carbonate, MeCN	 (73) er 97.5:2.5, (*S*)	187
	$Pd(OAc)_2$ (0.075 eq), dppe (0.075 eq), $MeOSnBu_3$ (0.3 eq), allyl methyl carbonate (1.55 eq), MeCN, reflux, 18 h	 (65)	182
	$Pd(OAc)_2$ (0.02 eq), MeCN, reflux, 4 h, 80°	 (76)	190, 191
	1. LHDMS, TMSCl, THF, –78°, 3 h 2. $Pd(OAc)_2$ (1.2 eq), MeCN, reflux, 50 h	 (67)	391

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

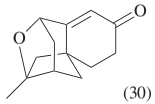
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	1. LDA, HMPA, TMSCl, THF, –80°, 0.25 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 18 h	 (75)	370
	1. HMDS, TMSI, CH_2Cl_2, 0° to rt, 6 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 5 h	 (64) +  (35)	392
	1. LDA, TMSCl, THF, –78°, 1 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 12 h	 (87)	393
	1. LDA, TMSCl, THF, –78° to rt, 2 h 2. $Pd(OAc)_2$ (1.1 eq), MeCN, 40°, 4 h	 (69)	394
	$Pd(OAc)_2$, DMSO, O_2	 (49)	395



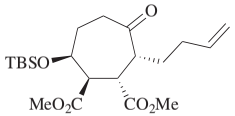
1. HMDS, LiI, TMSCl, CH_2Cl_2, 0°, 3 h
2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 5 h


(60)

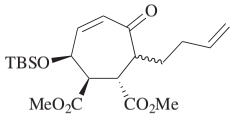
+


(30)

285

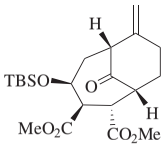


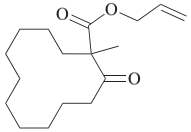
1. KHMDS, TMSCl, THF, –78°, 0.5 h
2. $Pd(OAc)_2$ (1.6 eq), MeCN, rt, 3 h


(35)

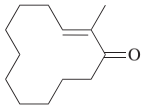
268

+

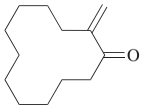

(30)



$Pd(OAc)_2$ (0.02–0.1 eq),
dppe (0.02–0.1 eq),
MeCN, reflux, 1 h



+



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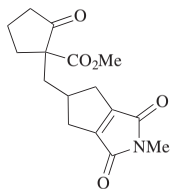
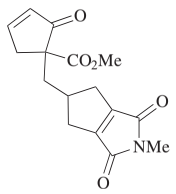
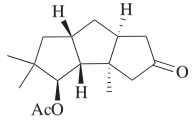
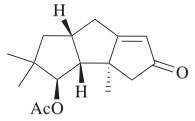
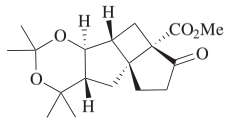
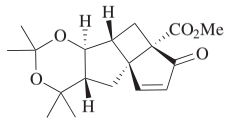
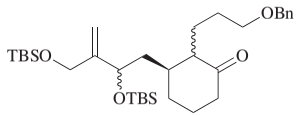
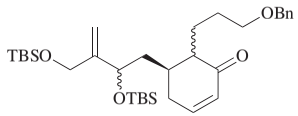
I **I** + **II** (79), **I**/**II** = 5:3 **II**

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	1. NEt_3, $TMSOTf$, CH_2Cl_2, 0°, 0.5 h 2. $Pd(OAc)_2$ (*x* eq), oxidant, solvent		180, 126

x	Oxidant	Solvent	Temp	Time (h)	
0.05–0.1	O_2 (1 atm)	DMSO	—	—	(25)
0.5	1,4-benzoquinone (0.5 eq)	MeCN	—	—	(53)
1	—	DMSO	rt	16	(87)

 **I**	1. 2,6-Lutidine, $TMSOTf$, CH_2Cl_2, 0°, 4 h 2. $Pd(OAc)_2$ (2 eq), 1,4-benzoquinone (1 eq), MeCN, rt, 16 h		(54) + **I** (15)	137
 **I**	1. $TMSCH_2CO_2Et$, TBAF (cat.), THF, rt, 40 min 2. $Pd(OAc)_2$ (1 eq), 1,4-benzoquinone (2 eq), MeCN, rt, 72 h		(56) + **I** (15)	131
	1. NEt_3, $TMSOTf$, CH_2Cl_2, 0°, 1 h 2. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 10 h		(68)	396

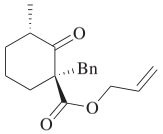
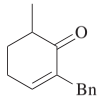
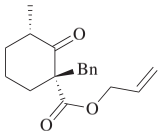
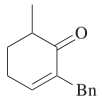
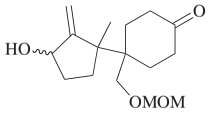
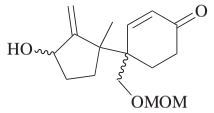
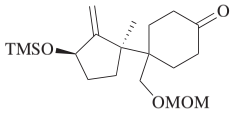
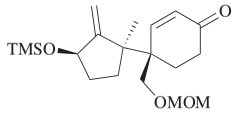
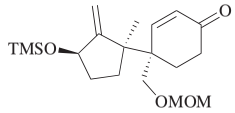
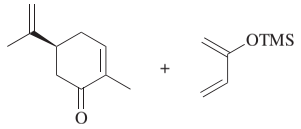
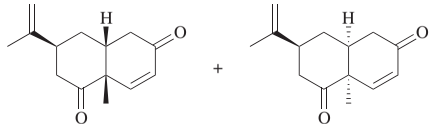
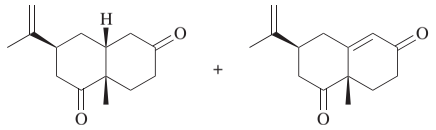
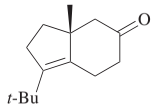
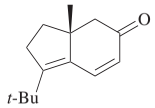
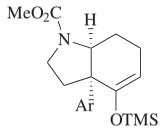
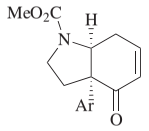
	$Pd(OAc)_2$ (0.02–0.1 eq), dppe (0.02–0.1 eq), MeCN, reflux, 40 min		(80)	46
	$Pd(OAc)_2$ (0.02–0.1 eq), dppe (0.02–0.1 eq), MeCN, reflux, 40 min		(89)	46
	1. NEt_3, TMSCl, 100° 2. $Pd(OAc)_2$, MeCN		(79)	397
	1. Lithium (*S*,*S*)-α,α-bis(phenethyl)amide, NEt_3, TMSCl, –78°, 0.5 h 2. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 9 h	 **I** +  **II**	**I** + **II** (88), **I**/**II** = 66:34	398

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	1. $EtAlCl_2$, PhMe, 0° to rt, 4 h 2. $Pd(OAc)_2$ (1 eq), DMSO, 0° to rt, 4.5 h	 **I** **I + II** (64), **I/II** = 19:1 **II**	122
	1. $EtAlCl_2$, PhMe, 0° to rt, 4 h 2. PhMe, 100° 3. $Pd(OAc)_2$ (1 eq), DMSO, 0° to rt, 4.5 h	 (30) (20)	122
	1. LHMDS, TMSCl, THF, –78° to rt 2. $Pd(OAc)_2$ (1.1 eq), MeCN, rt, 2 h	 (50)	278
 **I** Ar = 2-$O_2NC_6H_4$	$Pd(OAc)_2$ (2 eq), MeCN, 75°, 4 h	 (34) + **I** (47)	115

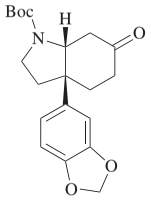
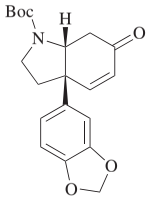
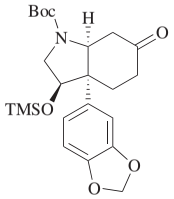
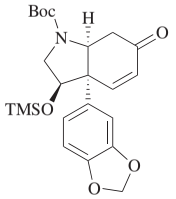
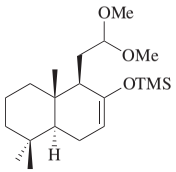
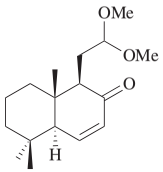
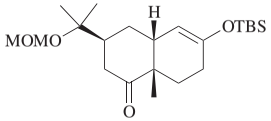
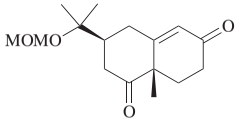
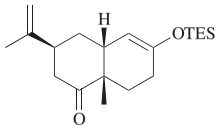
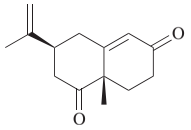
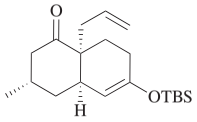
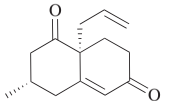
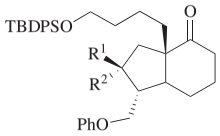
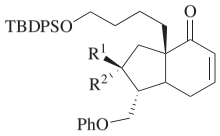
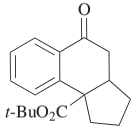
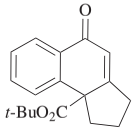
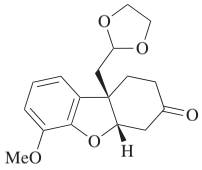
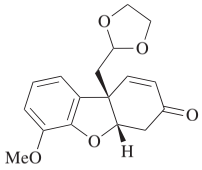
	1. LDA, TMSCl, THF, –78 to –20°, 1.5 h 2. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 12 h	 (85)	399
	1. LDA, TMSCl, THF, –78 to –20° 2. $Pd(OAc)_2$ (1.6 eq), MeCN, rt, 12 h	 (70)	400
	$Pd(OAc)_2$ (1.2 eq), MeCN, rt, 3 h	 (75)	401
	$Pd(OAc)_2$ (1.1 eq), MeCN, rt	 (80)	53

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	$Pd(OAc)_2$ (1 eq), DMSO, 0° to rt, 12 h	 (81)	122
	$Pd(OAc)_2$ (1.1 eq), MeCN, rt	 (71)	53
	1. LDA, TMSCl, THF, –78°, 20 min 2. $Pd(OAc)_2$ (1.05 eq), DMSO, O_2 (1 atm), 55°, 12 h		146
	1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0°, 1 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 12 h	 (69)	402
 **I**	1. LDA, TMSCl, THF, –78 to 0° 2. $Pd(OAc)_2$ (1.3 eq), Na_2CO_3 (1.3 eq), MeCN, rt, 12 h	 (63) + **I** (17)	403

R^1	R^2	
H	MeO	(85)
MeO	H	(61)

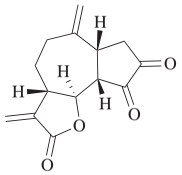
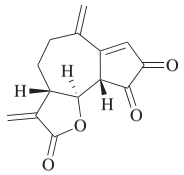
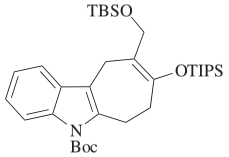
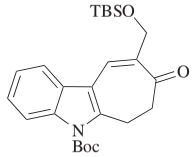
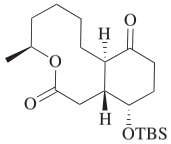
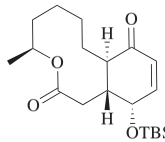
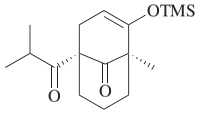
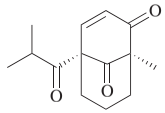
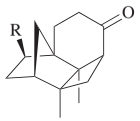
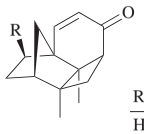
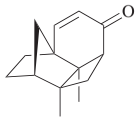
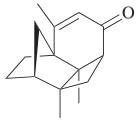
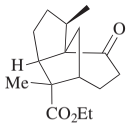
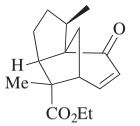
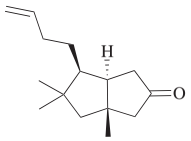
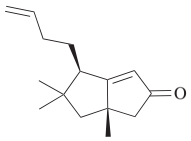
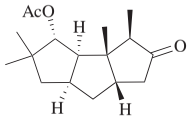
	1. HMDS, TMSI, CH_2Cl_2, –20°, 0.25 h 2. $Pd(OAc)_2$ (1 eq), DMSO (6 eq), MeCN, sonication for 2 min; then 40° for 60–80 min		(>49)	100
	$Pd(OAc)_2$ (1 eq), MeCN, 50°, 12 h		(55)	70
	1. NaHMDS, TESCl, –78°, 0.5 h 2. $Pd(OAc)_2$ (5.4 eq), MeCN, rt, 24–72 h		(61–74)	277, 404
	$Pd(OAc)_2$		(—)	405

