CHAPTER 1

THE McMURRY COUPLING AND RELATED REACTIONS

TAKESHI TAKEDA AND AKIRA TSUBOUCHI

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

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takeda-t@cc.tuat.ac.jp

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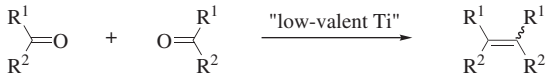
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INTRODUCTION

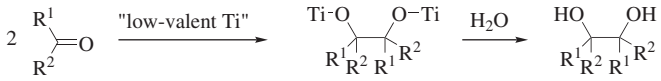
Reductive coupling of carbonyl compounds leading to pinacols or alkenes is a powerful synthetic transformation. The deoxygenative coupling of carbonyl compounds leading to the formation of alkenes is a rather newly developed synthetic method relative to other transformations such as the classical pinacol coupling. In 1970 Schreibmann first reported the formation of alkenes as minor products in the pinacol coupling of aromatic carbonyl compounds with aluminum amalgam.[1] The reductive coupling of both aromatic and aliphatic aldehydes and ketones using low-valent tungsten species generated by treatment of WCl_6 with two equivalents of BuLi was described shortly thereafter.[2] Although the process remains inefficient for the preparation of aliphatic alkenes, it works well to provide various stilbenes. The seminal deoxygenative carbonyl coupling with highly oxophilic titanium species was reported independently in 1973 and 1974 by Mukaiyama,[3] Tyrlik,[4] and McMurry.[5] The $TiCl_3$–$LiAlH_4$ system developed by McMurry was the first synthetically useful transformation of aliphatic carbonyl compounds into alkenes, demonstrating the versatility of the coupling system.

After four decades of study, a variety of low-valent titanium species have been found to promote the reductive coupling of a range of both aromatic and aliphatic aldehydes and ketones to furnish alkenes in inter- and intramolecular reactions (Scheme 1). Consequently, the McMurry coupling has been recognized as one of the most efficient methods for the synthesis of alkenes from carbonyl compounds.



Scheme 1

The initial studies shed light on the reagent- and substrate-dependence of reactivity. The concomitant or preferential formation of pinacols via titanium pinacolates, which are typically recognized as intermediates of the McMurry coupling, is observed in certain cases (Scheme 2). This chapter discusses the direct deoxygenative transformation of carbonyl compounds into alkenes and excludes the sequential formation of alkenes via pinacols and related compounds.



Scheme 2

The low-valent titanium reagents were initially prepared by the reduction of $TiCl_4$ or $TiCl_3$ with Zn dust or $LiAlH_4$. Further development of $TiCl_3(DME)_{1.5}$–Zn/Cu has improved yields and reproducibility, and extended the range of application.[6] More recent accounts describe highly active titanium reagents such as the $TiCl_3$–C_8K system,[7] permitting the intramolecular coupling of carboxylic acid derivatives with ketones or aldehydes. A variety of low-valent metal species other than titanium, including aluminum, zirconium, niobium, molybdenum, indium, tungsten, and samarium, have also been found to promote the reductive coupling of carbonyl compounds. Details of the low-valent metal reagents used in the McMurry coupling will be reviewed in the "Scope and Limitations" section.

Numerous synthetic applications of the coupling reaction, including the preparation of sterically congested and strained alkenes, as well as the formation of medium- and large-ring compounds, have been reported. In addition to these theoretically interesting alkenes, the preparation of biologically active targets and compounds useful in materials science using the McMurry coupling as a key step has been investigated extensively, and these results are summarized in the Tabular Survey. All these studies have been outlined in earlier reviews.[8–25]

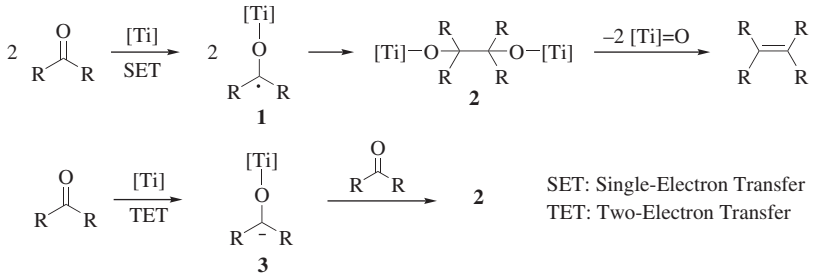
Despite the achievements described in this chapter, several challenges still remain in the deoxygenative coupling of carbonyl compounds. These include the control of double-bond geometry in the construction of highly substituted alkenes as well as the selective mixed-coupling of two distinct carbonyl compounds, particularly the intermolecular coupling of carboxylic acid derivatives. In this regard, the low-valent metal-mediated mixed-coupling of carbonyl equivalents such as thioacetals and *gem*-dihalides with various carbonyl compounds will be

briefly described in the "Scope and Limitations" section as carbonyl substitutes in the mixed McMurry coupling.

Recent theoretical studies suggest that the coupling follows alternative reaction pathways other than those involving pinacolate intermediates.[26] It is expected that the design of new low-valent metal reagents based on such theoretical insights into the McMurry coupling may provide solutions for the remaining problems.

MECHANISM

The reaction mechanism for the McMurry coupling remains unknown. Most mechanistic studies suggest that the reaction is composed of two processes: (1) formation of pinacolate intermediates **2**, and (2) deoxygenation of the pinacolates **2** leading to the formation of alkenes (Scheme 3).[26] When aliphatic ketones are employed, the formation of **2** is thought to proceed by the dimerization of ketyl radicals **1** by one-electron reduction of the carbonyl groups with low-valent titanium reagents. In the coupling of more active aromatic ketones, a two-electron reduction may take place to give dianions of ketones **3**, which then undergo nucleophilic addition to other ketones to furnish the pinacolate intermediates **2**.



Scheme 3

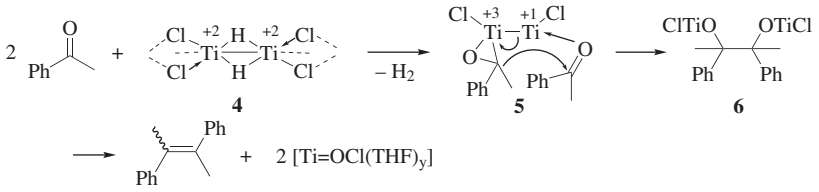
The mechanism composed of the above two distinct steps is supported by the observation that the pinacols may be isolated by carrying out the reaction at low temperature, whereas alkenes are produced at higher temperature using the same carbonyl coupling mediated by low-valent titanium reagents.[3,5] It has been proposed by McMurry that the pinacolate intermediates, coordinated to the same surface of a zero-valent titanium particle, but not to the same titanium atom, undergo stepwise cleavage of the C–O bonds and form the C=C bond.[27] Although the Ti–pinacolate intermediates could not be characterized because of the heterogeneous nature of the conditions, the pinacolate intermediates have been isolated in the reactions of carbonyl compounds with titanocene(III) dihalides[28] and titananorbornadiene complexes.[29]

The McMurry coupling is usually performed using inorganic low-valent titanium species, prepared in situ by reduction of titanium halides such as $TiCl_4$ or

$TiCl_3$ with various reductants. It has been assumed that finely dispersed particles of titanium are the active species in these reactions. However their oxidation states and structures have not been definitively identified. A zero-valent titanium species is proposed to be the active species in the coupling of ketones with the $TiCl_3$–Li, K, or Mg system,[30] and a mixture of Ti(0), Ti(I), and Ti(II) with the $TiCl_3$–$LiAlH_4$ system.[30] Conversely, it has been proposed that the McMurry coupling of ketones occurs on the ensemble of reduced titanium cations (+1, +2, and +3) on the TiO_2 (001) surface via the formation of pinacolate intermediates.[31]

The active species for the practical coupling using the $TiCl_3$–$LiAlH_4$ system has been isolated and characterized as $[HTiCl(THF)_{0.5}]_n$ (**4**) (Eq. 1).[32] That species possesses a chain-like structure composed of repeating units of dimeric or trimeric titanium atoms bridged through hydrogen. The titanium hydride **4**, which acts as a two-electron reductant, promotes the deoxygenative coupling of acetophenone to give 2,3-diphenyl-2-butene (Scheme 4).[33] As such, the reaction is thought to proceed through the formation of the ketone dianion intermediate **5** that is converted into pinacolate intermediate **6** by way of nucleophilic addition. In this regard, it is a prerequisite to reduce the $TiCl_3$ with $LiAlH_4$ completely before addition of carbonyl substrates.

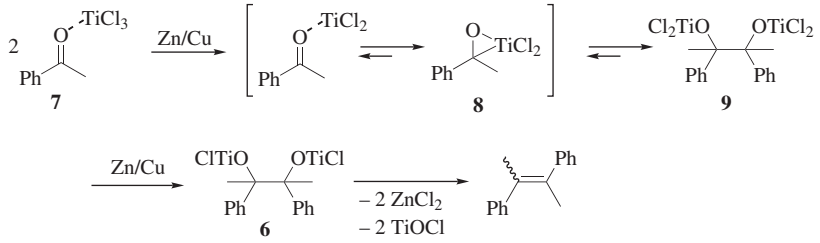
$$[TiCl_3(THF)_3]_n + 0.5n\ LiAlH_4 \longrightarrow [HTiCl(THF)_{0.5}]_n\ (\mathbf{4}) + 0.5n\ H_2 + 0.5n\ LiCl + 0.5n\ AlCl_3 \qquad \text{(Eq. 1)}$$



Scheme 4

When employing the $TiCl_3(DME)_{1.5}$–Zn/Cu system, the reduction of $TiCl_3$ with zinc takes place only in the presence of carbonyl substrates.[33] This observation indicates that no low-valent titanium species are formed in the absence of the carbonyl groups, and therefore, pre-reduction of the titanium halide prior to carbonyl addition is unnecessary. A proposed reaction mechanism for the McMurry coupling of acetophenone using this system is illustrated in Scheme 5.[33] The reaction is presumed to begin with the reduction of the acetophenone–$TiCl_3$ complex **7** with Zn/Cu by lowering the reduction potential of $TiCl_3$ through coordination to the Lewis basic oxygen. The "side-on" coordinated carbonyl complex of $TiCl_2$ **8**, a ketone dianion intermediate, is proposed as a precursor of the pinacolate **6**. The reduction of Ti^{3+} to Ti^{2+} by zinc is involved in both the conversion of the ketone to the pinacolate **9** and the pinacolate **9** to the alkene.

A similar mechanism involving the formation of ketone dianion intermediates like **8** by a two-electron transfer process has been proposed for the coupling of



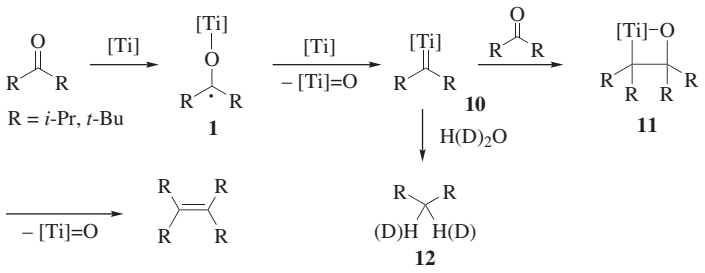
Scheme 5

aromatic ketones with $TiCl_2$, generated by the reaction of $TiCl_4$ with 2 equivalents of BuLi.[34] For the reactions in Schemes 4 and 5, the "side-on" coordinated carbonyl complex of $TiCl_2$ **8** is also proposed as a precursor for the pinacolates and, in the carbon–carbon bond formation step, the nucleophilic mechanism is operative rather than the radical mechanism. Ab initio calculations support the nucleophilic mechanism.[35]

By contrast, ketyl radical intermediates have been detected by ESR in the reductive coupling of aromatic ketones with the $TiCl_3$–Mg and $TiCl_3$–$LiAlH_4$ reagent systems.[30] The ketyl radicals on titanium complexes are also produced by the reaction of aliphatic ketones and aldehydes with $Ti(OSi\textit{t}\text{-}Bu_3)_3$, generated by the reduction of $Ti(OSi\textit{t}\text{-}Bu_3)_3Cl$ with Na(Hg). These have been characterized by ESR, although the radicals could not dimerize to form the pinacolates due to steric congestion.[36]

An alternative mechanism proposed for the McMurry coupling of hindered ketones involves titanium carbene intermediates rather than pinacolates. This hypothesis is supported by the observation that the pinacols are never obtained by the reductive coupling of diisopropyl ketone[37,38] and di-*tert*-butyl ketone[38,39] with the low-valent titanium species generated from the $TiCl_4$–Li/Hg system. Furthermore, it was demonstrated that the titanium pinacolates, $Cl_3TiOC(i\text{-}Pr)_2$–$(i\text{-}Pr)_2COTiCl_3$, prepared by transmetalation of the corresponding lithium pinacolate with $TiCl_4$, rapidly decomposes into diisopropyl ketone and $TiCl_3$ without formation of alkene.[37] These observations are consistent with the involvement of a titanium carbene mechanism in which the ketyl radicals **1,** formed by one-electron reduction of the ketones, undergo deoxygenative reduction to form the [Ti] intermediate **10**, probably due to steric hindrance (Scheme 6).[26] Intermediate **10** then reacts with the ketone to give the oxatitanacyclobutane intermediates **11** that lead to the formation of alkenes by metathesis-type degradation. When the reaction of di-*tert*-butyl ketone is quenched with D_2O, the dideuterated alkane **12** is produced, further supporting the presence of a titanium carbene intermediate.