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	1. LHMDS, NEt_3, TMSCl, THF, –70°, time 1 2. $Pd(OAc)_2$, MeCN, rt, time 2		406, 407

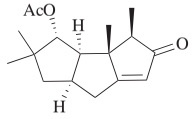
R	Time 1 (h)	Time 2 (h)	
H	3	3.5	(100)
BzO	2	4	(80)

	1. Me_2CuLi, NEt_3, TMSCl, –70°, 2 h 2. $Pd(OAc)_2$, MeCN, rt, 24 h	 (93)	407
	1. NEt_3, TMSOTf, CH_2Cl_2, 0° to rt, 2 h 2. $Pd(OAc)_2$ (0.12 eq), DMSO, O_2 (1 atm), 50°, 17 h	 (76)	344, 345
C_{15} 	1. $TMSCH_2CO_2Et$, TBAF (cat.), THF, –78° to rt, 1 h 2. $Pd(OAc)_2$ (0.98 eq), 1,4-benzoquinone (2 eq), MeCN, 12 h	 (89)	129



I

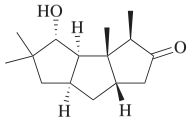
1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0°, 5 h
2. $Pd(OAc)_2$ (2 eq), 1,4-benzoquinone (*x* eq), MeCN, rt



II + **I**

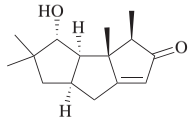
x	Time (h)	**II**	**I**
0 or 1	16	(81)	(19)
2	18	(77)	(—)

136, 137



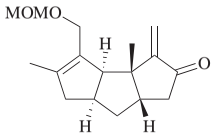
I

1. LDA, TMSCl, THF, –78°, 0.25 h
2. $Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 2 h
3. $AcOH/H_2O/THF$ (3:1:1)

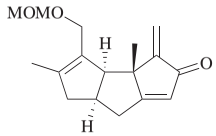


(80) + **I** (20)

408

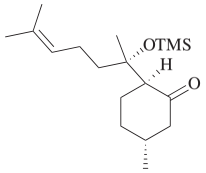


1. LDA, DMPU, TMSCl, THF, –10°, 6 h
2. $Pd(OAc)_2$, MeCN, rt, 5 h

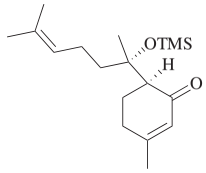


(50)

409



1. LDA, TMSCl, THF, –78°
2. $Pd(OAc)_2$ (0.3 eq), DMSO, O_2 (1 atm), 50°, 36 h



(61)

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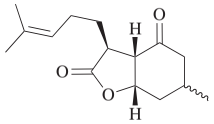
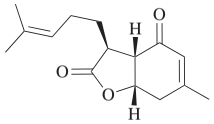
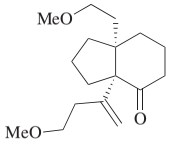
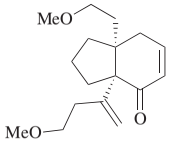
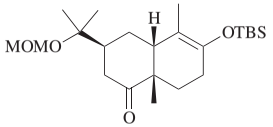
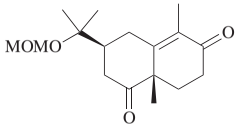
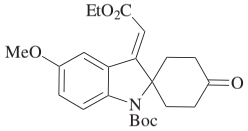
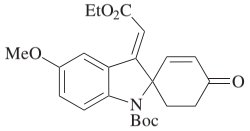
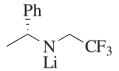
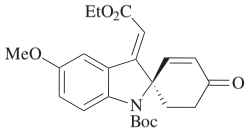
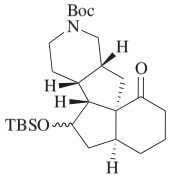
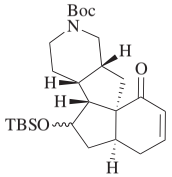
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	1. NEt_3, TMSCl, Et_2O, 0°, 1.5 h 2. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 16 h	 (67)	337
	1. NEt_3, TMSOTf, CCl_4, rt, 6 h 2. $Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, 30°, 16 h 3. $Pd(OAc)_2$ (0.3 eq), 29 h	 (53)	410
	$Pd(OAc)_2$ (1.1 eq), MeCN, rt	 (79)	53
	1. LHMDS, TMSCl, THF, –78°, 1 h 2. $Pd(OAc)_2$ (0.25 eq), DMSO, O_2 (1 atm), rt, 15 h	 (>71)	411
	1. TMSCl,  THF, –100°, 5 min 2. $Pd(OAc)_2$ (3.5 eq), MeCN, rt, 12 h	 (91) er 93.5:6.5, (*R*)	216

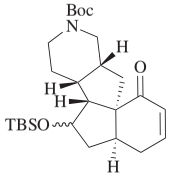


1. LDA, TMSCl, THF, –78°
2. $Pd(OAc)_2$, MeCN, 80°

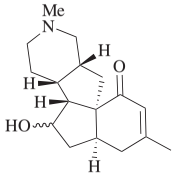


(85)

412, 413

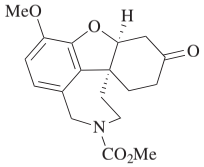


1. $LiMe_2Cu$, TMEDA, TMSCl, –78 to 0°
2. $Pd(OAc)_2$, MeCN, 80°

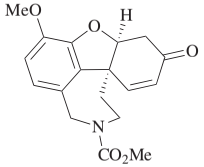


(>68)

412, 413



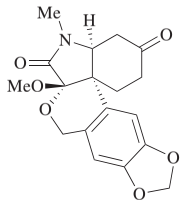
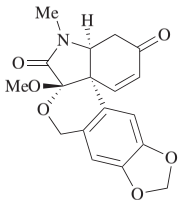
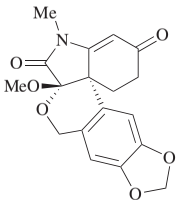
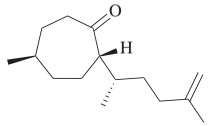
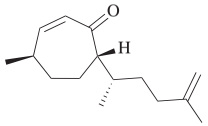
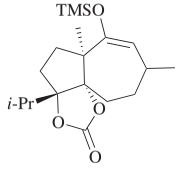
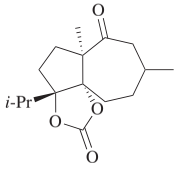
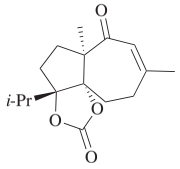
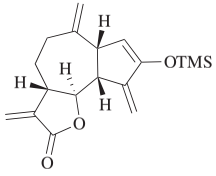
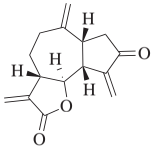
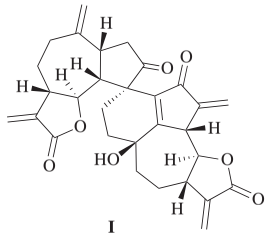
1. NEt_3, TBSOTf, CH_2Cl_2, temp 1, time 1
2. $Pd(OAc)_2$ (1.5 eq), 1,4-benzoquinone (1.5 eq), MeCN, temp 2, 48 h



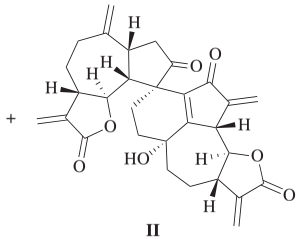
64, 65

Temp 1 (°)	Time 1 (h)	Temp 2 (°)	
–78	1	60	(51)
rt	3	50	(66)

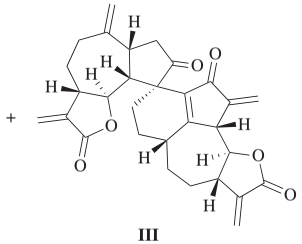
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	1. *i*-Pr_2NEt, TMSOTf, CH_2Cl_2, rt, 2 h 2. $Pd(OAc)_2$ (1.3 eq), MeCN, rt, 12 h	 (80) +  (19)	414
	1. LDA, TMSCl, THF, –78°, 1.5 h 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 16 h	 (86)	415
	$Pd(OAc)_2$ (1.4 eq), MeCN, reflux, 12 h	 (44) +  (21)	286
	 (*x* eq), $Pd(OAc)_2$ (1 eq), CuCl (*y* eq), DMSO, air, sonication, 1 min; then 50°, 19–24 h	 **I**	232

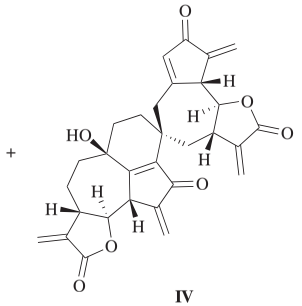
x	*y*	**I**	**II**	**III**	**IV**
2	0	(16)	(2)	(6)	(20)
4	0	(31)	(4)	(7)	(14)
4	0.1	(6)	(27)	(5)	(6)
6	0	(40)	(6)	(9)	(11)
6[a]	0	(0)	(0)	(14)	(0)



II

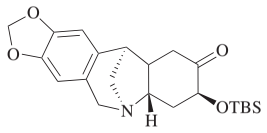
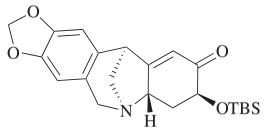
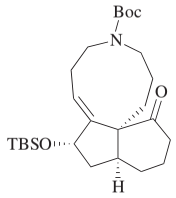
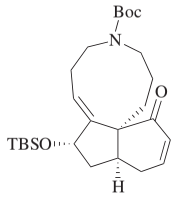
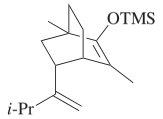
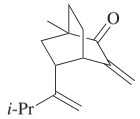
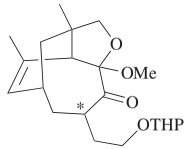
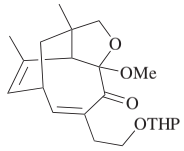


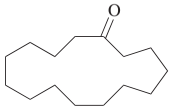
III



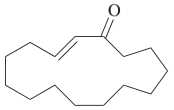
IV

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}  **I**	1. LDA, TMSCl, THF, –78°, 1 h 2. $Pd(OAc)_2$ (10 eq), MeCN, rt, 50 h	 (67) + **I** (17)	416, 282
	1. LHMDS, TMSCl, THF, –78°, 3 h 2. $Pd(OAc)_2$ (1.6 eq), MeCN, rt, 36 h	 (68)	280
	$Pd(OAc)_2$, MeCN	 (—)	417
 *dr 1:1	1. KH, TMSCl 2. $Pd(OAc)_2$, MeCN	 (78)	418



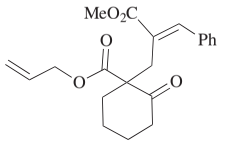
1. LDA, TMSCl, THF, –78° to rt
2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 24 h



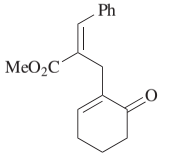
(89)

362, 179

C_{16}

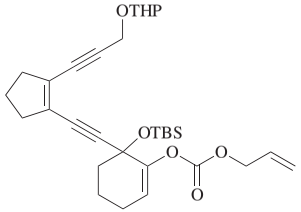


$Pd(OAc)_2$ (0.1 eq), PPh_3 (0.1 eq), MeCN, reflux, 1 h

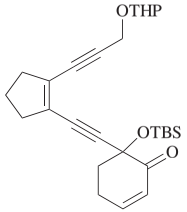


(78)

196

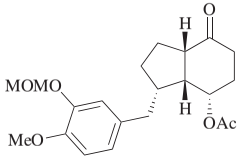


$Pd(OAc)_2$ (cat.), MeCN, reflux

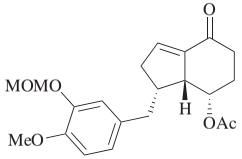


(83–98)

190



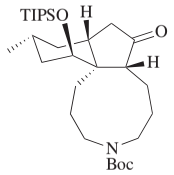
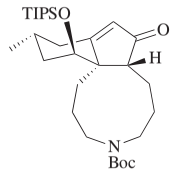
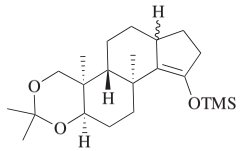
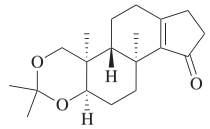
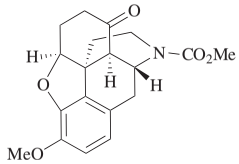
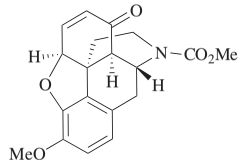
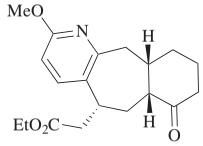
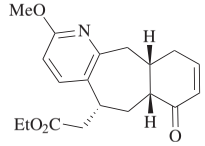
1. HMDS, TMSCl, LiI, CH_2Cl_2, 0°, 3 h
2. $Pd(OAc)_2$ (1.04 eq), MeCN, 5°, 15 h



(50)

419

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	1. LDA, TMSCl, NEt_3, THF, 0°, 2 h 2. $Pd(OAc)_2$ (2 eq), MeCN, rt, 21 h	 (73)	420
	$Pd(OAc)_2$, MeCN, rt	 (73)	421
	1. LHMDS, TMSCl, THF, 0°, 40 min 2. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 2 h	 (92)	422
	1. LDA, TMSCl, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (0.5 eq), 2,6-*t*-Bu_2-4-methylpyridine (1.4 eq), DMSO, O_2 (1 atm), rt, 16 h	 (72)	423, 424

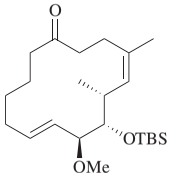
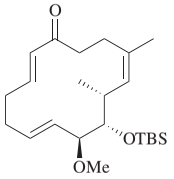
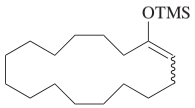
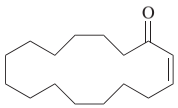
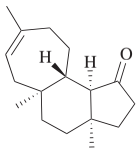
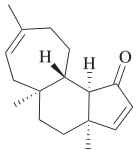
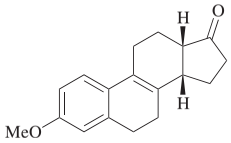
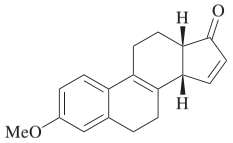
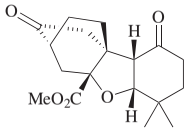
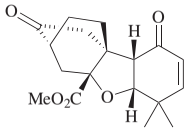
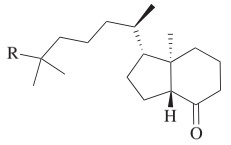
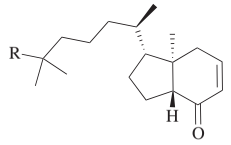
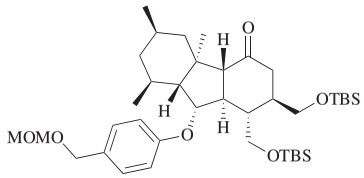
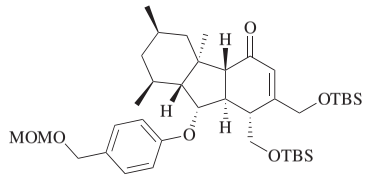
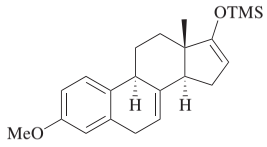
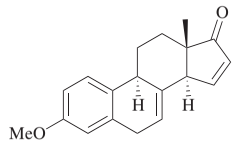
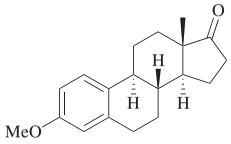
	1. TMSCl, LHMDS, THF, 0°, 2 h 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 3 h		(64–78)	425
	$Pd(OAc)_2$ (1 eq), MeCN, rt, 12 h		(87)	179
C_{17} 	1. LDA, TMSCl, THF, –78° to rt, 1 h 2. $Pd(OAc)_2$ (1.1 eq), MeCN, 40°, 2.5 h		(52–61)	426
	1. LDA, TMSCl, THF, –78°, 10 min 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 2 h		(72)	427
	1. LHMDS, TMSCl, THF, –78°, 0.5 h 2. $Pd(OCOCF_3)_2$ (10 eq), MeCN, rt, 8 h		(52)	119

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

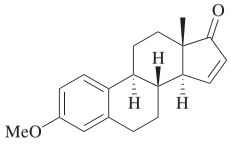
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	1. LDA, TMSCl, THF, temp 2. $Pd(OAc)_2$ (*x* eq), solvent, rt, time		428, 429, 430, 431

R	Temp (°)	*x*	Solvent	Time (h)	
H	—	—	—	—	(85)
TESO	−75 to rt	1	MeCN/THF	24	(84)
MOMO	−78 to rt	1.1	MeCN	20	(94)

	1. LDA, TMSCl, THF, −78°, 3 h 2. $Pd(OAc)_2$, MeCN, 50°, 10 h	 (>58)	378
	$Pd(OAc)_2$ (1.1 eq), MeCN, rt, 1 h	 (78)	432

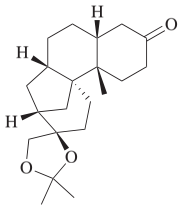


1. LHMDS, TMSCl, 0° to rt, 2 h
2. $Pd(OAc)_2$ (*x* eq), MeCN, rt, time

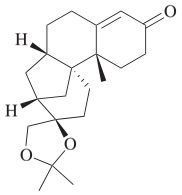


x	Time (min)	
1	25	(79)
1.1	180	(76)

433, 434

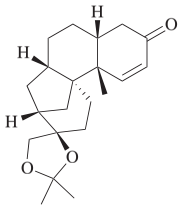


1. KH, NEt_3, TMSCl, THF, rt, 12 h
2. $Pd(OAc)_2$ (1.7 eq), MeCN, rt, 24 h



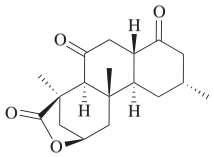
(90)

+

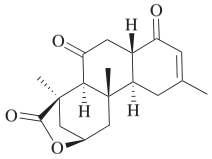


(4)

435, 436



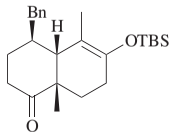
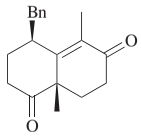
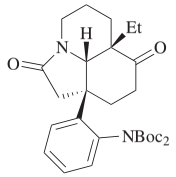
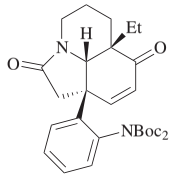
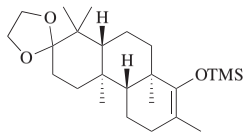
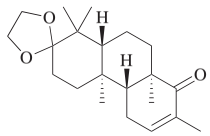
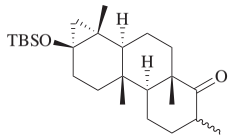
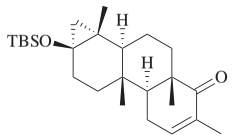
1. Base, TMSCl, THF, temp
2. $Pd(OAc)_2$ (*x* eq), MeCN, 50°, time

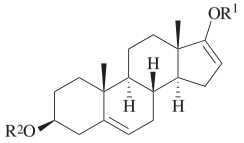


Base	Temp (°)	*x*	Time (h)	
LHMDS	–65	1.5	1.5	(93)
LDA	–70	4	—	(>42)

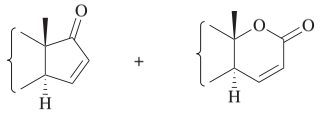
229, 437

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19} 	$Pd(OAc)_2$ (1.1 eq), MeCN, rt	 (58)	53
	1. KHMDS, TMSCl, THF, –78° to rt, 1 h 2. $Pd(OAc)_2$ (0.2 eq), DMSO, O_2 (1 atm), 70–75°, 16 h	 (80)	438
	$Pd(OAc)_2$ (1.45 eq), DMSO, O_2 (1 atm), 80°, 15 h	 (75)	145
	1. LDA, HMPA, TMSCl, –78° to rt 2. $Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 60°, 70 h	 (82)	439



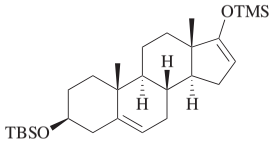
$Pd(OAc)_2$ (0.1 eq),
$DMSO/CH_2Cl_2$ (x:y), O_2 (1 atm)



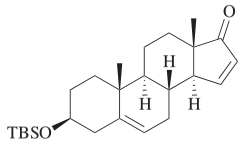
I + **II**

54

R^1	R^2	x	y	Temp (°)	**I**	**II**
TMS	TBDPS	1	1	0	(30)	(56)
TMS	Me	1	1	0	(38)	(54)
TMS	Me	3	2	rt	(46)	(39)
TES	Me	1	1	0	(46)	(44)



$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq),
Na_2HPO_4 (1 eq),
MeCN, O_2 (1 atm), 45°, 18 h



(63)

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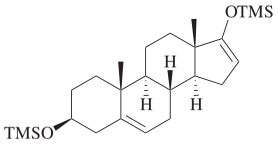
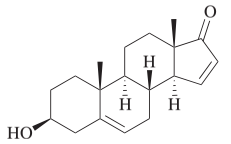
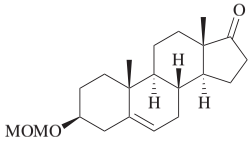


$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq),
diallyl carbonate (2 eq),
PhCN, reflux, 1–3 h

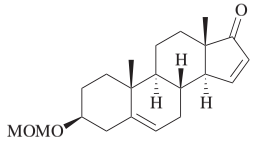


(52)

159, 39



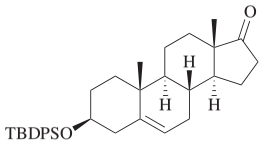
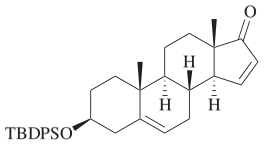
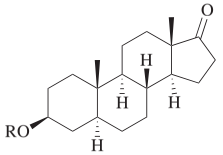
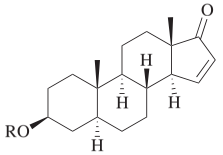
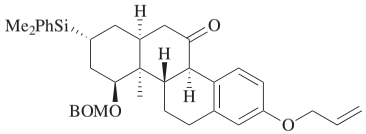
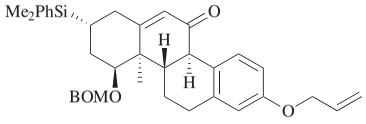
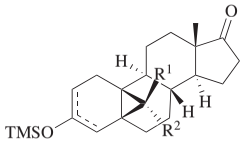
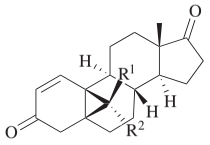
1. LDA, TMSCl, THF, –78°, 1 h
2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 14 h



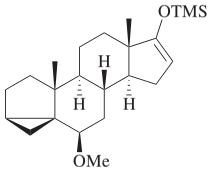
(92)

440

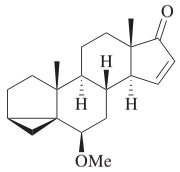
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19} 	1. LDA, TMSCl 2. $Pd(OAc)_2$ (0.1 eq), $CHCl_3$/DMSO, O_2 (1 atm), heat	 (84)	441
	1. LDA, TMSCl, NEt_3, THF, –78° to rt 2. $Pd(OAc)_2$ (1.05 eq), $MeCN/CH_2Cl_2$ (1:3), rt–40°, 2–3 h	 R: MOM (96); TMS (100)	442, 443
	1. LDA, TMSCl, –78°, 40 min 2. $Pd(OAc)_2$ (0.1 eq), 2,6-*t*-Bu_2-4-methylpyridine (1.5 eq), DMSO, O_2 (1 atm), rt, 12 h	 (72)	444
	$Pd(OAc)_2$ (*x* eq), MeCN		445

R^1	R^2	*x*	Temp (°)	Time (h)	
H	AcO	1.2	50	5.5	(24)
AcO	H	1.03	40	0.5	(32)

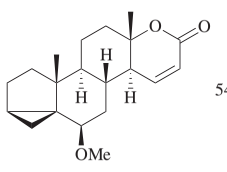


$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm)



I

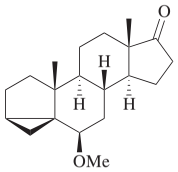
+



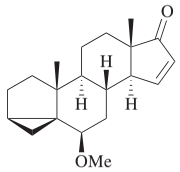
II

54

Temp (°)	**I**	**II**
rt	(45)	(35)
60	(75)	(6)



1. LDA, TMSCl, THF, –78° to rt, 2 h
2. $Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), DMSO, rt, 24 h



(86)

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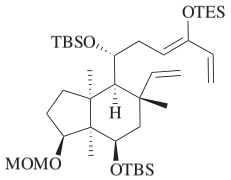
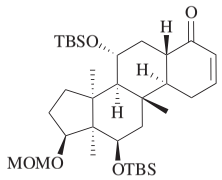
C_{20}