In view of the similarities in structure and reactivity of uranium and titanium, the reductive coupling of ketones with uranium compounds has been investigated as model reactions to obtain more details about the mechanism of the McMurry coupling. The above-mentioned mechanism involving the pinacolate intermediates is supported by these studies. Thus, the uranium pinacolates of

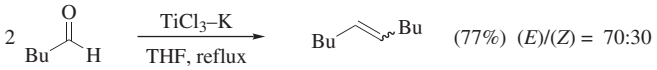


Scheme 6

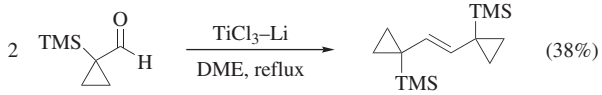
benzophenone[40] and acetone[41,42] have been isolated and characterized as intermediates, which undergo the deoxygenation to produce the corresponding alkenes upon heating the reaction mixtures at reflux temperatures.

STEREOCHEMISTRY

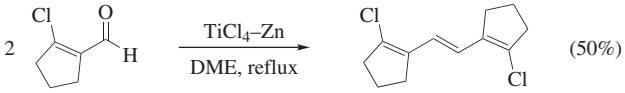
In general, the McMurry coupling of aldehydes and unsymmetrical ketones furnishes mixtures of (*E*)- and (*Z*)-isomers. The (*E*)/(*Z*) ratio is dependent on the reagents and structure of the substrates. The preferential formation of (*E*)-isomers is observed in the homocoupling of both aliphatic and aromatic aldehydes. The (*E*)/(*Z*) ratio of the alkene thus produced is improved with bulkier substituents. When pentanal is subjected to the coupling with the $TiCl_3$–K system, 5-decene is formed with a diastereomeric ratio of (*E*)/(*Z*) = 70:30 (Eq. 2).[27] By contrast, sterically hindered aldehydes such as cycloalkanecarbaldehydes (Eqs. 3 and 4)[43,44] and aromatic aldehydes afford only (*E*)-alkenes.



(Eq. 2)



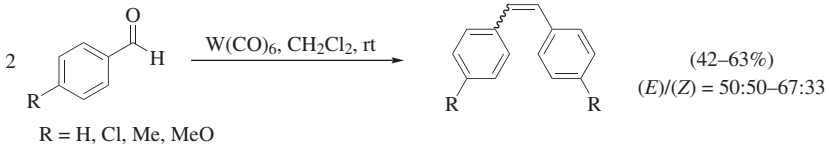
(Eq. 3)



(Eq. 4)

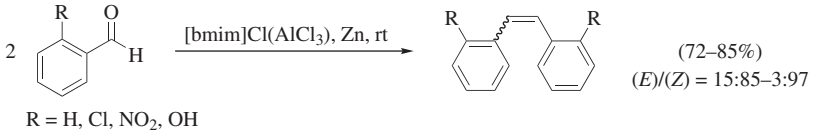
The (*E*)-selectivity is dramatically decreased when $W(CO)_6$ is employed in the reductive coupling of substituted benzaldehydes (Scheme 7).[45] It is proposed that the reaction proceeds through the formation of carbene intermediates generated by the reaction of low-valent tungsten with the aryl-substituted aldehyde.

By contrast, the homocoupling of aromatic aldehydes using the ionic liquid, 1-butyl-3-methylimidazolium chloroaluminate [bmim]$ClAlCl_3$ in combination with



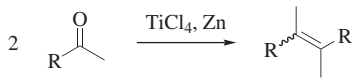
Scheme 7

zinc exhibits preferential formation of (*Z*)-stilbenes (Scheme 8),[46] although the reasons for this are not clear.



Scheme 8

The homocoupling of unsymmetrical aliphatic ketones generally affords (*E*)-alkenes. Increasing the size difference of the two alkyl groups improves the selectivity. As shown in Scheme 9, the coupling of methyl ethyl ketone with the $TiCl_4$–Zn–Py system furnishes an (*E*)/(*Z*) mixture of 3,4-dimethyl-3-hexene with a slight excess of the (*E*)-isomer, whereas only the (*E*)-alkene is formed by the coupling of *tert*-butyl methyl ketone under similar conditions.[47]

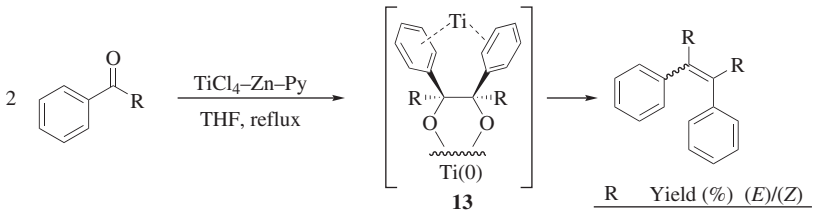


R	Yield (%)	(*E*)/(*Z*)
Et	65	1.1:1
Pr	61	1.4:1
i-Pr	46	1.5:1
neopentyl	48	100:0
t-Bu	62	100:0

Scheme 9

When sterically less encumbered alkyl aryl ketones, such as acetophenone, are subjected to the conventional McMurry coupling conditions, (*Z*)-stilbenes are preferentially obtained (Scheme 10).[48] This selectivity has been attributed to the complexation of the aromatic ring with titanium in the pinacolate intermediates **13**, in which the two phenyl rings adopt a *syn* configuration. The coupling of the sterically hindered isopropyl phenyl ketone results in preferential formation of the (*E*)-alkene.

A π–π pre-association of the aromatic rings in a transition state or at a pinacolate intermediate stage may also explain the (*Z*)-selective formation of

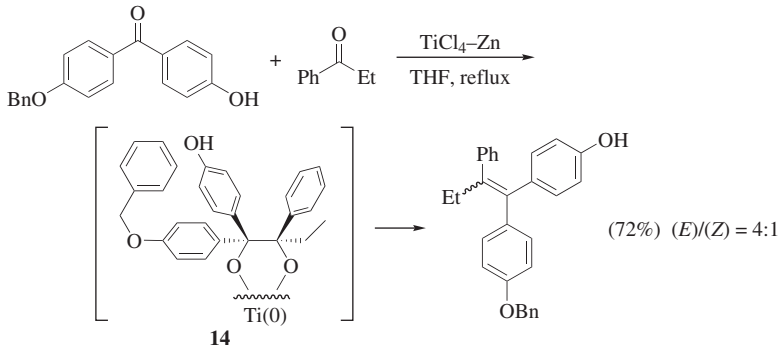


R	Yield (%)	(*E*)/(*Z*)
Me	81	26:74
Et	59	27:73
Pr	55	11:89
i-Pr	25	88:12

Scheme 10

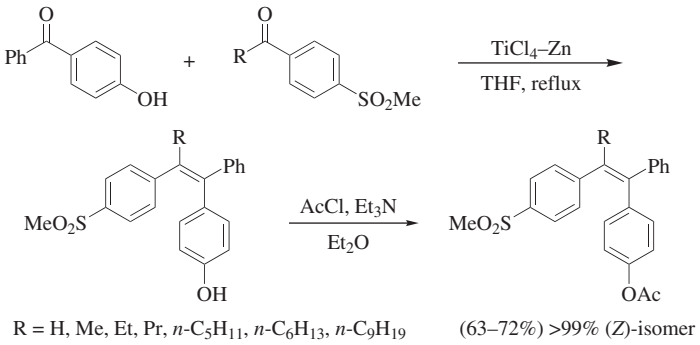
the stilbenes. Such a $\pi-\pi$ stacking interaction has also been suggested for the non-negligible formation of the (*Z*)-isomer in the coupling of large π-electron systems such as porphyrin[49]- and chlorin[50]-based aldehydes.

The stereoselectivity of the double bond formation by the mixed McMurry coupling is also affected by the steric demand of the substituents proximal to the carbonyl groups. The mixed-coupling of unsymmetrical 4,4′-disubstituted benzophenones with propiophenone generally exhibits (*E*)-selectivity when the sizes of the two substituents are significantly different.[51–55] For example, the reaction with 4-benzyloxy-4′-hydroxybenzophenone produces the corresponding alkene in an (*E*)/(*Z*) ratio of 4:1 (Scheme 11).[53] The observed selectivity can be ascribed to the pinacolate intermediate **14**. Because of steric hindrance, the phenyl ring bearing the larger substituent and the ethyl group are positioned on the same side to give (*E*)-alkenes. In contrast, the reaction of 4-benzyloxy-4′-perfluorotolyloxybenzophenone results in only a slightly higher (*E*)/(*Z*) ratio, because of a small difference in bulkiness of the two substituents. A substituent at the *ortho* position of a benzophenone significantly improves the (*E*)-selectivity in the McMurry coupling of propiophenone.[56]



Scheme 11

High levels of (*Z*)-selectivity have been achieved in the McMurry coupling between benzophenones and alkanophenones bearing hydroxyl and methylsulfonyl functionalities at the *para*-position of the arene ring of each coupling component. This outcome is obtained regardless of whether the alkanophenones possess a hydroxy or methylsulfonyl group.[57–59] For example, the mixed McMurry coupling between 4-methylsulfonylalkanophenones and 4-hydroxybenzophenone furnishes the triarylethenes with complete (*Z*)-selectivity (Scheme 12).[58] Less selective formation of (*Z*)-alkenes is observed in the reaction of *para*-acetoxy substituted alkanophenones with 4-methylsulfonylbenzophenone.[57]



R = H, Me, Et, Pr, *n*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_9H_{19} (63–72%) >99% (*Z*)-isomer

Scheme 12

SCOPE AND LIMITATIONS

Coupling Reagents

Various low-valent metal reagents promote the reductive coupling of two carbonyl compounds to form alkenes.[60] Due to the oxophilicity of titanium, the most common reagents in the McMurry coupling are those prepared by the reduction of Ti(III) or Ti(IV) chlorides with a range of reducing agents ($LiAlH_4$, Li, Na, Mg, K, Zn, Zn/Cu). Depending on the reducing agents, additives, and conditions, various low-valent titanium species with different oxidation states and reactivities are generated. The most commonly used reagents are described below.

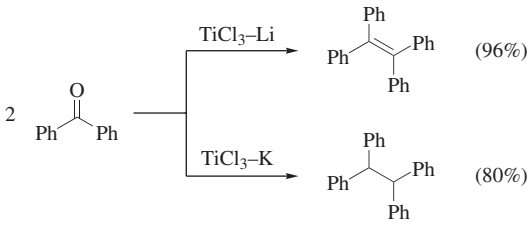
Low-Valent Titanium-Based Reagents

The $TiCl_4$–Zn System. The $TiCl_4$–Zn system couples aromatic aldehydes and ketones at elevated temperature to furnish substituted alkenes. Heat is essential because the treatment of these compounds with low-valent titanium species at ambient temperature results in the exclusive formation of pinacol derivatives.[3] Similar treatment of aliphatic carbonyl compounds produces only pinacols, even at higher temperature. Several modified reagent systems, such as $TiCl_4$–Zn/Cu, $TiCl_4$–Zn–CuCl, and $TiCl_4$–Zn–CuI, are also employed for the McMurry coupling.