1. Pyridine, PhMe, sealed tube, 210°, 16 h
2. $Pd(OAc)_2$ (0.2 eq), DMSO, O_2 (1 atm), 70°, 5.5 h



(69)

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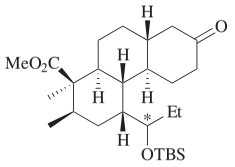
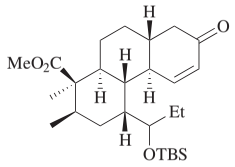
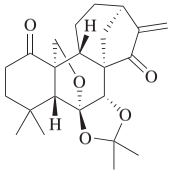
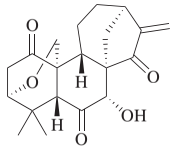
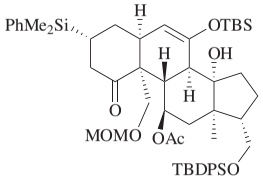
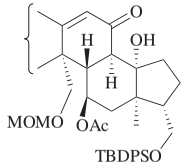
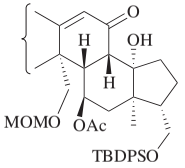
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}  *dr 1:0	1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0° 2. $Pd(OAc)_2$ (1 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 30 h	 (79)	133
	1. TMSOTf, Et_3N, CH_2Cl_2, 60°, 1 h 2. $Pd(OAc)_2$ (4 eq), MeCN, rt, 3 h 3. aq HCl, THF, rt, 12 h	 (54)	235
 **I**	$Pd(OAc)_2$ (cat.), 2,6-*t*-Bu_2-pyridine, DMSO, O_2, rt	 **II** +  **III** **II + III** (68)	66
	$Pd(OAc)_2$, 2,6-*t*-Bu_2-4-methylpyridine, DMSO	**II + III + I** (18) **II + III** (55), **II/III** = 1.33:1	66
	$Pd(OAc)_2$, DMSO	**II + III + I** (25) **II + III** (44), **II/III** = 2.44:1	66

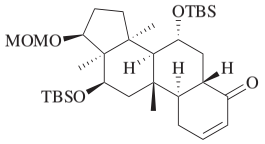
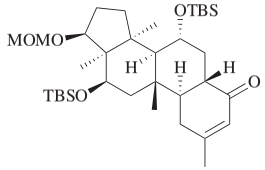
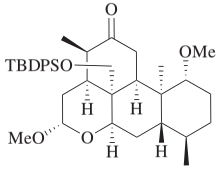
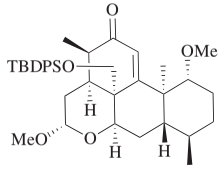
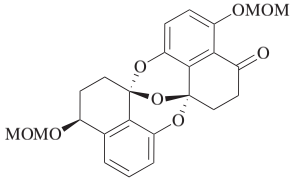
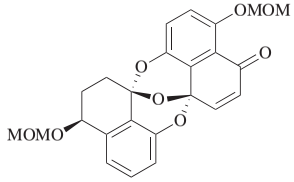
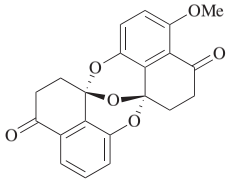
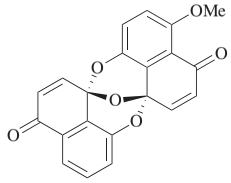
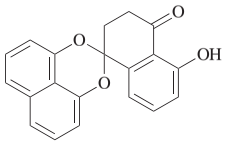
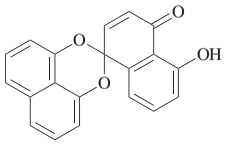
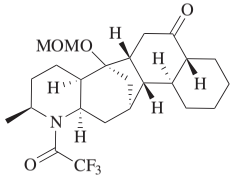
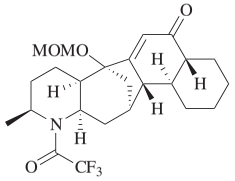
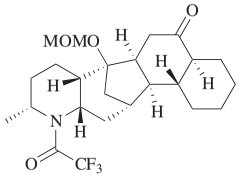
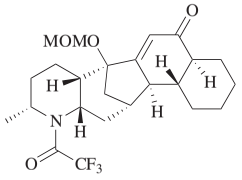
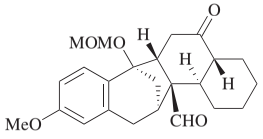
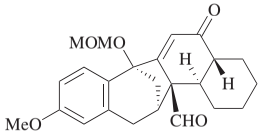
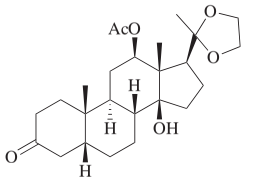
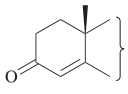
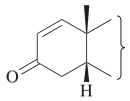
	$Pd(OAc)_2$ (2 eq), HOAc (0.25 eq), DMSO, rt, 48 h	**II** + **III** + **I** (60) **II** + **III** (30), **II**/**III** = 7.34:1		66
	1. MeLi, CuBr•SMe_2, HMPA, TMSCl, THF, –78 to –42°, 1 h 2. $Pd(OAc)_2$ (1 eq), MeCN, 60°, 10 h		(78)	56
	1. LDA, TMSCl, THF, –78° 2. $Pd(OAc)_2$, Na_2CO_3, MeCN, 45°		(86)	447
 **I**	1. NaHMDS, TMSCl, THF, –40° to rt, 5 h 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 15 h		(75) + **I** (25)	177
	1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0° to rt, 1.25 h 2. $Pd(OAc)_2$ (2.1 eq), MeCN, rt, 18 h		(91)	176, 177

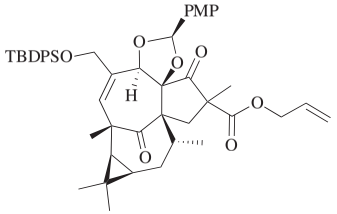
TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0°, 1 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 16 h	 (60–78)	358
	1. LDA, TMSCl, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (1.5 eq), DMSO/MeCN (3:2), rt, 16 h	 (82)	448
	1. LDA, TMSCl, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (1.5 eq), DMSO/MeCN (3:2), rt, 16 h	 (82)	127
C_{21}  **I**	1. LDA, TMSCl, THF, –78°, 1 h 2. $Pd(OAc)_2$ (1 eq), DMSO, 70°, 12 h	 (63) + **I** (34)	448

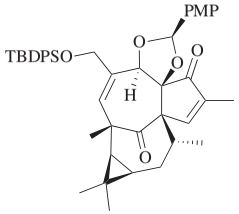


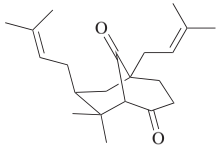
1. LHMDS, TMSCl, NEt_3,
   THF, –78°, 0.5 h
2. $Pd(OAc)_2$ (5 eq), MeCN, rt, 1 h


(79) + 
(8) 449

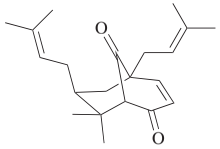


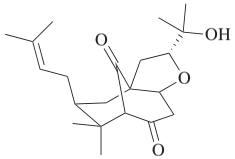
$Pd(OAc)_2$ (0.64 eq), MeCN, reflux, 2 h


(>23) 193



1. NEt_3, DMAP, TMSOTf,
   CH_2Cl_2, 0°, 1 h
2. $Pd(OAc)_2$ (1.18 eq), MeCN, 55°, 6 h


(59) 450



1. NEt_3, DMAP, TMSOTf,
   CH_2Cl_2, 0°, 1 h
2. $Pd(OAc)_2$ (1.5 eq), MeCN, 55°, 6 h

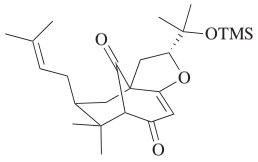
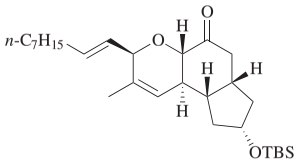
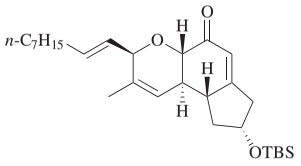
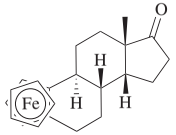
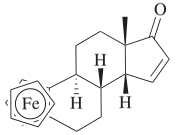
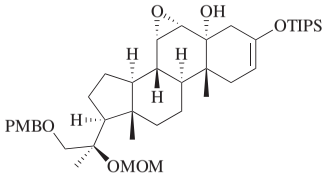
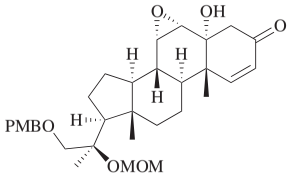
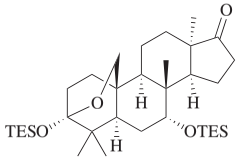
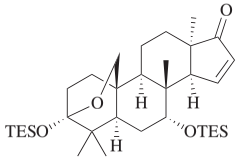
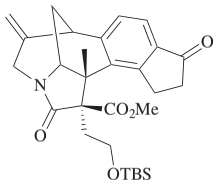
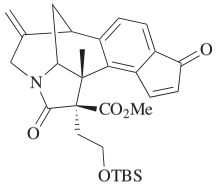

(55) 450

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

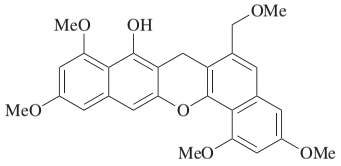
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}			
	1. LDA, TMSCl, 0°, 0.5 h 2. $Pd(OAc)_2$ (1.1 eq), DMSO, rt, 2 h	 (53)	451
	1. NEt_3, TESOTf, CH_2Cl_2, –78°, 3.5 h 2. $Pd(OAc)_2$ (1.05 eq), $Cu(OAc)_2$ (2.6 eq), MeCN, O_2 (1 atm), 50°, 20 h	 (78)	55
	$Pd(OAc)_2$ (1 eq), MeCN, rt, 8 h	 (54)	69
	1. TBSCl, LHMDS, NEt_3, THF, –78° to –60°, 0.75 h 2. $Pd(OAc)_2$ (2 eq), MeCN, rt, 9 h	 (92)	452



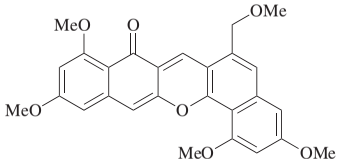
1. NEt_3, TMSOTf, CH_2Cl_2, –78°, 10 min
2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 1 h



(81) 453

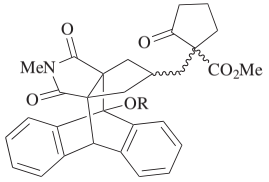


1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0°, 2.5 h
2. $Pd(OAc)_2$ (1 eq), MeCN, reflux, 12 h



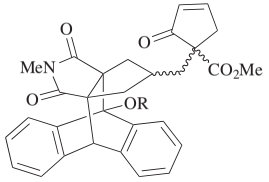
(56) 454

C_{28}



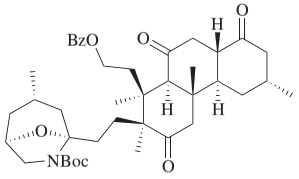
R = benzyloxymethyl

1. NEt_3, TMSOTf, CH_2Cl_2, 0.5 h
2. $Pd(OAc)_2$ (1 eq), DMSO, rt, 16 h

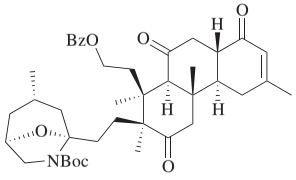


(84) 126

C_{29}

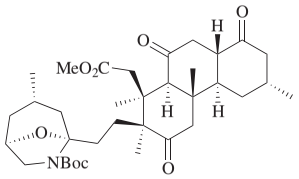
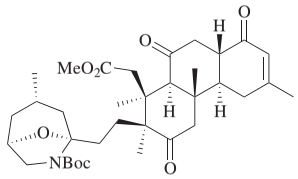


1. LHMDS, TMSCl, THF, –78°, 0.5 h
2. $Pd(OAc)_2$ (0.58 eq), DMSO, O_2 (1 atm), 60°, 11 h

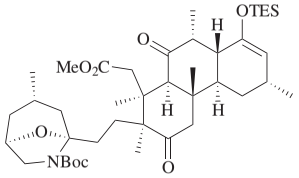
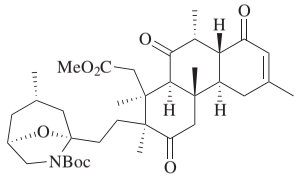
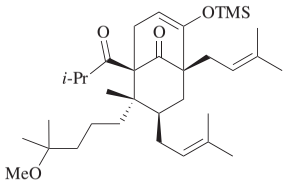
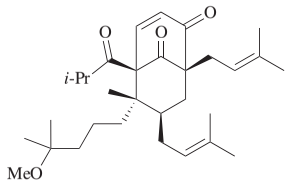


(74) 231

TABLE 1B. CYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29} 	1. LHMDS, TMSCl, THF, temp 1, time 1 2. $Pd(OAc)_2$ (*x* eq), MeCN, temp 2, time 2		230, 455, 50

Temp 1 (°)	Time 1 (h)	*x*	Temp 2 (°)	Time 2 (h)	
—	—	—	—	—	(96)
–65	1	3.5	50	2	(96)

C_{30} 	$Pd(OAc)_2$ (1.4 eq), NMP, 55°, 4 h		(>37)	50
	$Pd(OAc)_2$ (2 eq), DMSO, O_2 (1 atm), rt, 10.5 h		(100)	456, 457

[a] The reaction was run under anaerobic conditions.

TABLE 1C. HETEROCYCLIC 2,3-EN-1-ONES

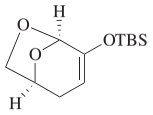
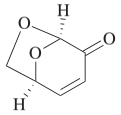
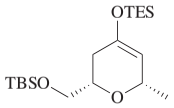
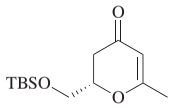
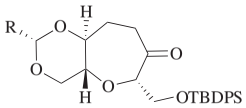
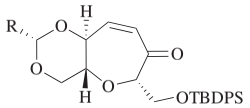
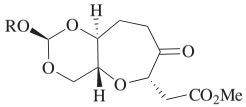
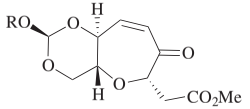
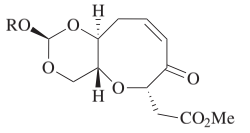
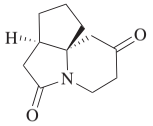
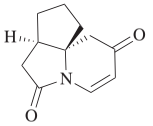
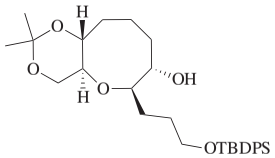
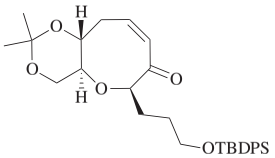
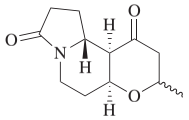
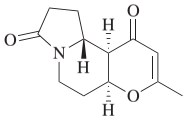
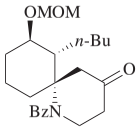
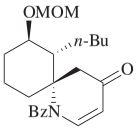
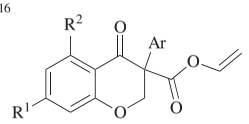
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), 80°, 48 h	 (77)	68
C_7		$Pd(OAc)_2$ (0.15 eq), DMSO, O_2 (1 atm), rt to 40°, 6 h	 (93)	57
C_8	 R = 4-methoxyphenyl	1. LHMDS, $TMSCl$, NEt_3, THF, –78° 2. $Pd(OAc)_2$, MeCN, rt	 (86)	458
C_9	 R = 3-methoxyphenyl	1. $KN(TMS)_2$, $TMSCl$, NEt_3, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (2 eq), MeCN, rt, 0.5 h	 (93)	459
		1. $AlMe_3$, $TMSCHN_2$, CH_2Cl_2/hexane, 4 Å MS, –90 to –10°, 4.5 h 2. PhMe, sealed tube, 140°, 1.5 h 3. $Pd(OAc)_2$ (1.1 eq), MeCN, 70°, 0.5 h	 (51)	459

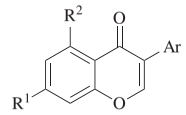
TABLE 1C. HETEROCYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	1. NEt_3, TMSOTf, CH_2Cl_2, rt, 12 h 2. $Pd(OAc)_2$	 (75)	460
	1. Dess-Martin periodinate, CH_2Cl_2, rt 2. KHMDS, TMSCl, NEt_3, THF, –78° 3. $Pd(OAc)_2$, MeCN, rt	 (72)	461
C_{12} 	1. LHMDS, TMSCl, THF, –78° 2. $Pd_2(dba)_3$ (0.1 eq), diallyl carbonate (2 eq), MeCN, rt	 (70)	169
C_{14} 	1. LTMP, TMSCl, THF, –78° to rt, 3 h 2. $Pd(OAc)_2$ (1.2 eq), MeCN/DMSO (3:1), rt, 41 h	 (84)	462

$C_{15–16}$



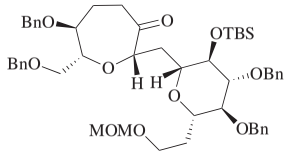
$Pd(OAc)_2$ (0.05 eq),
dppe (0.05 eq),
MeCN, reflux, 4 h



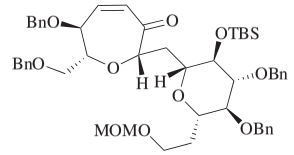
195

Ar	R^1	R^2	
Ph	H	H	(72)
Ph	MeO	H	(74)
Ph	MeO	MeO	(84)
4-$MeOC_6H_4$	H	H	(74)
4-$MeOC_6H_4$	MeO	H	(73)
4-$MeOC_6H_4$	MeO	MeO	(83)
2,4-$(MeO)_2C_6H_3$	H	H	(83)
2,4-$(MeO)_2C_6H_3$	MeO	H	(82)
2,4-$(MeO)_2C_6H_3$	MeO	MeO	(68)
2,4,6-$(MeO)_3C_6H_2$	H	H	(83)
2,4,6-$(MeO)_3C_6H_2$	MeO	H	(81)
2,4,6-$(MeO)_3C_6H_2$	MeO	MeO	(72)
4-MeC_6H_4	H	H	(82)
4-MeC_6H_4	MeO	H	(90)
4-MeC_6H_4	MeO	MeO	(77)

C_{15}



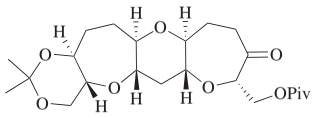
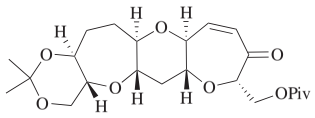
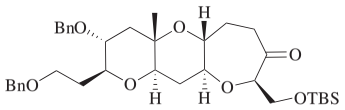
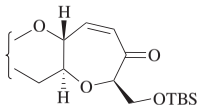
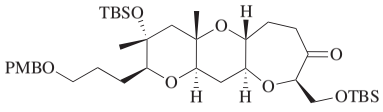
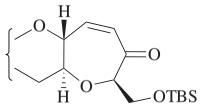
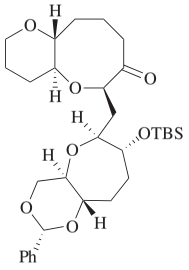
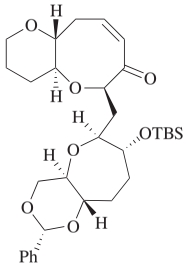
1. LHMDS (2.0 eq),
TMSCl (2.0 eq),
NEt_3 (2.0 eq), THF,
–78°, 10 min
2. $Pd(OAc)_2$ (2.5 eq),
MeCN, rt, 0.5 h



(96)

281, 227

TABLE 1C. HETEROCYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	1. LHMDS, TMSCl, NEt_3, THF, –78°, 25 min 2. $Pd(OAc)_2$ (1.8 eq), MeCN, rt, 15 h	 (96)	463, 464, 227
C_{16} 	1. LHMDS, TMSCl, NEt_3, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (5 eq), MeCN, rt, 50 min	 (92)	225
C_{18} 	1. LHMDS, TMSCl, NEt_3, THF, –70°, 1 h 2. $Pd(OAc)_2$ (2.5 eq), MeCN, rt, 2 h	 (90)	221
	1. LHMDS, TMSCl, NEt_3, THF, –78° 2. $Pd(OAc)_2$, MeCN, 60°	 (77)	465, 227

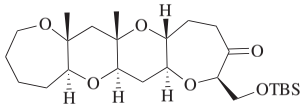
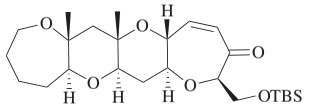
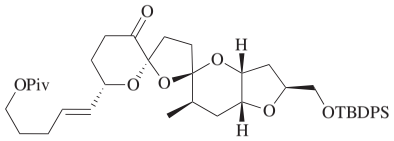
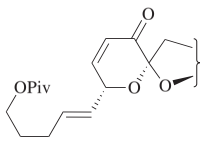
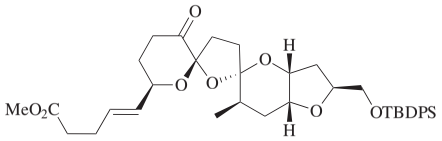
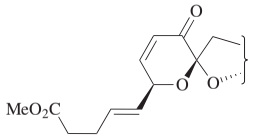
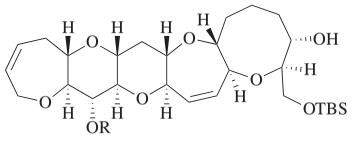
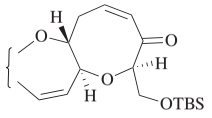
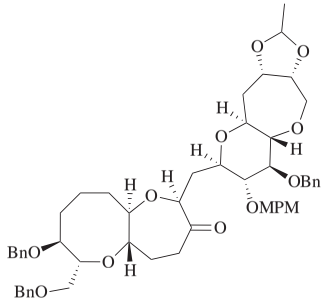
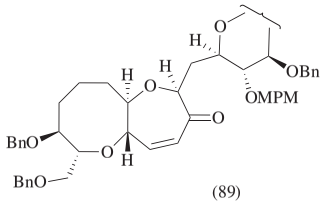
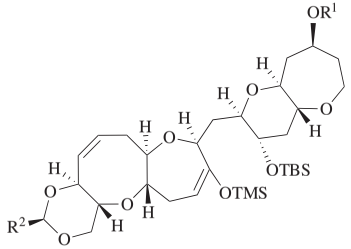
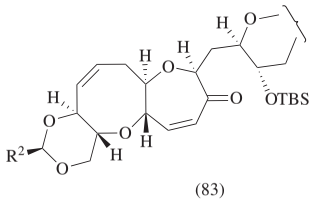
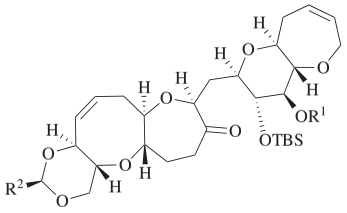
C_{19} 	1. LHMDS, TMSCl, NEt_3, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (3 eq), MeCN, rt, 40 min		(100)	466
C_{21} 	1. KHMDS, TMSCl, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (2 eq), DMSO, rt, 48 h		(55)	269
	1. KHMDS, TMSCl, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (5 eq), DMSO, rt, 72 h		(55)	269
C_{22}  R = 2-naphthylmethyl	1. TPAP, NMO, CH_2Cl_2, 4 Å MS, rt 2. LHMDS, TMSCl, NEt_3, THF, –78° 3. $Pd(OAc)_2$, MeCN, rt		(74)	467

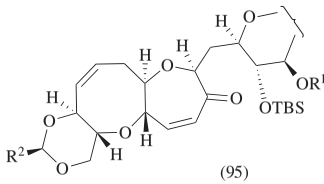
TABLE 1C. HETEROCYCLIC 2,3-EN-1-ONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	1. LHMDS, TMSCl, NEt_3, THF, –78° 2. $Pd(OAc)_2$, MeCN, rt	 (89)	467
 R^1 = 2-naphthylmethyl, R^2 = 3-methoxyphenyl	$Pd(OAc)_2$, MeCN, rt	 (83)	468



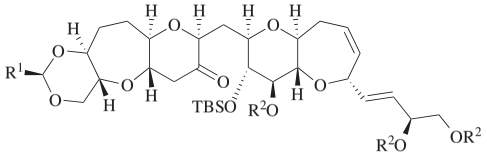
R^1 = 2-naphtylmethyl, R^2 = 3-methoxyphenyl