The $TiCl_3$–Zn/Cu System. The $TiCl_3$–Zn/Cu system was first employed for the intramolecular coupling of aliphatic as well as aromatic diketones.[61] This reagent is a safer and more effective alternative to low-valent titanium reagents generated by reduction with either potassium or lithium reagents (see below). An optimized procedure for the preparation of this reagent involves the reduction of $TiCl_3(DME)_{1.5}$ with a Zn/Cu couple. The low-valent titanium species thus formed is one of the most widely used low-valent titanium reagents.[6] An additional advantage of this procedure is that $TiCl_3(DME)_{1.5}$ is stable and may be purified by crystallization.

The $TiCl_3$–$LiAlH_4$ System. The $TiCl_3$–$LiAlH_4$ system was first employed by McMurry to carry out the deoxygenative coupling of both saturated and unsaturated ketones. The reagent can be employed for the preparation of β-carotene from retinal.[5] The procedure remains problematic such that successful results seem to be dependent on the specific batches of reagent used.[62] However, the intramolecular coupling of oxo esters is readily performed with the $TiCl_3$–$LiAlH_4$ system in the presence of triethylamine.[63]

The $TiCl_3$–Alkali or Alkaline Earth Metal System. The low-valent titanium reagent generated by the reduction of $TiCl_3$ with potassium metal according to Rieke's procedure[64] is a good alternative to the $TiCl_3$–$LiAlH_4$ system for the coupling of saturated aliphatic ketones.[62] To avoid the use of hazardous potassium for the preparation of low-valent titanium species, an improved procedure using lithium metal was developed. The reagent thus formed is equally effective for the deoxygenative coupling of a variety of carbonyl compounds in both inter- and intramolecular reactions. A difference between the two reagents is shown in Scheme 13: the titanium reagent prepared by the reduction of $TiCl_3$ with lithium affords tetraphenylethylene in high yield whereas the similar reaction using the $TiCl_3$–K system results in the formation of tetraphenylethane.[27]



Scheme 13

One of the earliest studies on deoxygenative coupling employed the $TiCl_3$–Mg system that promotes the coupling of both aliphatic and aromatic ketones. Despite further studies on this reagent,[3,65,66] only limited applications for the McMurry coupling have been reported.

The $TiCl_3$–Lithium Arene System. The preparation of low-valent titanium reagents by the reduction of $TiCl_3$ with Li–arenes has been investigated and the study reveals that the reagent prepared by using the Li–naphthalene combination is reactive enough to carry out the transformation of carbonyl compounds into alkenes under milder conditions as compared with the conventional $TiCl_3$–Li system.[67]

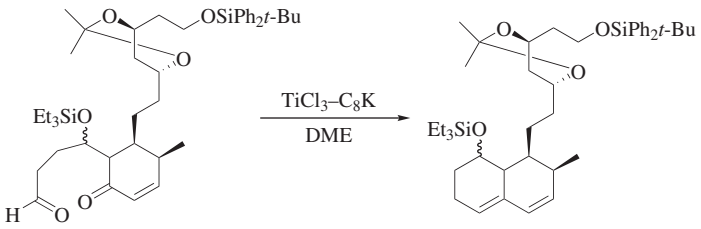
The $TiCl_4$–BuLi System. Treatment of $TiCl_4$ with two equivalents of BuLi in THF produces an isolable, and well-characterized, divalent titanium species (Eq. 5).[34] This reagent promotes the reductive coupling of aromatic aldehydes and ketones to form the corresponding (*E*)-alkenes with high levels of stereoselectivity. A similar reagent generated from TiF_4 is also capable of promoting the same coupling reaction.[68]

$$TiCl_4 + 2\,BuLi \xrightarrow[-\,2\,LiCl]{THF} TiCl_2(THF)_2 + BuH + EtCH{=}CH_2 \qquad \text{(Eq. 5)}$$

Supported Titanium Reagents. A major disadvantage of the $TiCl_3$–alkali metal system is the low efficacy and the need for the use of pyrophoric reducing agents. By contrast, sodium deposited on inorganic supports such as Al_2O_3, TiO_2, or NaCl are readily available nonpyrophoric reducing agents for $TiCl_3$.[69] Consequently, these reagents are useful for the inter- and intramolecular McMurry coupling of aromatic carbonyl compounds. Both the inter- and intramolecular coupling reactions of acyltrimethylsilanes were first realized by the use of these reagents.[70]

The intercalation compound potassium in graphite (C_8K) acts as a powerful reducing agent toward transition-metal halides dissolved or suspended in THF.[71] The low-valent titanium generated by the reduction of $TiCl_3$ with C_8K is highly useful for all types of McMurry coupling reactions,[72–77] including the intramolecular reaction of oxo amides.[7,78–83] The $TiCl_3/C_8K$ ratio is crucial for the preparation of a highly activated form of titanium. Although the initially reported titanium reagent generated by the reduction of $TiCl_3$ with three equivalents of C_8K (formally a Ti(0) species) is successfully employed for the various coupling processes, the reagent generated by the reduction of $TiCl_3$ with two equivalents of C_8K (formally a Ti(+1) species) is much more reactive and provides more reproducible results for the cyclization of the keto aldehyde shown in Scheme 14.[84]

Titanium Powder. Commercial titanium powder exhibits exceptional resistance to chemical attack. The treatment of titanium powder with TMSCl in boiling THF or DME for dozens of hours removes a thin oxide layer on its surface and the activated Ti(0) species can be employed for the McMurry coupling. The reagent effectively promotes the coupling reactions of aromatic and α,β-unsaturated aldehydes or ketones as well as the intramolecular mixed-coupling leading to aromatic heterocyclic compounds.[83,85] However, aliphatic carbonyl compounds are not good substrates for this reagent.



$TiCl_3/C_8K$	Substrate/$TiCl_3$	Yield (%)
1.00:4.07	1.00:10.00	0
1.00:3.00	1.00:10.00	30
1.00:2.09	1.00:17.14	85

Scheme 14

Other Titanium-Based Reagents. Several well-defined low-valent titanium species are known to promote the deoxygenative coupling of carbonyl compounds. The reductive coupling of aromatic aldehydes and ketones with $Cp_2Ti(CO)_2$ produces alkenes along with the corresponding pinacols.[86] For example, the intramolecular coupling of 2-(benzoylamino)benzophenone is promoted with the Ti(0) species such as electrochemically generated Ti-clusters, $Ti(PhMe)_2$, and Ti(biphenyl)$_2$, as well as the Ti(II) compound $Cp_2Ti(PMe_3)_2$.[7] The treatment of aromatic aldehydes and acetophenone with the reagent system $Ti(O\textit{i}\text{-}Pr)_4$–TMSCl–Mg–$Et_3N$ affords the McMurry coupling products.[87]

Low-Valent Metals Other Than Titanium

Aluminum and Zinc Reagents. The reagent generated by the treatment of $AlCl_3$ with zinc promotes the coupling of aromatic and aliphatic aldehydes and ketones with (*E*)-stereoselectivity at reflux in MeCN.[88] Conversely, the treatment of benzophenone derivatives with the $AlCl_3$–Zn system in MeCN at 35° under ultrasonic irradiation results in the exclusive formation of benzopinacolones via reductive coupling–rearrangement, except for some bridged benzophenones such as xanthone.[89]

In certain cases, zinc alone promotes the deoxygenative coupling of carbonyl compounds. The treatment of steroidal conjugated dienones with zinc dust activated by HCl in THF under reflux affords the desired deoxygenative coupling products.[90] The reagent system Zn–TMSCl can be applied to both the coupling of aryl and α,β-unsaturated carbonyl compounds to alkenes,[91] and the McMurry-type coupling of metallocenyl ketones. A very low concentration of HCl must be present to obtain satisfactory results.[92] Zinc dust in combination with the acidic ionic liquid 1-butyl-3-methylimidazolium chloroaluminate converts aromatic aldehydes and ketones to alkenes with (*Z*)-stereoselectivity.[46]

Zirconium Reagents. Similarly to titanium, the low-valent zirconium reagent generated by the reduction of $ZrCl_4$ with lithium reacts with aromatic

aldehydes and ketones to produce alkenes with (*E*)-stereoselectivity. Bicyclohexylidene is obtained in moderate yield by the reaction of cyclohexanone using this procedure.[93]

Vanadium and Niobium Reagents. The treatment of 9-fluorenone with VCl affords the deoxygenative coupling product in quantitative yields although its use for the McMurry-type coupling is largely restricted.[94] The active niobium reagent generated by the reduction of $NbCl_5$ with $NaAlH_4$ is effective for the coupling of aromatic aldehydes and ketones to produce arylethenes. 2-Heptanone is transformed into 6,7-dimethyl-6-dodecene by treatment with this reagent but in moderate yield.[95] The reduction of $NbCl_5$ with one equivalent of MeLi or metallic potassium gives an active low-valent niobium reagent which reacts with aromatic carbonyl compounds to give the corresponding alkenes. The $NbCl_5-K$ system is more reactive than $NbCl_5-MeLi$ and it transforms cycloheptanone into the dimerized alkene in good yield.[96] (Arene)tricarbonylchromium ketones undergo reductive coupling to produce mixtures of mono- and di-metallated alkenes when treated with $NbCl_3$(DME). Mono-metallated alkenes are obtained exclusively by the similar reaction of (arene)tricarbonylchromium aldehydes.[97]

Molybdenum and Tungsten Reagents. $Mo(CO)_6$[45] and $W(CO)_6$[45,98] promote the deoxygenative coupling of benzaldehyde in appropriate solvents but the yields are only moderate. The low-valent tungsten reagent generated by the reduction of WCl_6 with BuLi mediates the coupling of aromatic carbonyl compounds.[2] This reagent also performs the coupling of aliphatic carbonyl compounds, albeit with lower efficiency. Similar results are also obtained by taking advantage of the reagent prepared by treatment of WCl_6 with $LiAlH_4$.[45] Various aromatic and aliphatic aldehydes and ketones are transformed into alkenes by treatment with ditungsten hexaalkoxides such as $W_2(OCH_2CMe_3)_6Py_2$.[99,100] The reaction proceeds via the initial formation of tungsten alkylidene-bridged intermediates.[101,102] The reagent produced by electrochemical reduction of WCl_6 promotes the coupling of aromatic carbonyl compounds but it cannot be used for the reductive coupling of aliphatic counterparts.[103]

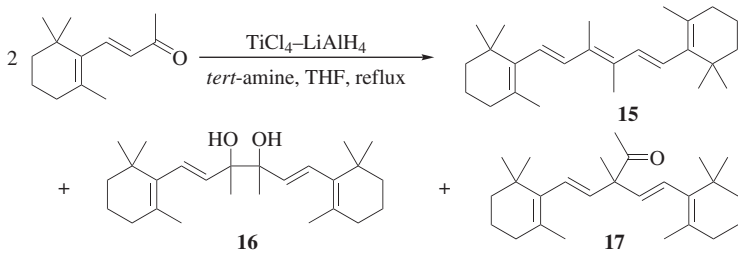
Indium Reagents. The system $InCl_3-Zn$ reductively couples aromatic and aliphatic aldehydes and aromatic ketones in MeCN at ambient temperature with (*E*)-stereoselectivity.[104]

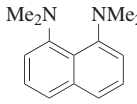
Samarium and Ytterbium Reagents. Although the deoxygenative coupling of two carboxylic acid derivatives is not achieved by the conventional McMurry coupling, *vic*-diaminoalkenes are obtained by the treatment of amides with the $Sm-SmI_2$ system.[105] However, with some amides bearing a double bond at an appropriate position, the major course of the reaction is cyclopropanation of the double bond. The system can be applied to the intermolecular coupling between aromatic amides and diaryl ketones.[106] The SmI_2-Mg system is also employed for the same intermolecular coupling.[107] The $Yb-YbI_2$ system shows similar reactivity to the $Sm-SmI_2$ system and can be applied to the coupling of amides.[108]