1. $KN(TMS)_2$, $TMSCl$, NEt_3, THF, –78°
2. $Pd(OAc)_2$ (5 eq), MeCN, rt, 1 h



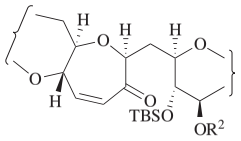
(95) 469

C_{24}



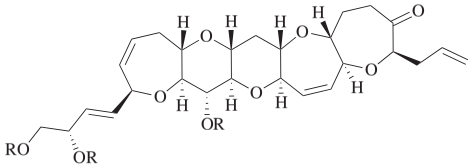
R^1 = 4-methoxyphenyl, R^2 = 2-naphthylmethyl

1. $TMSCHN_2$, $AlMe_3$, CH_2Cl_2, 4 Å MS, –90 to –30°, 1 h
2. PhMe, sealed tube, 140°, 3 h
3. $Pd(OAc)_2$ (2 eq), rt, 1 h



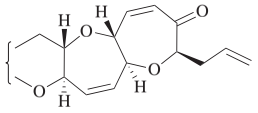
(59) 458

C_{27}



R = 2-naphthylmethyl

1. LHMDS, $TMSCl$, NEt_3, THF, –78°, 1 h
2. $Pd(OAc)_2$ (4 eq), MeCN, rt, 0.5 h



(70) 458

TABLE 1C. HETEROCYCLIC 2,3-EN-1-ONES (*Continued*)

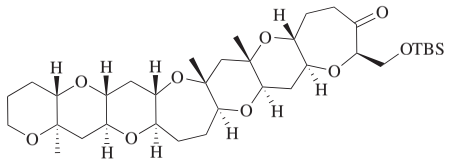
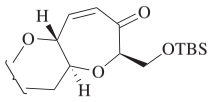
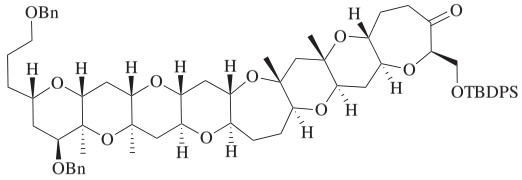
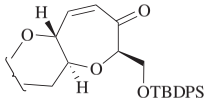
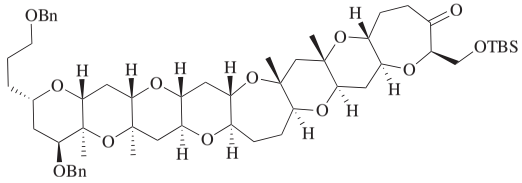
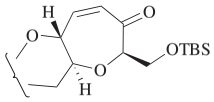
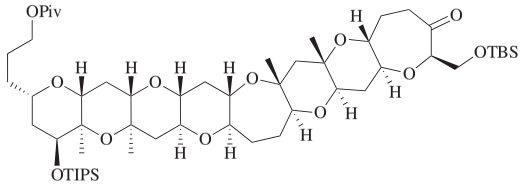
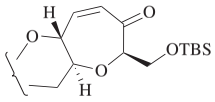
Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{29} 	1. LHMDS, TMSCl, NEt_3, THF, –78°, 0.5 h 2. $Pd(OAc)_2$ (3 eq), MeCN, rt, 2 h		(98)	466
C_{36} 	1. LHMDS, TMSCl, NEt_3, THF, –80°, 40 min 2. $Pd(OAc)_2$ (5 eq), MeCN, rt, 1.25 h		(98)	219, 218, 220
	1. LHMDS, TMSCl, NEt_3, THF, –78°, 1 h 2. $Pd(OAc)_2$ (5.2–10 eq), MeCN, rt, 1.25 h		(89–94)	224, 225, 227, 223, 220
	1. LHMDS, TMSCl, NEt_3, THF, –78°, 1 h 2. $Pd(OAc)_2$ (3 eq), MeCN, rt, 1 h		(92)	222, 223

TABLE 1D. CROSS-CONJUGATED DIENONES

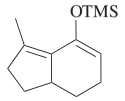
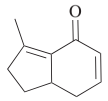
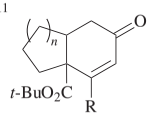
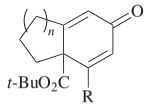
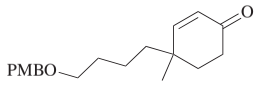
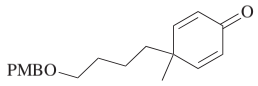
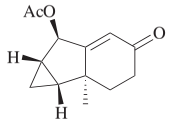
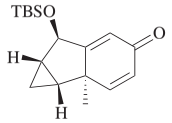
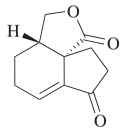
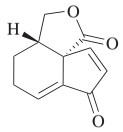
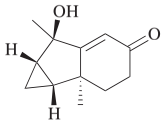
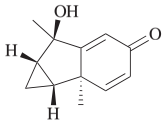
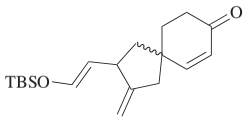
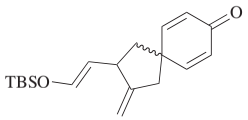
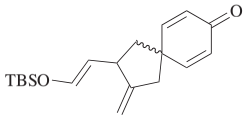
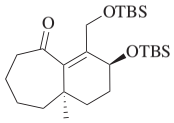
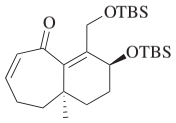
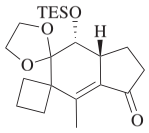
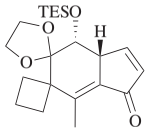
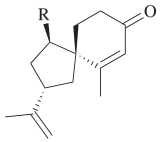
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	$Pd(OAc)_2$, MeCN, rt, 14 h	 (59)	470
C_{10-11} 	1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0°, 2 h 2. $Pd(OAc)_2$ (1 eq), MeCN, 12 h		402
		n R 1 H (70) 1 Me (62) 2 H (70)	
C_{11} 	1. LHMDS, TMSCl, THF, –78 to –20° 2. $Pd_2(dba)_3$•$CHCl_3$ (0.1 eq), diallyl carbonate (1 eq), MeCN, rt, 12 h	 (64)	167
	1. K_2CO_3, MeOH, 0° to rt, 1 h 2. NEt_3, TBSOTf, CH_2Cl_2, –78 to –30° 3. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 12 h	 (73)	471
	1. NEt_3, TMSOTf, CH_2Cl_2, 0°, 0.5 h 2. $Pd(OAc)_2$ (1.15 eq), MeCN, rt, 1 h	 (98)	472, 473

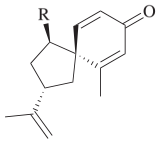
TABLE 1D. CROSS-CONJUGATED DIENONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	1. NEt_3, TBSOTf, CH_2Cl_2, –78° to rt 2. $Pd(OAc)_2$ (1.45 eq), MeCN, rt, 12 h	 (78)	471
C_{13} 	1. LHMDS, TMSCl, THF, –78°, 2 h 2. $Pd(OAc)_2$ (1.1 eq), MeCN, rt, 1.5 h	 (68)	178
	1. LHMDS, TMSCl, THF, –78 to –20°, 1 h 2. $Pd_2(dba)_3$•$CHCl_3$ (0.1 eq), diallyl carbonate (2 eq), MeCN, rt, 2 h	 (93)	170
	1. TMSCl, LDA, NEt_3, THF, –78° to rt, 0.5 h 2. $Pd(OAc)_2$ (1 eq), MeCN/THF (2:1), rt, 120 h	 (73)	474
 **I**	1. LDA, TMSCl, NEt_3, THF, –78° 2. $Pd(OAc)_2$ (1 eq), MeCN/THF (5:3), rt, 3 h	 (65) + **I** (16)	475

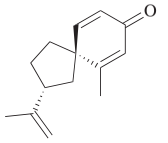
C_{14}



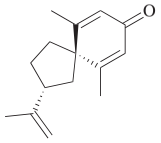
1. LHMDS, NEt_3, TMSCl, THF, –70°, 2–3 h
2. $Pd(OAc)_2$, MeCN, rt, 4 h



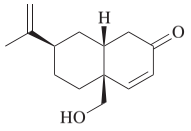
R		
H	(90)	407, 406
BzO	(80)	



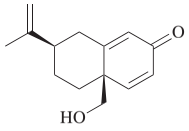
1. Me_2CuLi, NEt_3, TMSCl, Et_2O, –70°, 2 h
2. $Pd(OAc)_2$, MeCN, rt, 3 h



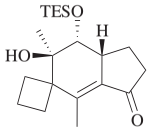
(90) 407



1. TBSOTf, NEt_3, CH_2Cl_2
2. $Pd(OAc)_2$ (1 eq, gradual addition), MeCN, 0°

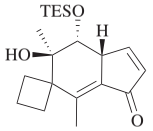


(81) 476

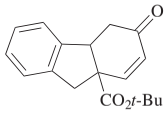


I

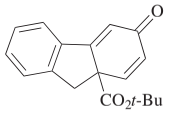
1. LDA, TMSCl, NEt_3, –78°, 1 h
2. $Pd(OAc)_2$ (1 eq), MeCN/THF (1:1), rt, 3 h



(65) + **I** (20) 475

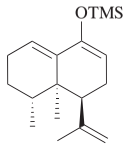
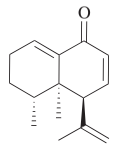
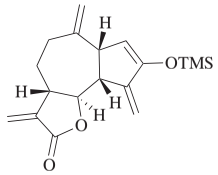
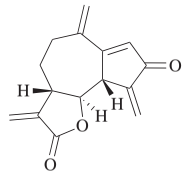
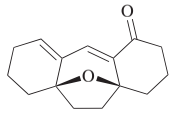
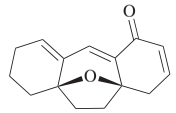
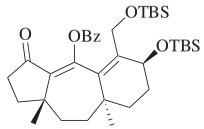
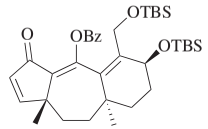


1. 2,6-Lutidine, TMSOTf, CH_2Cl_2, 0°, 2 h
2. $Pd(OAc)_2$ (1 eq), MeCN, 12 h



(62) 402

TABLE 1D. CROSS-CONJUGATED DIENONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	$Pd(OAc)_2$ (1.3 eq), MeCN, rt, 20 h	 (16)	477
	$Pd(OAc)_2$ (1 eq), DMSO (6 eq), MeCN, sonication for 2 min; then 40° for 60–80 min	 (—)	100
	1. NEt_3, TMSOTf, –78 to 0°, 1.5 h 2. $Pd(OAc)_2$ (1.5 eq), MeCN, rt, 15 h	 (43)	91
C_{17} 	1. TMSI, HMDS, CH_2Cl_2, 0°, 1 h 2. $Pd(OAc)_2$ (1.5 eq), diallyl carbonate (25 eq), MeCN/THF (2:1), 50°, 40 h	 (81)	474

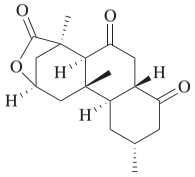
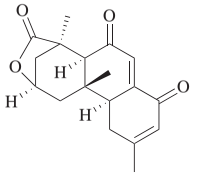
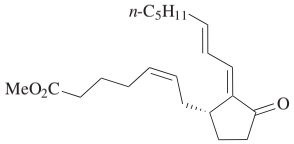
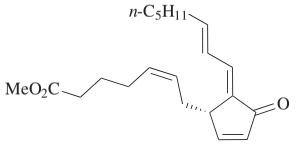
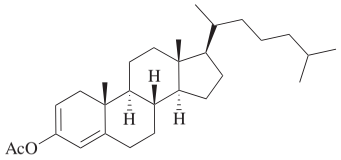
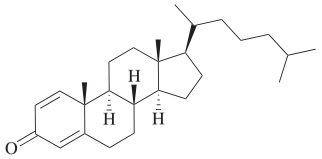
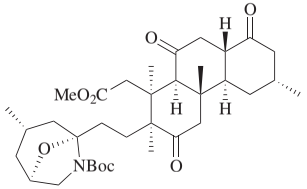
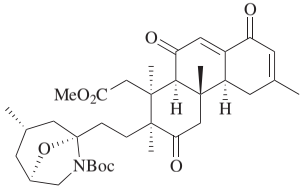
C_{18}		1. LDA, TMSCl, THF, –70°, 1 h 2. $Pd(OAc)_2$ (4 eq), MeCN, 50°, 1 h		(>42)	229
C_{20}		1. NEt_3, TMSOTf, CH_2Cl_2, 0° 2. $Pd(OAc)_2$ (5 eq), 1,4-benzoquinone (5 eq), MeCN, 0°, 4 h		(70)	135
C_{27}		$Pd(OAc)_2$ (0.1 eq), $MeOSnBu_3$ (0.2 eq), allyl methyl carbonate (2 eq), MeCN, reflux, 5–10 h		(69)	160, 39
C_{29}		1. LDA, TMSCl, THF, –70° 2. $Pd(OAc)_2$, MeCN, 50°		(99)	229

TABLE 1D. CROSS-CONJUGATED DIENONES (*Continued*)

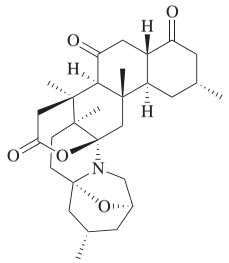
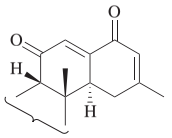
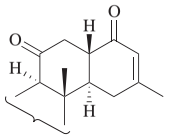
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29} 	1. LDA, TMSCl, THF, –78 to –50°, 1.5 h 2. $Pd(OAc)_2$ (4 eq), $CaCO_3$ (10 eq), MeCN, 55°, 1.5 h	 +  **I** **I + II** (>57), **I/II** = 50:3 **II**	229, 437, 455

TABLE 1E. PHENOLIC SYSTEMS

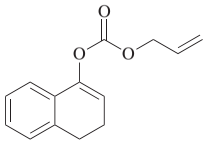
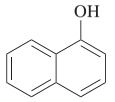
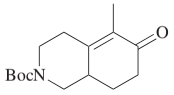
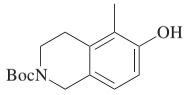
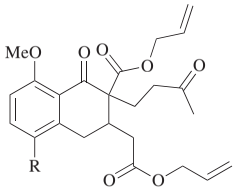
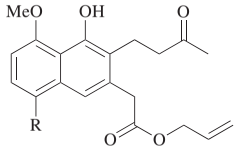
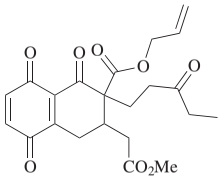
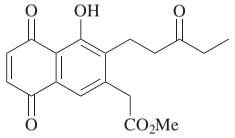
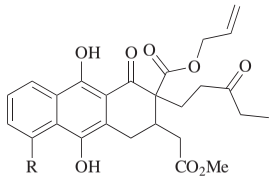
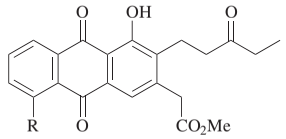
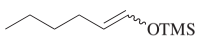
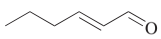
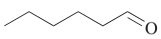
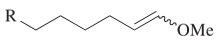
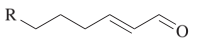
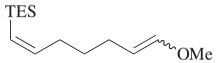
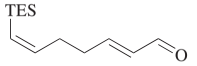
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	$Pd(OAc)_2$ (0.1 eq), MeCN, 80°	 (81)	160
	1. LiHMDS, TMSCl, THF, –78° 2. $Pd(OAc)_2$ (1.13 eq), THF, 0° to rt, 1 h	 (52)	128
C_{16} 	$Pd(OAc)_2$, dppe, MeCN, reflux, 1 h	 R: H (45); MeO (80)	478
C_{17} 	$Pd(OAc)_2$ (0.35 eq), dppe (1 eq), MeCN, reflux, 50 min	 (>42)	479

TABLE 1E. PHENOLIC SYSTEMS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21} 	$Pd(OAc)_2$ (*x* eq), dppe (*y* eq), MeCN, reflux		478, 479

R	*x*	*y*	Time (min)	
H	—	—	30	(62)
HO	0.56	0.65	40	(81–87)

TABLE 2. α,β-UNSATURATED ALDEHYDES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 3 h	 (92) +  (2)	12
C_{6-14} 	$Pd(OAc)_2$ (*x* eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH (4 eq), CH_2Cl_2, rt		42
C_7 	$Pd(OAc)_2$ (0.04 eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH (4 eq), CH_2Cl_2, rt, 24 h	 (67)	42

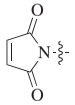
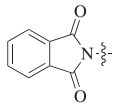
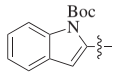
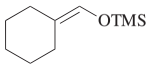
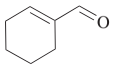
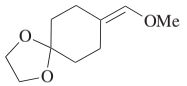
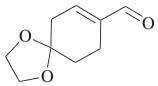
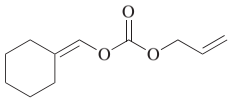
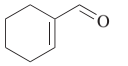
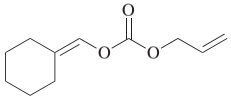
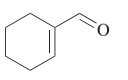
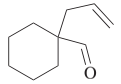
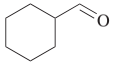
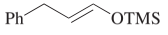
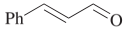
R	*x*	Time (h)	
TBSO	0.025	8	(57)
AcO	0.01	12	(79)
	0.025	8	(72)
n-C_7H_{15}	0.02	4	(65)
	0.025	7	(72)
	0.05	16	(44)

TABLE 2. α,β-UNSATURATED ALDEHYDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), diallyl carbonate (2 eq), MeCN, reflux, 1–3 h	 (74)	159, 39
	$Pd(OAc)_2$ (0.025 eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH (4 eq), CH_2Cl_2, rt, 18 h	 (76)	42
	$Pd(OAc)_2$ (0.1 eq), dppe (0.1 eq), MeCN, 80°, 1 h	 (90)	188
 **I**	$Pd(OAc)_2$ (0.01 eq), PPh_3 (0.01 eq), MeCN, reflux, 1.5 h	 +  **II** (82) **III** (—)	16
		+  + **I** (1) **II/III/IV** = 95:4:1 **IV** (—)	
C_9  (*E*)/(*Z*) > 20:1	$Pd(OAc)_2$ (0.2 eq), Oxone (1 eq) Na_2HPO_4 (1 eq), MeCN, O_2 (1 atm), rt, 18 h	 (69), (*E*)/(*Z*) > 20:1	33

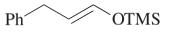
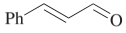
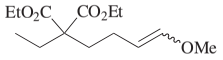
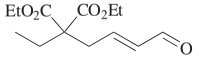
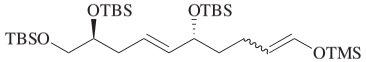
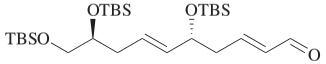
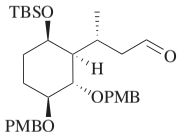
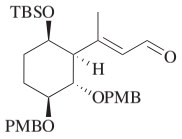
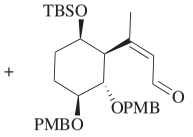
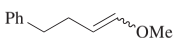
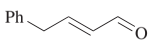
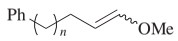
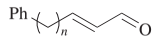
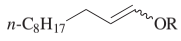
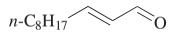
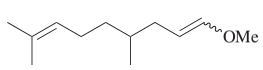
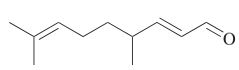
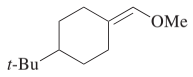
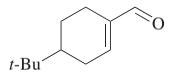
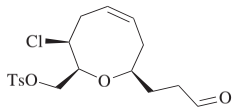
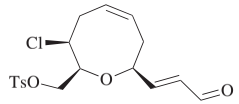
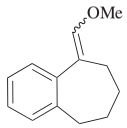
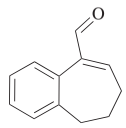
		$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), diallyl carbonate (2 eq), MeCN, reflux, 1–3 h		(80)	159, 39
		$Pd(OAc)_2$ (0.5 eq), $Cu(OAc)_2 \cdot H_2O$ (1 eq), $NaHCO_3$ (0.05 eq), MeCN, 0° to rt, 1.5 h		(94)	41
C_{10}		$Pd(OAc)_2$ (1.6 eq), MeCN/DMF (4:1), rt, 2.5 h		(99)	480
	 **I**	1. $KN(TMS)_2$, NEt_3, TMSCl, 0° 2. $Pd(OAc)_2$ (1.1 eq), MeCN, 0°, 12 h	 + 	(47) + (8) + **I** (12)	481, 482
		$Pd(OAc)_2$ (0.01 eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH (4 eq), CH_2Cl_2, rt, 4 h		(63)	42

TABLE 2. α,β-UNSATURATED ALDEHYDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{10–12}$ 	$Pd(OAc)_2$ (0.5 eq), $Cu(OAc)_2•H_2O$ (1 eq), $NaHCO_3$ (0.05 eq), MeCN, 0° to rt, 1.5–2 h	 *n*: 1 (83); 3 (92)	41
C_{11} 	$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt	 R: TMS, 72 h, (86); TBS, 84 h, (82)	27
	$Pd(OAc)_2$ (0.05 eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH (4 eq), CH_2Cl_2, rt, 16 h	 (72)	42
	$Pd(OAc)_2$ (0.02 eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH (4 eq), CH_2Cl_2, rt, 6 h	 (90)	42
	1. *i*-Pr_2NEt, TMSOTf, 0°, 0.5 h 2. $Pd(OAc)_2$ (1.33 eq), MeCN, rt, 1 h	 (81)	74
C_{12} 	$Pd(OAc)_2$ (0.05 eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH, 40°, 16 h	 (73)	42

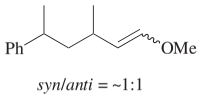
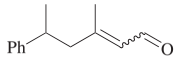
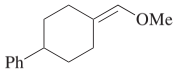
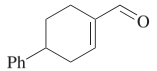
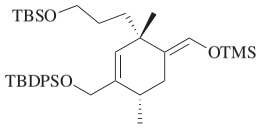
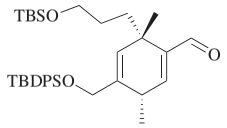
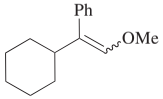
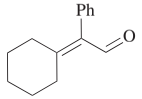
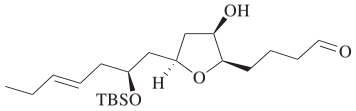
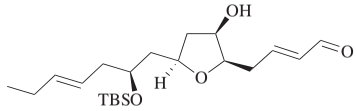
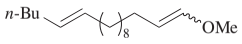
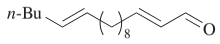
C_{13}	 *syn*/*anti* = ~1:1	$Pd(OAc)_2$ (0.5 eq), $Cu(OAc)_2 \cdot H_2O$ (1 eq), $NaHCO_3$ (0.05 eq), MeCN, 0° to rt, 3.25 h		(86)	41
		$Pd(OAc)_2$ (0.02 eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH (4 eq), CH_2Cl_2, rt, 8 h		(80)	42
		1. $Pd(OAc)_2$ (1.45 eq), MeCN, 80°, 1 h 2. $Pd(OAc)_2$ (0.55 eq), 80°, 20 h		(93)	483
C_{14}		$Pd(OAc)_2$ (0.1 eq), H_2O (1.1 eq), 1,4-benzoquinone (1.2 eq), AcOH, rt, 96 h		(57)	42
C_{15}		1. *i*-Pr_2NEt, TMSOTf, CH_2Cl_2, rt, 2 h 2. $Pd(OAc)_2$ (1.3 eq), MeCN, 23°, 1.5 h		(53)	484, 413
C_{17}		$Pd(OAc)_2$ (0.5 eq), $Cu(OAc)_2 \cdot H_2O$ (1 eq), $NaHCO_3$ (0.05 eq), MeCN, 0° to rt, 1.5 h		(96)	41

TABLE 2. α,β-UNSATURATED ALDEHYDES (*Continued*)

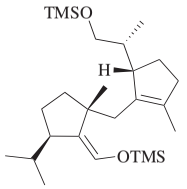
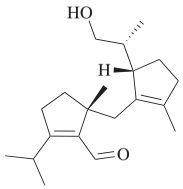
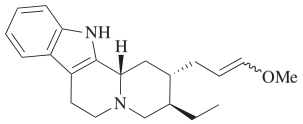
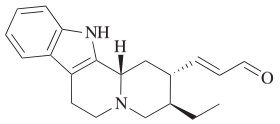
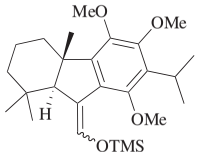
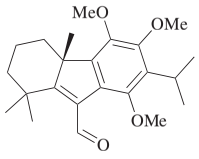
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	1. $Pd(OAc)_2$ (1.1 eq), rt, 72 h 2. HCl, Et_2O/H_2O	 (61)	97
	$Pd(OAc)_2$ (1 eq), CSA•H_2O (1 eq), MeCN, –16°, 1.3 h	 (80)	41
	$Pd(OAc)_2$ (1.5 eq), DMSO, 65°, 8 h	 (84)	485