Uranium and Thorium Reagents. The reduction of UCl_4 with [(TMEDA)$Li]_2$[Np] affords a highly reactive uranium metal powder that produces tetraphenylethylene in moderate yield on treatment with benzophenone.[17] The deoxygenative coupling of benzophenone is also observed, but in lower yield, when treated with thorium metal powder prepared similarly. Another method for the preparation of highly reactive uranium powder is the reduction of UCl_4 with Na–K alloy and 5–10% naphthalene. The reagent also converts benzophenone to tetraphenylethylene in refluxing DME.[109]

Effect of Additives

In general, the McMurry coupling is performed with a titanium source and a reducing agent in an appropriate solvent. In certain cases, the use of additives greatly improves the reactivity of the reagents. The effect of amines for the selective formation of alkenes was first reported by Mukaiyama.[110] In the coupling of β-ionone using the $TiCl_4$–$LiAlH_4$ system, the addition of tertiary amines enhances the yield of alkene **15** by suppressing the concomitant formation of pinacol **16** and its rearrangement product **17** (Scheme 15).[110]



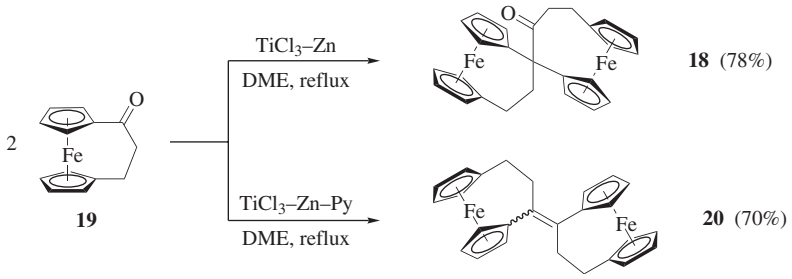
tert-Amine	**15** (%)	**16** (%)	**17** (%)
none	44	8	25
Bu_3N	91	0	0
Py	82	0	0
Et_3N	82	0	0
	94	0	0
DABCO	72	0	0

Scheme 15

The $TiCl_4$–Zn system also benefits from addition of pyridine. In its absence, reductive coupling of aliphatic ketones affords the pinacol coupling products exclusively,[3] whereas tetrasubstituted ethenes are produced when the reactions are run in the presence of pyridine.[111] The system $TiCl_4$–Zn–Py is one of the most widely used reagents for the McMurry coupling.

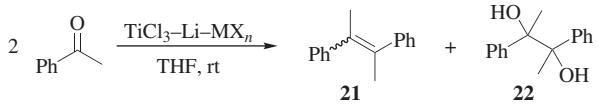
Another example of the suppression of pinacol rearrangement products is observed in the deoxygenative coupling using the $TiCl_3$–Zn system. Although

the reaction of ferrocenyl ketone **19** with this system results in the exclusive formation of the rearranged product **18**, the alkene **20** is selectively produced when pyridine is added (Scheme 16).[112] The intramolecular McMurry coupling of oxo esters by the $TiCl_3$–$LiAlH_4$ system is carried out in the presence of triethylamine.[63]



Scheme 16

Addition of Group 1 and 2 metal salts enhances the selectivity of the $TiCl_3$–Li system. The reductive coupling of acetophenone with the $TiCl_3$–Li system produces predominantly the pinacol **22**, but the combined use of KCl with the reagent system results in the exclusive formation of stilbene **21** (Scheme 17).[113,114]



MX_n	**21** (%)	**22** (%)
none	trace	89
$MgCl_2$	25	62
LiI	trace	75
CsCl	65	—
KCl	82	—
$ZnCl_2$	32	45

Scheme 17

Alternatively, activation of the $TiCl_3$–Li system is achieved by adding substoichiometric amounts of iodine. Although the conventional McMurry coupling with this system requires high temperatures and prolonged reaction times, the low-valent titanium species activated with iodine effects the deoxygenative coupling of aliphatic as well as aromatic carbonyl compounds at lower temperatures and in much reduced reaction times.[115]

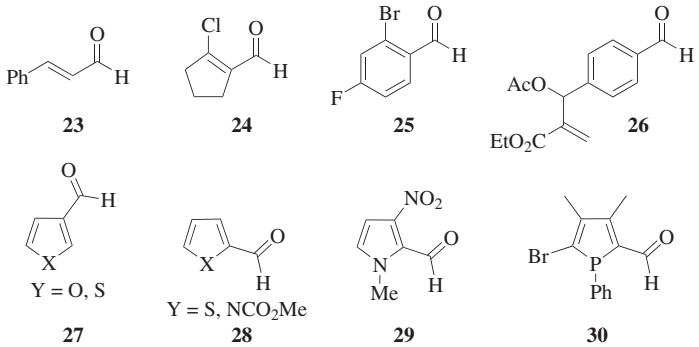
The Carbonyl Substrate

Although nearly all types of aldehydes and ketones are good substrates for the McMurry coupling, certain functional groups are not compatible with the reaction conditions as low-valent titanium species are highly reactive reducing agents. It is well known that the aqueous Ti(III) species are employed for the reductive

conversion of various organic compounds such as nitroalkanes, quinones, oximes, enedicarbonyl compounds, and α-halo ketones.[116] The reagent prepared by the reduction of $TiCl_3$ with $LiAlH_4$ converts epoxides and bromohydrins to alkenes, and allylic and benzylic alcohols are deoxygenated.[117] This reagent also reduces pinacol-containing compounds[27] as well as 2-ene-1,4-diols.[118] The reagent generated by the reduction of $TiCl_4$ with two equivalents of $LiAlH_4$ reduces acetals, thioacetals, sulfides, β-hydroxy sulfides, aryl halides, and alkenyl chlorides.[119] Various aromatic compounds, such as benzoic acid derivatives, halobenzenes, nitrobenzene, and diphenylacetylene, are also reduced by the low-valent titanium species generated under the reaction conditions.[120] β-Hydroxy sulfides and their benzoates are reductively transformed into alkenes by $TiCl_4$–Zn–Py systems.[119] Despite the possible reduction of functional groups under the McMurry conditions described above, aldehydes and ketones bearing such functional groups have been successfully employed for the McMurry coupling.

Relative to aldehydes and ketones, carboxylic acid derivatives are generally not effective substrates for the intermolecular McMurry coupling, and only a few examples of mixed-coupling between esters and ketones have been reported. Conversely, the intramolecular mixed-coupling of esters and amides with aldehydes and ketones is a useful method for the preparation of heterocyclic compounds. The homocoupling of amides is successfully achieved with Sm-based reagents.

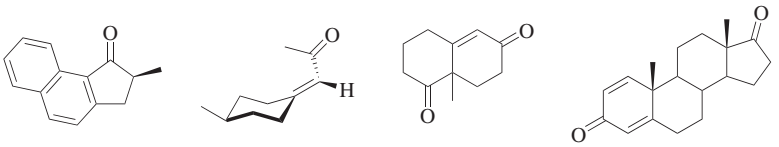
Aldehydes. The McMurry homocoupling of unsaturated aldehydes, such as cinnamaldehyde (**23**), with the $TiCl_4$–Zn–Py system proceeds with complete retention of configuration of the double bond.[121] Haloaldehydes **24**[5] and **25**[122] are coupled without reduction of the halogens using the $TiCl_4$–Zn system. The reaction of benzaldehyde **26** bearing ester and allylic acetate moieties with $TiCl_4$–Zn proceeds in good yield.[123] Most heterocycles, such as furan, thiophene, pyrrole, and pyridine, are compatible irrespective of the position of the formyl group as exemplified with **27** and **28**.[124] Even the pyrrole **29** bearing a nitro group is converted into the coupling product when treated with $TiCl_4$–Zn, albeit with unsatisfactory yields.[125] The bromophospholecarbaldehyde **30** is also successfully transformed into the phosphole-substituted ethene by the $TiCl_4$–Zn system-promoted coupling without loss of bromine.[126]



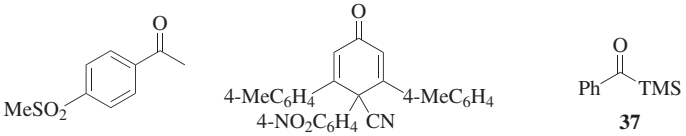
23 **24** **25** **26**

27 **28** **29** **30**

Ketones. Aliphatic, aromatic, α,β-unsaturated, acyclic, and cyclic ketones can be submitted to the McMurry conditions. Sterically congested ketones are transformed into the corresponding strained alkenes. The coupling of chiral α-substituted ketones such as **31** using the $TiCl_3-LiAlH_4$ system proceeds without epimerization.[127] The enantiomerically enriched enone **32** reacts with acetone in the presence of $TiCl_4-LiAlH_4$ to furnish the tetrasubstituted alkene without double bond isomerization.[128] Of note, the treatment of enone **33**[129] and dienone **34**[83] with the $TiCl_4-Zn$ or Ti powder–TMSCl system results in the selective coupling of the unsaturated carbonyl groups. In addition to halogens, sulfonyl groups are compatible with the McMurry conditions as indicated in the coupling of 4-methylsulfonylacetophenone (**35**).[58] The reaction of the dienone **36** demonstrates the tolerance of both cyano and nitro groups.[130] Acylsilanes such as **37** react with $TiCl_3-Na/Al_2O_3$ to produce 1,2-disilylethene derivatives with (*E*)-stereoselectivity.[70,131] Acyltrimethylsilane **37** also reacts with 9-fluorenone in the presence of ytterbium to form the corresponding alkenylsilane.[132]

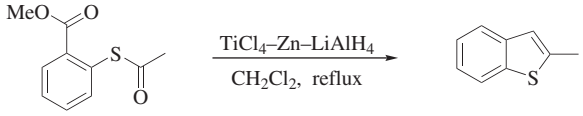


31 **32** **33** **34**



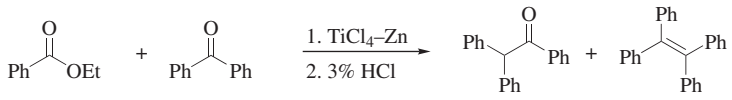
35 **36** **37**

Esters. To date, the deoxygenative coupling between two esters has not been reported. Benzothiophenes may be prepared via the intramolecular reaction of an ester with thioester groups with the reagent generated from $TiCl_4$, Zn, and $LiAlH_4$ (Eq. 6).[133]

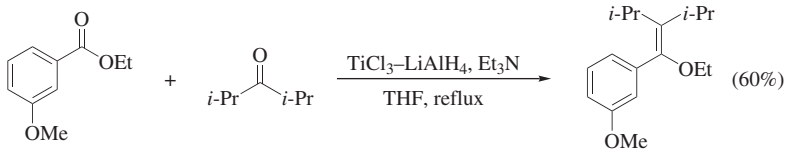


(Eq. 6)

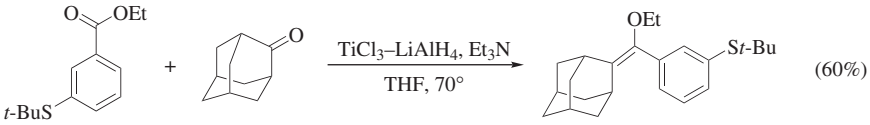
The intermolecular mixed-coupling of esters is possible with other carbonyl-containing compounds. Ketones are suitable partners in certain cases, although the homocoupling of ketones is always a side reaction; some examples are shown in Eqs. 7[134] and 8.[135] In this context, it is noteworthy that the reaction of ethyl 3-(*tert*-butylthio)benzoate with 2-adamantanone proceeds without formation of any homocoupling product (Eq. 9).[136]



(Eq. 7)

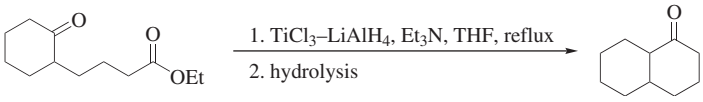


(Eq. 8)

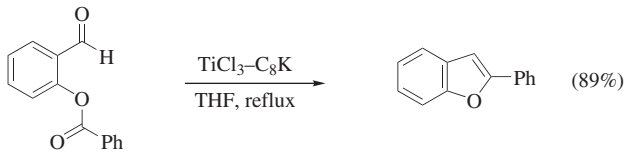


(Eq. 9)

Many intramolecular coupling reactions of esters with aldehydes and ketones have been studied. These reactions are useful and convenient for the preparation of a variety of cyclic ketones and furans (Eqs. 10[63] and 11[79]).

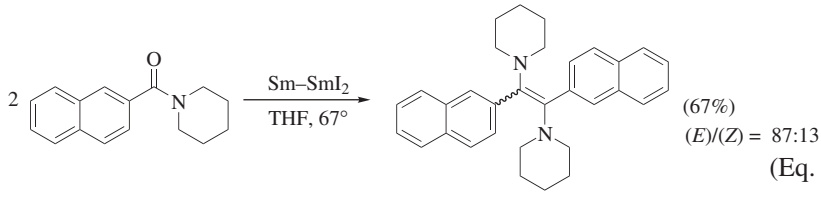


(Eq. 10)

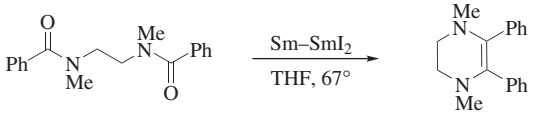


(Eq. 11)

Amides. The deoxygenative homocoupling of amides is performed by using the Sm–SmI_2 system. Both inter- and intramolecular processes have been delineated (Eqs. 12 and 13).[105] However, the yield decreases when aliphatic amides such as *N*,*N*-diethylpentanamide are employed.

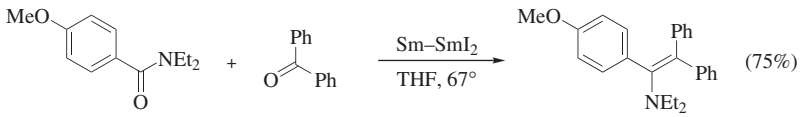


(Eq. 12)



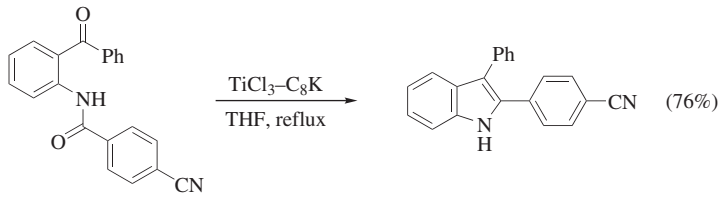
(Eq. 13)

The intermolecular, deoxygenative mixed-coupling between aromatic amides and benzophenone derivatives is promoted with the samarium-based systems, $Sm-SmI_2$[106] and SmI_2-Mg,[107] as shown in Eq. 14.[106]



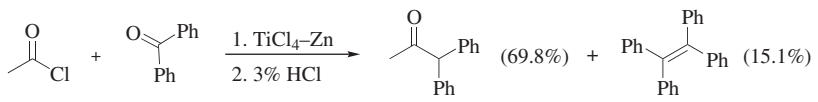
(Eq. 14)

The intramolecular coupling between amides and ketones has been extensively studied as a useful synthetic method for the preparation of various indole derivatives (Eq. 15).[79]

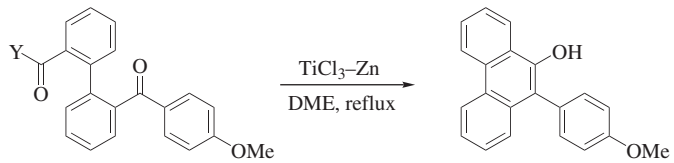


(Eq. 15)

Carboxylic Acids and Acid Halides. Only limited examples of the McMurry coupling of carboxylic acids and acyl halides are known. The $TiCl_4-Zn$ system-promoted intermolecular mixed-coupling of acetyl chlorides with benzophenone affords the corresponding ketones following acidic hydrolysis (Eq. 16).[134] The intramolecular reactions of benzoic acid and benzoic acid fluoride with the benzophenone moiety result in the formation of the corresponding phenols (Eq. 17).[137] It is suggested that the cleavage of the C–F bond in the latter reaction is the result of reductive elimination from the pinacolate intermediate during the coupling reaction.



(Eq. 16)

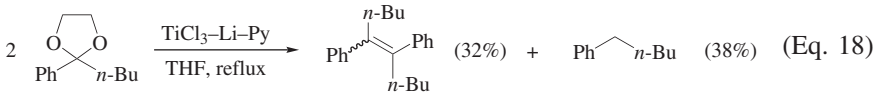


Y	Yield (%)
HO	86
F	90

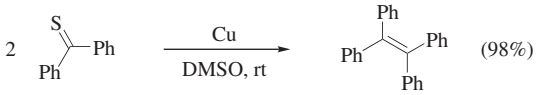
(Eq. 17)

Related Substrates. Benzylidene acetals are transformed into 1,2-diphenylethene derivatives under McMurry conditions. The yields are generally moderate due to the concomitant formation of arylalkanes (Eq. 18).[138] Treatment of

thiobenzophenone with copper powder in DMSO produces tetraphenylethylene (Eq. 19).[139] The desulfurizative coupling of thiobenzoylpiperidine and selenobenzoylpiperidine forming 1,2-dipiperidinostilbene is achieved with the Sm−SmI_2 system.[108]



(Eq. 18)

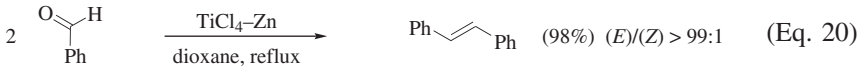


(Eq. 19)

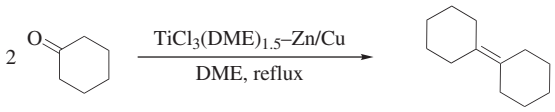
Mode of Coupling of Aldehydes and Ketones

Flexibility makes the McMurry coupling a useful method for the construction of a range of carbon skeletons. Except for intermolecular homocoupling, this process suffers from a narrow substrate scope and, particularly in intramolecular coupling and tandem cyclizations, the yields vary widely depending on the substitution of the substrates. The judicious choice of reaction conditions for a given mode of reaction is also of crucial importance for a successful McMurry coupling.

Homocoupling. Because of the highly oxophilic nature of titanium species, a range of aldehydes and ketones can be employed in homocoupling, which serves as a useful method for the preparation of symmetrical alkenes. Both aromatic and aliphatic cyclic and acyclic carbonyl compounds are good substrates for homocoupling reactions (Eqs. 20[3] and 21[140]).



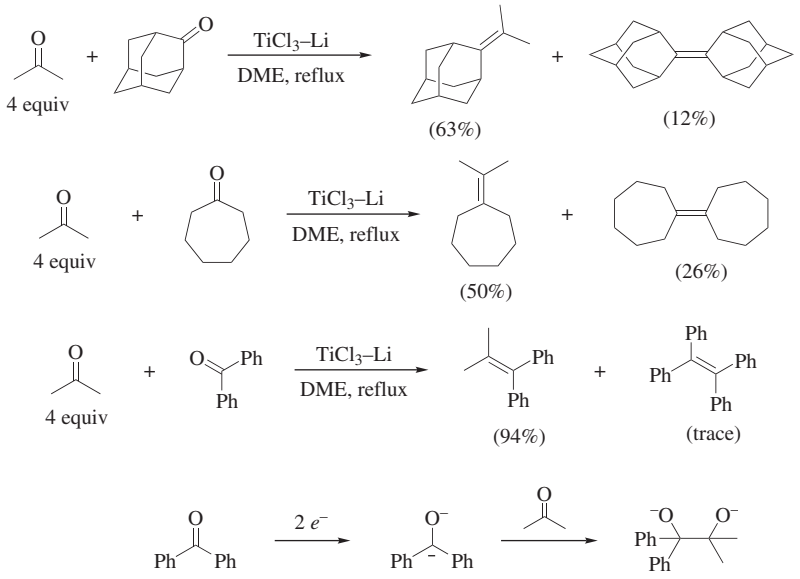
(Eq. 20)



(Eq. 21)

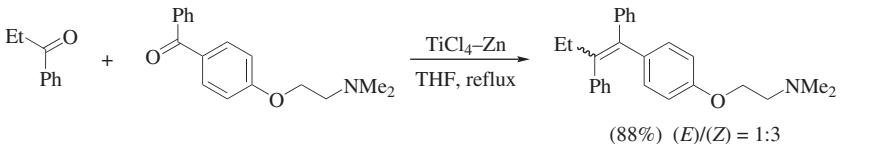
Mixed-Coupling. In general, the mixed-coupling of two carbonyl compounds produces a nearly statistical mixture of the mixed and two possible homocoupling products. Therefore, use of one of the coupling components in excess is often necessary to obtain reasonable yields of the mixed-coupling products. This approach is particularly useful when volatile and inexpensive ketones such as acetone are employed. For example, the mixed-coupling of adamantanone with excess acetone affords isopropylideneadamantane in good yield (Eq. 22).[27] The success of mixed-coupling is also dependent on the structure of the ketones. In the mixed-coupling of cycloheptanone, a considerable amount of homocoupling product is formed even when an excess amount of acetone is used (Eq. 23).[27] Conversely, a similar reaction of benzophenone predominantly gives the mixed-coupling product (Eq. 24).[27] The preferential formation of the

mixed-coupling product is explained by the formation of a dianion species by the two-electron reduction of benzophenone, whose reduction potential is 1.0–1.5 V less negative than that of acetone (Scheme 18).[141]

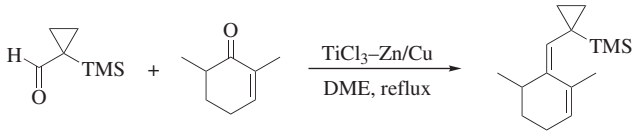


Scheme 18

Similar preferential formation of heterocoupled products is observed in the mixed-coupling of equimolar amounts of diaryl (Eq. 25)[142] or α,β-unsaturated ketones (Eq. 26)[143] with monoaryl ketones or their corresponding aliphatic counterparts. The success of these reactions is also attributable to the sufficiently different redox potentials of two coupling components.



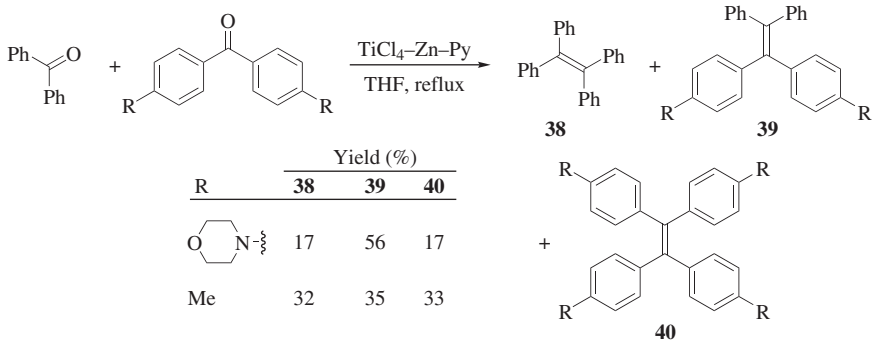
(Eq. 25)



(Eq. 26)

The preferential formation of mixed-coupling products is also observed when nitrogen- or oxygen-containing aryl or diaryl ketones are employed as one of the coupling components. Thus the reaction of benzophenone with an equimolar

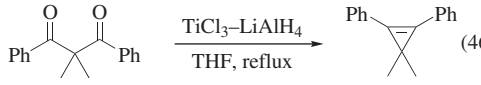
amount of 4,4′-dimorpholinobenzophenone yields the mixed-coupling product in a yield better than that expected from statistical probability whereas its reaction with 4,4′-dimethylbenzophenone affords no such selectivity as shown by the distribution of products **38**–**40** (Eq. 27).[144,145] It is believed that the strong affinity of the heteroatom substituents for the low-valent titanium surface is important for good selectivity.