TABLE 3. α,β-UNSATURATED ESTERS

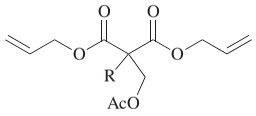
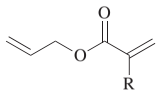
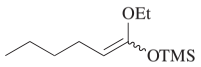
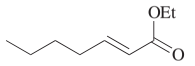
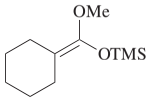
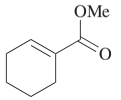
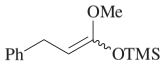
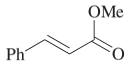
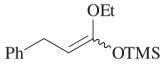
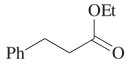
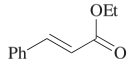
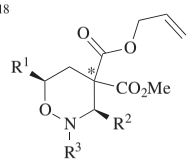
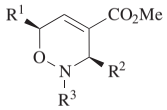
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-9} 	$Pd_2(dba)_3$•$CHCl_3$ (0.025 eq), PPh_3 (0.1 eq), MeCN, 40°, 0.25 h	 R: MeO_2C (83); n-C_5H_{11} (87)	203
C_6 	$Pd(OAc)_2$ (0.1 eq), allyl methyl carbonate (2 eq), MeCN, reflux, 2–6 h	 (79)	161, 39
C_7 	$Pd(OAc)_2$ (0.1 eq), allyl methyl carbonate (2 eq), PhCN, reflux, 2–6 h	 (75)	161, 39
C_9 	$Pd(OAc)_2$ (0.1 eq), allyl methyl carbonate (2 eq), PhCN, reflux, 2–6 h	 (69)	161, 39
	$Pd(OAc)_2$ (0.1 eq), DMSO, O_2 (1 atm), rt, 72 h	 (49) +  (40)	27
C_{10-18}  *dr ~1:1	$Pd_2(dba)_3$ (0.06 eq), MeCN, reflux, 3 h	 R^1 / R^2 / R^3: H / 2-C_4H_3S / Ph (76); H / Ph / Ph (85); Ph / Ph / Ph (66); Ph / 4-$O_2NC_6H_4$ / Ph (79); Ph / 4-$MeOC_6H_4$ / 4-MeC_6H_4 (79)	198

TABLE 3. α,β-UNSATURATED ESTERS (*Continued*)

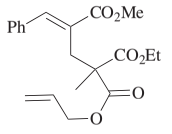
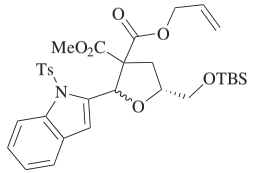
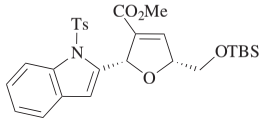
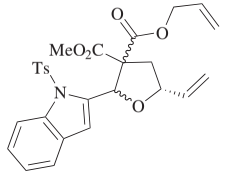
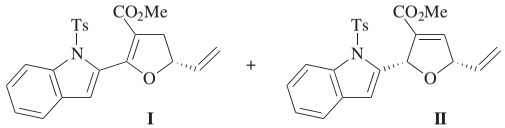
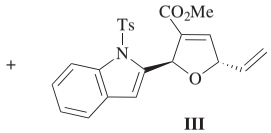
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	$Pd(OAc)_2$ (0.1 eq), PPh_3 (0.1 eq), DMF, 140–150°, 1 h	 **I** + **II** **I** + **II** (55), **I/II** = 3:2	196
C_{15} 	$Pd_2(dba)_3$ (0.05 eq), MeCN, reflux, 10 h	 (45–55)	197
C_{16} 	$Pd_2(dba)_3$, MeCN, reflux	 **I** + **II**  **III** **I** + **II** + **III** (94), **I/II/II** = 1:1:1	197

TABLE 4. α,β-UNSATURATED LACTONES AND LACTAMS

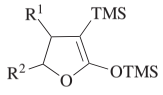
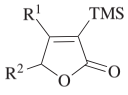
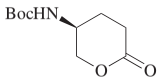
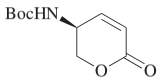
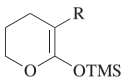
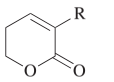
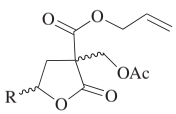
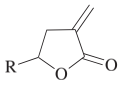
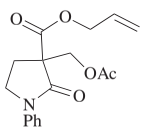
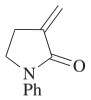
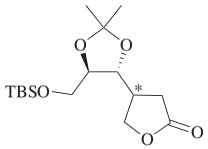
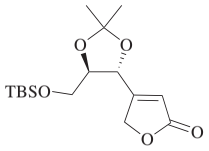
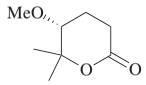
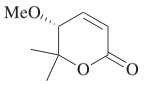
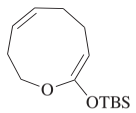
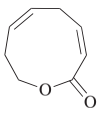
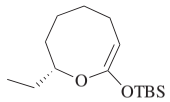
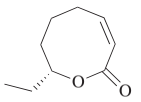
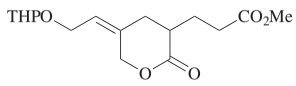
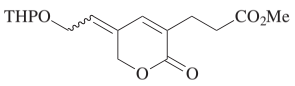
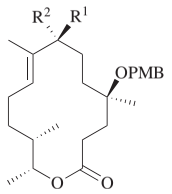
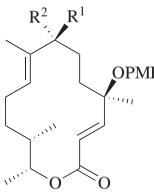
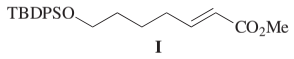
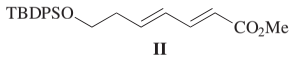
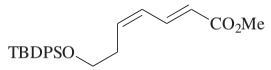
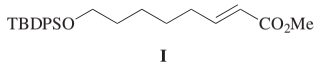
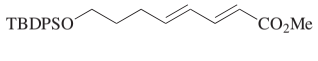
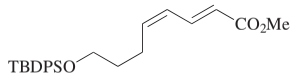
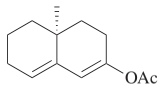
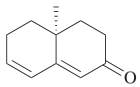
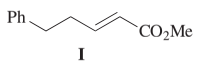
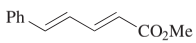
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{4–5}$ 	$Pd(OAc)_2$ (0.1 eq), allyl methyl carbonate (2 eq), MeCN, reflux, 2–6 h	 R^1 R^2: H H (90); H Me (90); Me H (85)	39
C_5 	1. LHMDS, TMSCl, –78°, 0.25 h 2. $Pd(OAc)_2$ (1.2 eq), MeCN, rt, 0.75 h	 (70)	486
	$Pd(OAc)_2$ (0.1 eq), allyl methyl carbonate (2 eq), MeCN, reflux, 2–6 h	 R: H (70); TMS (72)	161, 39
$C_{5–11}$ 	$Pd_2(dba)_3$•$CHCl_3$ (0.025 eq), PPh_3 (0.1 eq), MeCN, 50°, 0.25 h	 R: H (74); n-C_6H_{13} (93)	203
C_5 	$Pd_2(dba)_3$•$CHCl_3$ (0.025 eq), PPh_3 (0.1 eq), MeCN, 80°, 0.25 h	 (87)	203
C_7  * dr 1:0	1. LHMDS, TMSCl, THF, –78° to rt, 0.5 h 2. $Pd(OAc)_2$ (0.5 eq), 1,4-benzoquinone (0.5 eq), MeCN, rt, 36 h	 (74)	271

TABLE 4. α,β-UNSATURATED LACTONES AND LACTAMS (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7	 **I**	1. LHMDS, TMSCl, THF, –78°, 20 min 2. $Pd(OAc)_2$ (1 eq), MeCN, 0° to rt, 2–4 h	 (72) + **I** (28)	487
C_8		$Pd(OCOCF_3)_2$ (1 eq), CH_2Cl_2/MeCN, rt, 16 h	 (72)	120
C_9		$Pd(OAc)_2$ (cat.), allyl methyl carbonate, MeCN, reflux, 6 h	 (83)	488
C_{10}		1. LHMDS, TMSCl, THF, –78° 2. $Pd(OAc)_2$, MeCN, rt	 (65)	489
C_{17}		1. LiHMDS, TMSCl, THF, –78° 2. $Pd(OAc)_2$, 3 Å MS, MeCN, rt		490

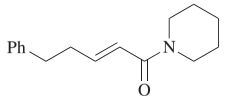
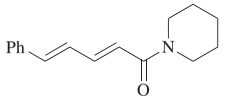
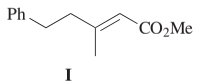
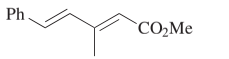
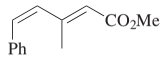
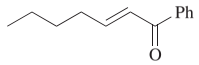
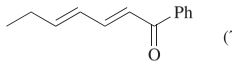
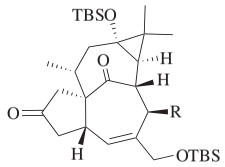
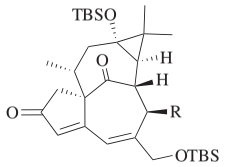
R^1	R^2	
H	TBDPSO	(59)
TBDPSO	H	(38)

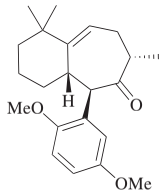
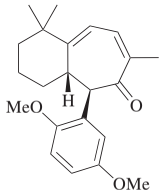
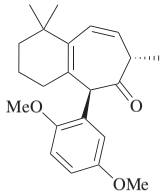
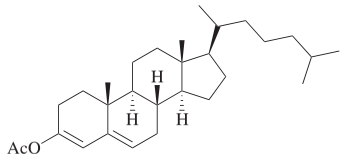
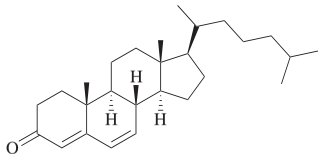
TABLE 5. α,β,γ,δ-UNSATURATED KETONES, ESTERS, AND AMIDES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7  **I**	1. NEt_3, TIPSOTf, CH_2Cl_2, rt, 1 h 2. $Pd(OAc)_2$ (*x* eq), 1,4-benzoquinone (*y* eq), K_2CO_3 (*z* eq), $MeCN/CH_2Cl_2$ (1:1), rt, time	 **II** +  **III** + **I** (16)	491
C_8  **I**	1. NEt_3, TIPSOTf, CH_2Cl_2, rt, 1 h 2. $Pd(OAc)_2$ (2 eq), K_2CO_3 (5 eq), $MeCN/CH_2Cl_2$ (1:1), rt, 12 h	 (48) +  (5) + **I** (14)	491
C_{11} 	$Pd(OAc)_2$ (0.05 eq), dppe (0.05 eq), $MeOSnBu_3$ (0.2 eq), allyl methyl carbonate (1.7 eq), MeCN, reflux, 20 h	 (70)	492, 493
 **I**	1. NEt_3, TIPSOTf, CH_2Cl_2, rt, 3 h 2. $Pd(OAc)_2$ (2 eq), K_2CO_3 (5 eq), $MeCN/CH_2Cl_2$ (1:1), rt, 12 h	 (62) + **I** (11)	491

x	*y*	*z*	Time (h)	**II**	**III**
0.2	2	1	15	(27)	(27)
2	—	5	18	(51)	(—)

TABLE 5. α,β,γ,δ-UNSATURATED KETONES, ESTERS, AND AMIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	1. NEt_3, TIPSOTf, CH_2Cl_2, rt, 0.5 h; then reflux, 1 h 2. $Pd(OAc)_2$ (2 eq), K_2CO_3 (5 eq), $MeCN/CH_2Cl_2$ (1:1), reflux, 8 h	 (56)	491
C_{12}  **I**	1. NEt_3, TIPSOTf, CH_2Cl_2, rt, 50 min 2. $Pd(OAc)_2$ (2 eq), K_2CO_3 (5 eq), $MeCN/CH_2Cl_2$ (1:1), rt, 14 h	 (28) +  (25) + **I** (32)	491
C_{13} 	1. NEt_3, TIPSOTf, CH_2Cl_2, rt, 1 h 2. $Pd(OAc)_2$ (2 eq), K_2CO_3 (5 eq), MeCN, 50°, 35 h	 (73)	491
C_{19} 	1. LHMDS, TMSCl, NEt_3, THF, –78°, 2–3.5 h 2. $Pd(OAc)_2$ (*x* eq), MeCN, rt, 18–19 h	 R *x* H 4.4 (95) PhSe 5.4 (64)	494, 125

C_{20}		1. NEt_3, TMSOTf, CH_2Cl_2, 0° to rt, 5 h 2. $Pd(OAc)_2$ (1 eq), MeCN, rt, 10 h	 (46) +  (29)		495, 496
C_{27}		$Pd(OAc)_2$ (0.1 eq), $MeOSnBu_3$ (0.2 eq), allyl methyl carbonate (2 eq), MeCN, reflux, 5–10 h		(78)	160, 39

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