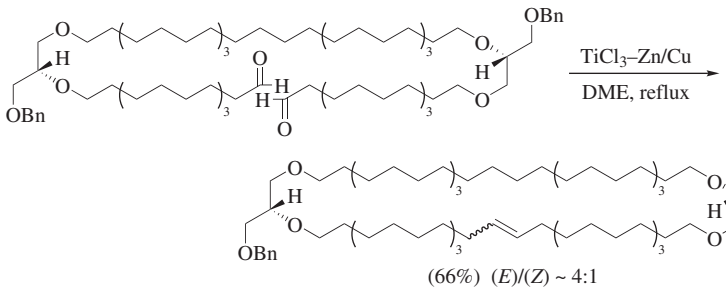
R	Yield (%) 38	39	40
O N-	17	56	17
Me	32	35	33

(Eq. 27)

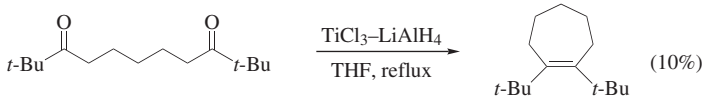
Intramolecular Coupling. A variety of intramolecular deoxygenative coupling reactions of aldehydes and ketones have been studied as useful methods for the construction of cyclic and macrocyclic compounds. Three (Eq. 28[146]) to 72-membered ring derivatives (Eq. 29[147]) have been synthesized to date. The McMurry coupling is particularly effective for the preparation of medium-size rings (Eqs. 30[148] and 31[61]).



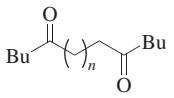
(Eq. 28)



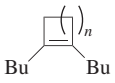
(Eq. 29)



(Eq. 30)



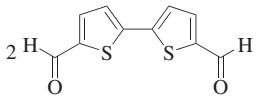
$TiCl_3$–Zn/Cu, DME, reflux



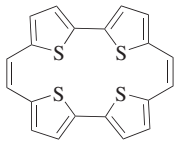
n	Yield (%)
5	67
6	68

(Eq. 31)

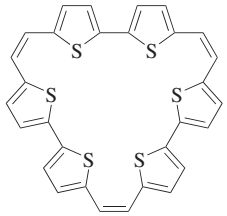
Tandem Cyclizations (Annulations). The tandem cyclization reaction consists of initial intermolecular coupling followed by subsequent intramolecular coupling. For the selective formation of cyclic dimers, a significant side reaction is the oligomerization of starting materials, as exemplified in Eq. 32.[149] In certain cases, the mode of the reaction is dependent on the distance between the two carbonyl groups. The exclusive formation of dimer **41** over intramolecular coupling product **42** is observed when the tether connecting the two 1′-acetonaphthone moieties contains one or two carbons, whereas the intramolecular coupling proceeds selectively if the carbon number is three (Eq. 33).[150]



$TiCl_4$–Zn–Py, THF/CH_2Cl_2, reflux

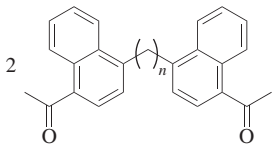


(10.5%) +



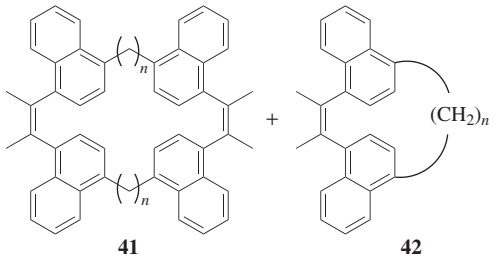
(13.6%)

(Eq. 32)



$TiCl_4$–Zn/Cu, DMF, reflux

(Eq. 33)

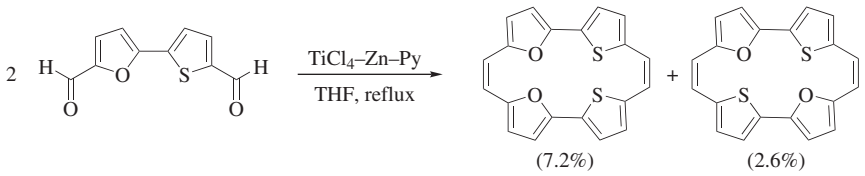


41 **42**

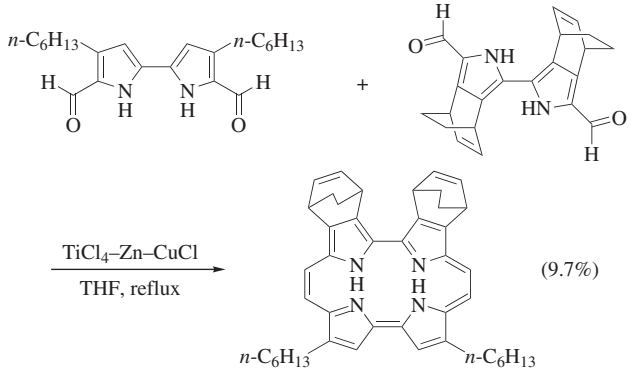
	Yield (%)	
n	**41**	**42**
1	64	—
2	40	—
3	trace	41

In the reaction of unsymmetrical dicarbonyl compounds, constitutional isomers should be formed (Eq. 34).[151] The tandem cyclization of two distinct dicarbonyl

compounds has also been investigated (Eq. 35).[152]



(Eq. 34)

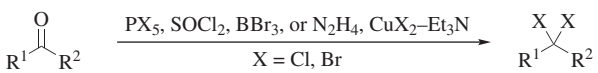


(Eq. 35)

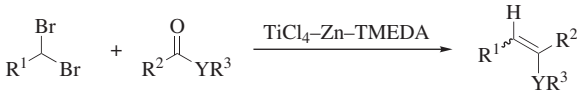
Related Reactions

Although the McMurry coupling is a versatile tool for the preparation of unsaturated compounds, several limitations arise in applying it to the mixed-coupling of two different carbonyl compounds. A major drawback is that the selective mixed-coupling between ketones and aldehydes is generally difficult to achieve in useful yields. The mixed-coupling of ketones or aldehydes with carboxylic acid derivatives is also largely restricted. Although the intramolecular coupling of carboxylic acid derivatives such as esters and amides is a useful route to heteroatom-substituted alkenes and heterocyclic compounds, only a limited number of examples of the intermolecular McMurry coupling using carboxylic acid derivatives as one of the coupling components are known (see Table 2D). In such cases, the low-valent titanium-promoted reactions of carbonyl compounds with various carbonyl equivalents such as *gem*-dihalides and thioacetals are useful complements to the mixed McMurry coupling.

Carbonyl Olefination with *gem*-Dihalides. Carbonyl compounds are transformed into *gem*-dihalides by using various reagents such as PX_5[153,154], $SOCl_2$[155,156], BBr_3[157], or $N_2H_4/CuX_2–Et_3N$[158]) (Scheme 19). The selective mixed-coupling of *gem*-dibromides with carbonyl compounds to furnish alkenes is successfully achieved using the $TiCl_4–Zn–TMEDA$ system (Eq. 36).[159]

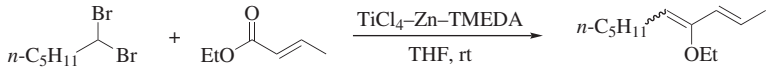


Scheme 19

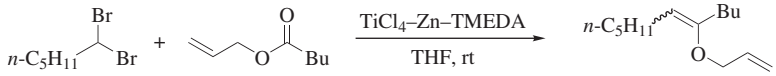


(Eq. 36)

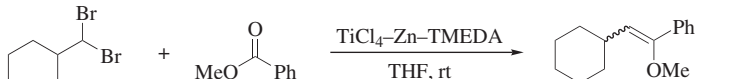
The advantage of this method is that it is applicable to the alkenylation of carboxylic acid derivatives such as esters, thioesters, and amides, as well as aldehydes and ketones (Eqs. 37–39,[160] 40,[161] and 41[162]). It is desirable to use pyrometallurgy-grade zinc that contains 0.04–0.07 mol % of lead based on zinc.[163]



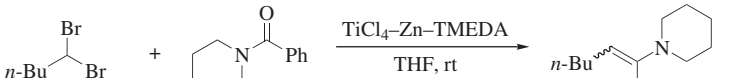
(90%) (*E*)/(*Z*) = 6:94 (Eq. 37)



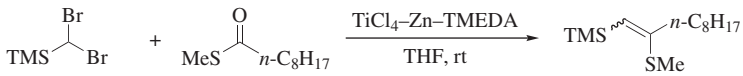
(52%) (*E*)/(*Z*) = 8:92 (Eq. 38)



(61%) (*E*)/(*Z*) = 10:90 (Eq. 39)

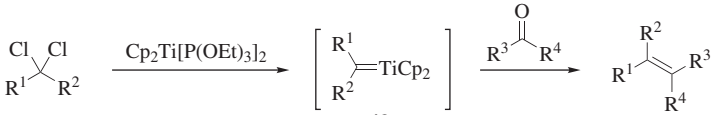


(80%) (*E*)/(*Z*) = 96:4 (Eq. 40)



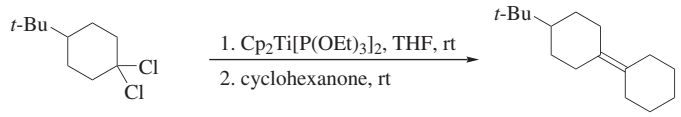
(80%) (*E*)/(*Z*) = 34:6 (Eq. 41)

An alternative method for the mixed-coupling of *gem*-dihalides with carbonyl compounds employs $Cp_2Ti[P(OEt)_3]_2$, which is prepared by the reduction of Cp_2TiCl_2 with magnesium in the presence of triethyl phosphite and 4 Å molecular sieves (Scheme 20). A variety of tetrasubstituted alkenes are obtained by the mixed-coupling between highly substituted *gem*-dichlorides and carbonyl compounds including aldehydes, ketones, esters, and lactones (Eqs. 42,[164] 43,[165] and 44[164]). The reaction is assumed to proceed via the formation of titanium carbene complexes **43**. Ketene equivalents, 1,1-dichloroalkenes, may be also employed in the mixed-coupling with aldehydes and ketones (Eqs. 45 and 46).[166]

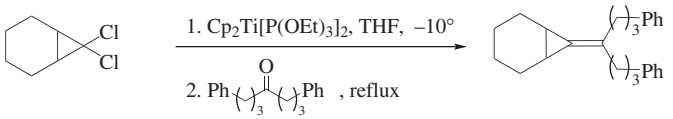


43

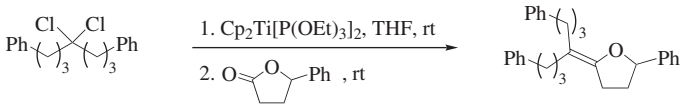
Scheme 20



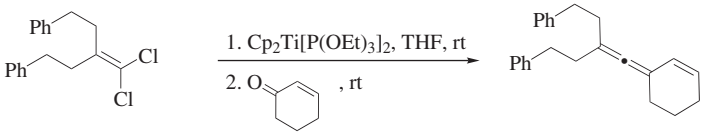
(73%) (Eq. 42)



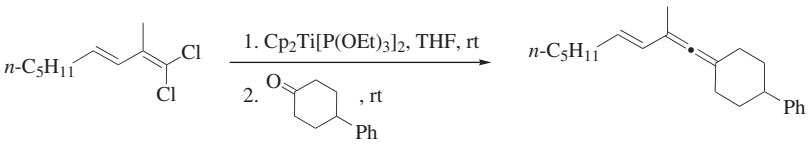
(64%) (Eq. 43)



(72%) (Eq. 44)



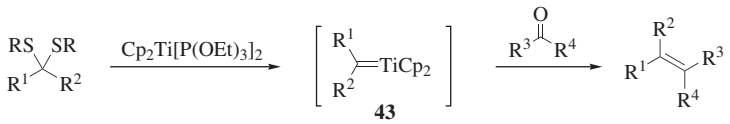
(70%) (Eq. 45)



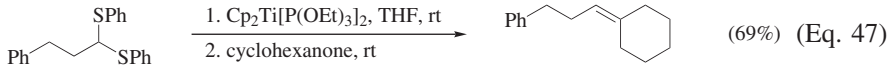
(60%)

(Eq. 46)

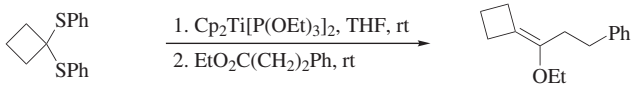
Carbonyl Olefination with Thioacetals. The titanocene(II)-promoted reaction of thioacetals with carbonyl compounds is also a good substitute for the McMurry coupling of two different carbonyl compounds. This reaction also proceeds by the formation of titanium carbene complexes **43** (Scheme 21).[167–169] Since thioacetals are readily prepared by the treatment of aldehydes and ketones with thiols in the presence of an appropriate acid catalyst and further derivatization of thioacetals, this method enjoys wide synthetic application (Eqs. 47,[170] 48,[171] 49,[170] 50,[172] and 51.[173] Although the mixed-coupling readily proceeds with diphenyl thioacetals of aldehydes, the reaction using thioketals produces alkenes only when thioketals of sterically less-congested ketones such as acetone and cyclobutanone are employed.



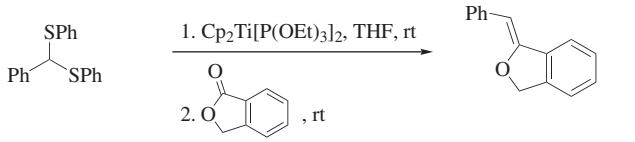
Scheme 21



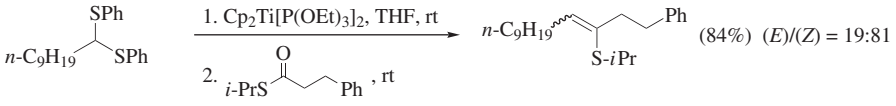
(Eq. 47)



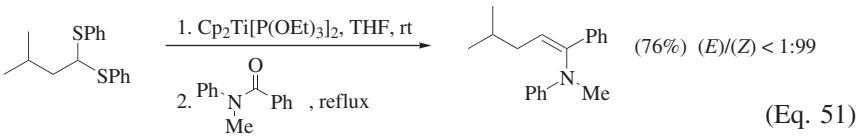
(Eq. 48)



(Eq. 49)

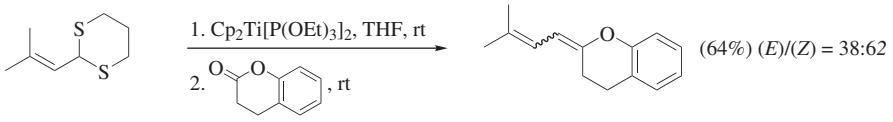


(Eq. 50)

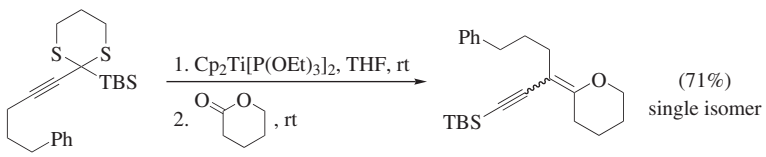


(Eq. 51)

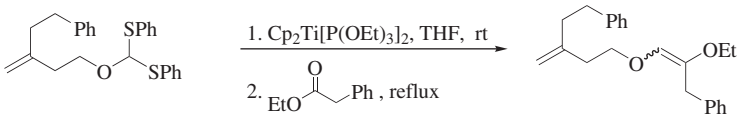
The reaction of thioacetals of unsaturated aldehydes with carbonyl compounds provides a method for the preparation of 1,3-dienes (Eq. 52).[170] Thioacetals of alkynyl silyl ketones may also be subjected to coupling with carbonyl compounds (Eq. 53).[174,175] Reactions using dithio- and trithio orthoesters may be regarded as a mixed-coupling of formic acid esters with carbonyl compounds (Eqs. 54[176] and 55[177]).



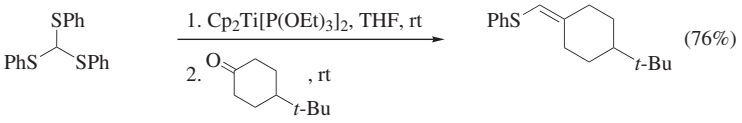
(Eq. 52)



(Eq. 53)

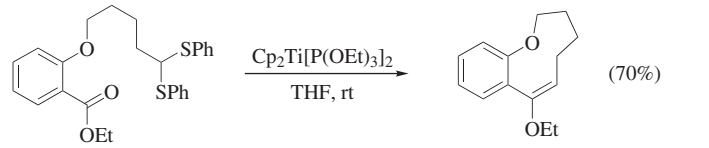


(Eq. 54)

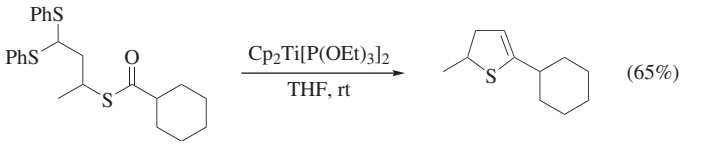


(Eq. 55)

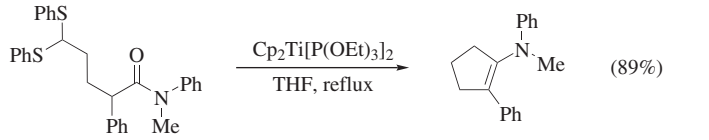
The titanocene(II)-promoted, intramolecular coupling between thioacetals and carboxylic acid derivatives furnishes unsaturated cyclic compounds. The reaction is applicable to the preparation of a variety of heterocyclic and heteroatom-substituted cyclic compounds with different ring sizes (Eqs. 56,[178] 57,[179] and 58[180]).



(Eq. 56)



(Eq. 57)



(Eq. 58)

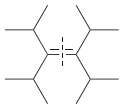
APPLICATIONS TO SYNTHESIS

Applications of the McMurry coupling include the preparation of sterically congested and strained alkenes that are otherwise difficult to prepare by conventional methods. Another synthetic use is for the preparation of theoretically interesting and structurally unique alkenes. These include polyenes, ethylene-bridged porphyrins, rigid stilbenes, and 1,2-(bis)metallocenylethenes. Intramolecular couplings of dicarbonyl compounds are used for the preparation of cyclophan-1-enes, dihydropyrroles and thiophenes, and condensed polyaromatics. Compounds bearing medium and large rings are also synthesized effectively by intramolecular coupling of dicarbonyl compounds. In this regard, construction of cyclic natural products with various ring sizes has been achieved. Tandem cyclizations have been employed to synthesize π-conjugate macrocycles such as ethylene-bridged cyclic bi- and ter-aryls and their heterocyclic analogues. Biologically

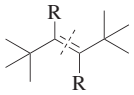
active triphenylethene derivatives such as tamoxifen (an antagonist of the estrogen receptor in breast tissue) and cyclooxygenase inhibitors are widely prepared by the mixed McMurry coupling.

Synthesis of Sterically Hindered and/or Strained Alkenes

In general, simple dialkyl ketones and cycloalkanones are converted into the corresponding alkenes in good to high yields by homocoupling with the low-valent titanium reagents. The homocoupling of sterically encumbered acyclic aliphatic ketones provides convenient access to strained tetrasubstituted alkenes, some of which are difficult to prepare by other methods. Thus, tetraisopropylethene (**44**) is obtained by the deoxygenative coupling of diisopropyl ketone using the $TiCl_3(DME)_{1.5}$–Zn/Cu system in 87% yield.[6] The homocoupling of *tert*-butyl methyl ketone[181] using the $TiCl_3$–Zn system and *tert*-butyl ethyl ketone[182] using the $TiCl_3$–$LiAlH_4$ system produces the corresponding alkene **45** with excellent (*E*)-selectivity. However, the preparation of the elusive tetra-*tert*-butylethene by the McMurry coupling has not yet been reported.

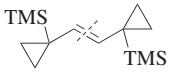


44 (87%)

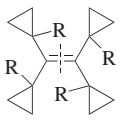


45
R = Me (65%), (*E*) only
R = Et (47%) (*E*)/(*Z*) = 12:1

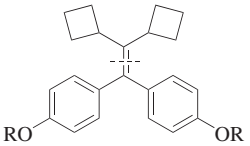
The McMurry coupling of aldehydes and ketones bearing strained small rings provides access to alkenes containing such rings. For example, the homocoupling of cyclopropyl aldehydes and ketones furnishes alkenes bearing cyclopropyl rings **46**[43] and **47**.[183,184] The dicyclobutyl ketone can be employed for the mixed-coupling the acetophenones to produce the dicyclobutylethenes **48**.[185]



46 (38%)

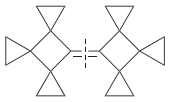


47
R = H (15%); R = Me (13%)

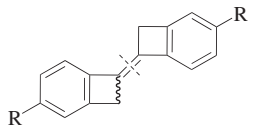


48
R = H (18%); R = Me (87%)

The McMurry coupling of strained cyclic ketones constitutes a convenient route to strained alkenes. The homocoupling of trispiro[2.0.2^4.0.2^7]decan-10-one furnishes the fully spirocyclopropanated bi(cyclobutylidene) **49**.[186] Similarly, benzocyclobutanones afford the bi(cyclobutylidenes) **50** as (*E*)/(*Z*) mixtures.[187,188] Cyclobutanone can also be applied to the mixed-coupling with 4,4′-methoxybenzophenone to give the corresponding alkene **51** in 87% yield.[189]

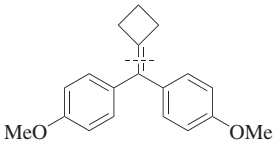


49 (28%)



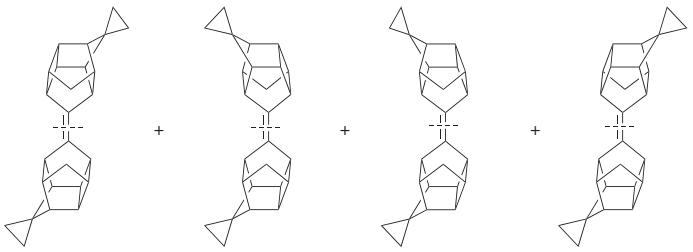
50

R = H (22%) (*E*)/(*Z*) = 1:1
R = Me (6%) (*E*)/(*Z*) = —



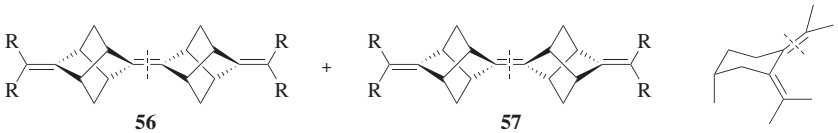
51 (87%)

The McMurry coupling is frequently employed for the preparation of sterically crowded alkenes having unique and/or unusual structures. The highly compact and often strained polycyclic cage hydrocarbons connected with carbon–carbon double bonds are prepared by the low-valent titanium-promoted deoxygenative coupling of polycyclic ketones.[190–193] These compounds are of interest as potential materials for high-energy/high-density fuels. Thus, the coupling of 4-(spirocyclopropyl)pentacyclo[5.4.0.0.^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one leads to an isomeric mixture of alkene dimers **52**–**55**.[191] The titanium-promoted deoxygenative coupling of 6-alkylidenetricyclo[3.3.0.0^{3,7}]octan-2-ones yields a mixture of the racemic (**56**) and meso isomers (**57**) of distella-2,2′,6,6′-trienes. These alkenes are considered as models for investigation of through-space interaction of isolated double bonds.[194,195] The highly twisted bis-exocyclic cisoid diene **58** is prepared by the coupling between acetone and (+)-pulegone.[196]



52 **53** **54** **55**

52 + **53** + **54** + **55** (46%)



56 **57**

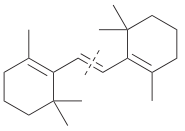
R = H, **56** + **57** (12%), **56**/**57** = 98:2
R = Me, **56** + **57** (1.3%), **56**/**57** = 98:2

58 (50%)

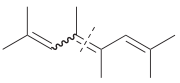
Synthesis of Highly Conjugated Molecules

The homocoupling of enals and enones is a useful method for the preparation of symmetrical acyclic polyenes. For example, aliphatic trienes **59**[110] and **60**[129] can be synthesized by the titanium-mediated coupling of the corresponding

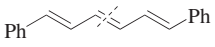
enal and enone respectively. Similarly, the trienes having phenyl ((*E*,*E*,*E*)-**61**)[121] and 1-azulenyl (**62**)[197] groups at either end are also obtained with the all (*E*)-configuration of the triene moiety. When the $NbCl_5$–Li system is used for the coupling of cinnamyl aldehyde, the triene **63** is formed with the (*E*,*Z*,*E*)-configuration.[96]



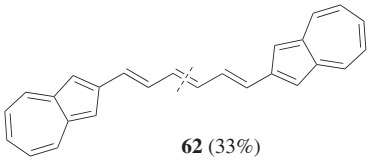
59 (94%)



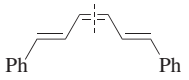
60 (*E*)-isomer (60%) + (*Z*)-isomer (25%)



61 (83%)

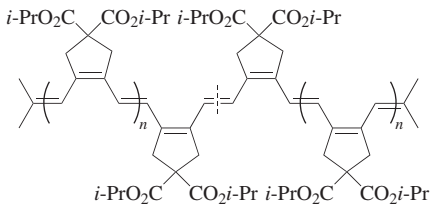


62 (33%)



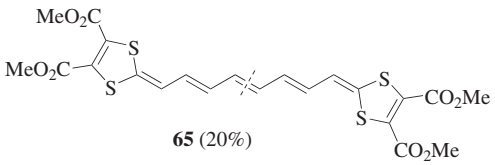
63 (55%)

The McMurry coupling can be applied to the preparation of a wide variety of symmetrical pentaenes and higher polyenes. The deoxygenative homocoupling of the corresponding dienal, tetraenal, and hexaenal yields the pentaene **64** ($n = 0$), nonaene **64** ($n = 1$), and tridecaene **64** ($n = 2$).[198] The polyenic analogue of tetrathiafulvalene **65**, in which two dithiole moieties are separated by a pentaene moiety, has also been synthesized.[199] Fully cross-conjugated pentaene **66** is obtained by the coupling of 4,4-dimethylcyclohexa-2,5-diene.[200]

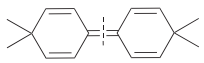


64

n	Yield (%)
0	61
1	82
2	25



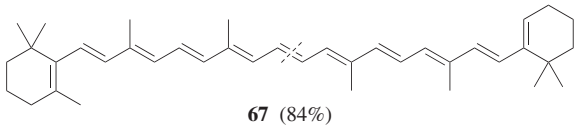
65 (20%)



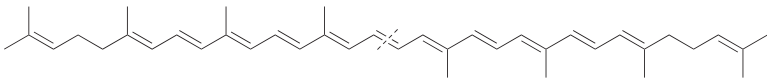
66 (97%)

β-Carotene (**67**) and lycopene (**68**) are synthesized by treatment of retinal and γ-retinal in 84 and 75% yields, respectively, with the $TiCl_3$–$LiAlH_4$ system.[201] Other titanium reagents such as $TiCl_4$–Zn,[202] titanium powder–TMSCl,[83] and

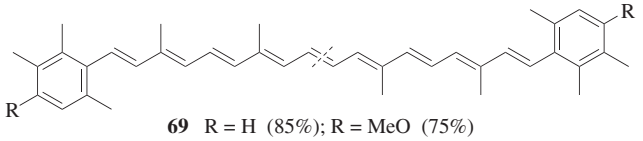
$TiCl_3$–Li[27] have been used for the β-carotene synthesis. Isorenieratenes (**69**) (carotenide light-harvesting pigments) are prepared in a similar manner.[203] The unsymmetrical heptaene **70** is synthesized as a stereoisomeric mixture by the mixed-coupling of the tetraenone and dienone using the $TiCl_4$–Zn system.[204]



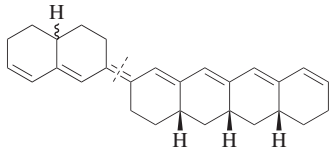
67 (84%)



68 (75%)



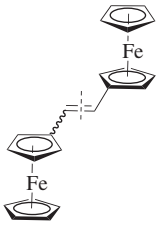
69 R = H (85%); R = MeO (75%)



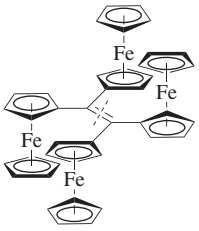
70 (40.8%)

Metallocenes and related structural units are tolerant to the McMurry coupling conditions. Thus, the homocoupling of metallocene-substituted aldehydes and ketones and related compounds provides access to symmetrical alkenes with metallocene units or η^5-cyclopentadienyl complexes. 1,2-Diferrocenylethene (**71**)[205] and tetraferrocenylethene (**72**)[206] can be prepared from ferrocenecarbaldehyde and diferrocenyl ketone, respectively, by low-valent titanium-promoted deoxygenation. The η^4-1,3-cyclobutadienyl-iron complex substituted ethene **73** is obtained with (*E*)-stereoselectivity by the $TiCl_3$–$LiAlH_4$ system-promoted homocoupling of the corresponding aldehyde.[207] The (*Z*)-alkenes **74** (R = Me) having a phosphacyclopentadienyl manganese unit are formed as *rac*/*meso* mixtures by the coupling of the corresponding methyl ketone (R = Me).[208] When the corresponding phenyl ketone is subjected to similar coupling conditions, the (*Z*)-isomer **74** (R = Ph) is selectively obtained. Cynchridene is transformed into (*E*)-1,2-bis[(η^5-cyclopentadienyl)dicarbonylnitrosylchromium]ethene (**75**) in a similar manner.[205]

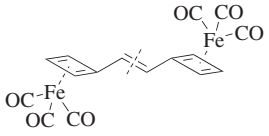
Alkenes bearing nitrogen-containing heteroaromatic units may be synthesized by McMurry methods. *N*-Alkoxycarbonylpyrrolecarbaldehyde undergoes deoxygenative coupling using the $TiCl_3$–Li system to give the di(2-pyrrolyl)ethenes **76**,[124] whereas the coupling of the *N*-unsubstituted 2-pyrrolecarbaldehyde under



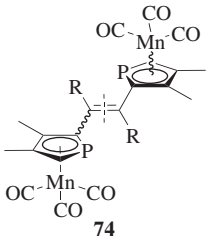
71 (25%) (*E*)/(*Z*) = 3.5:1



72 (75%)

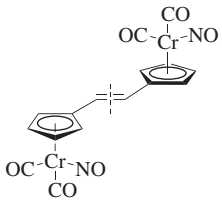


73 (56%)



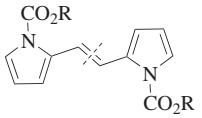
74

R = Me (*Z*)-*rac* (45%) + (*Z*)-*meso* (27%)
R = Ph (*E*)-*rac* (41%)



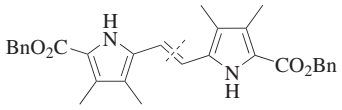
75 (36%)

similar conditions results in the formation of a complex mixture. Using 2-pyrrolecarbaldehydes bearing an ester group at the 5-position leads to di(*N*-unsubstituted pyrrolyl)ethenes **77**.[209,210] By contrast, the use of the corresponding 3-pyrrolecarbaldehydes lowers the yield of the alkenes.[211] Pyridine-substituted alkenes **78** and **79** are obtained by the homocoupling of 3-[212] or 4-pyridinecarbaldehyde, respectively.[124] Treatment of 4,5-diazafluorenone with the $TiCl_3$–$LiAlH_4$ system gives bis(4,5-diazafluorenylidene) (**80**), but a similar reaction of the 1,8-diaza-isomer fails to produce the corresponding alkene.[213]

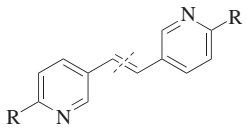


76

R = Me (50%); R = Et (30%)

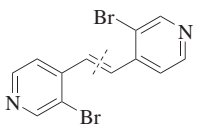


77 (81%)

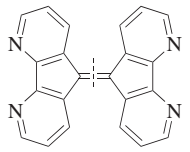


78

R = MeO (40%); R = MeS (30%)

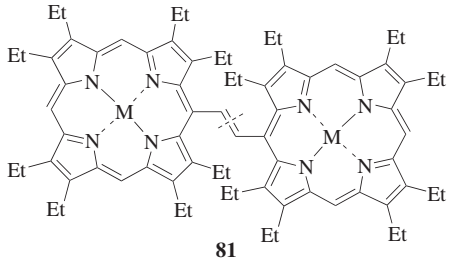


79 (30%)



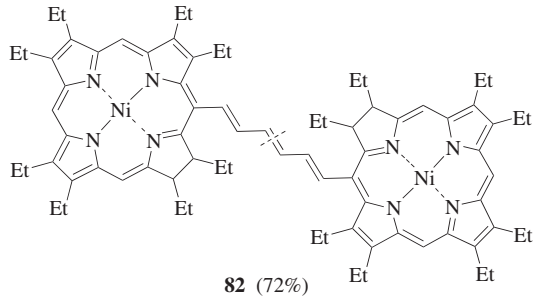
80 (20%)

Deoxygenative coupling can be applied to form porphyrin or chlorin dimers linked by conjugate systems. These compounds are of importance for understanding the processes of photosynthesis. Metalloporphyrin and chlorin substructures are compatible with the McMurry coupling conditions; thus, the ethene-bridged prophyrins **81**,[49,214] triene-bridged porphyrins **82**,[215] and their chlorin counterparts **83**[215] are obtained from the corresponding aldehydes. The reaction frequently provides (*E*)/(*Z*) mixtures with regard to the newly formed double bond and, in some cases, the (*Z*)-isomers predominate. This selectivity likely results from a strong π-π pre-association of the large conjugate system.

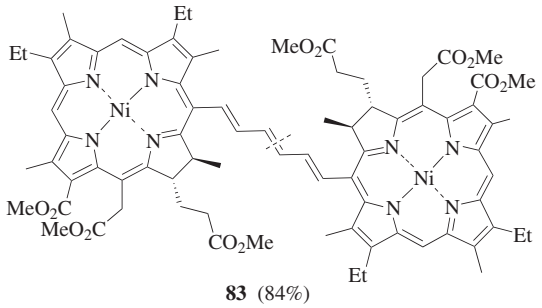


81

M	Yield (%)	(*E*)/(*Z*)
Ni	72	39:33
Cu	70	0:100

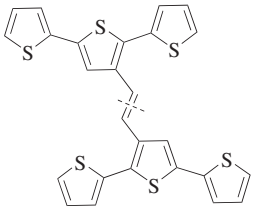


82 (72%)

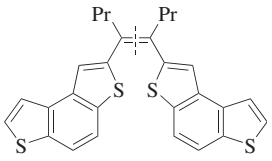


83 (84%)

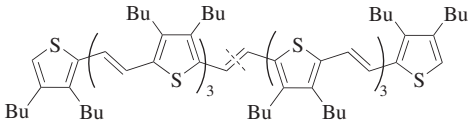
Aldehydes containing various thiophene substructures are amenable to the McMurry coupling. Such substructures include not only simple thiophenes but also oligothiophenes **84**,[216] condensed thiophenes **85**,[217] oligo(thienylenevinylene)s **86**,[218] or more complex structures.



84 (66%)



85 (*E*) isomer (7%)
+ (*Z*) isomer (93%)

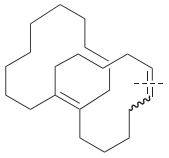


86 (52%)

Synthesis of Ring Compounds with Unique Structures

Cycloalkenes of ring sizes 3–16 and larger are prepared by the intramolecular McMurry coupling of dicarbonyl compounds. The yields of medium-sized and larger rings are remarkably high relative to other methods.[23] Construction of simple and saturated ring systems are described in the "Scope and Limitations" section. This section focuses on the preparation of rings with unique structures.

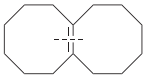
Bicyclic systems such as the chiral *trans*-fused (*R*)-(+)-[10.10]betweenanene **87**,[219] the bridgehead alkene **88**,[220] and bicyclo[6.6.0]tetradec-1(8)-ene (**89**)[221] have been prepared by the intramolecular McMurry coupling of the corresponding dicarbonyls. Compound **88**, which is difficult to prepare by other methods, has been converted to a cation in order to investigate a bent three-center, two-electron, C–H–C bond. The tricyclodecadiene **90** has also been synthesized for the study of the through-space interaction of two π systems, located perpendicular to each other.[222] These results demonstrate that this process is effective for the construction of medium rings with strained structures.



87 (44%)



88 (36%)

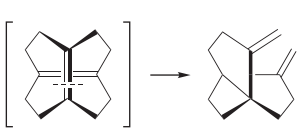


89 (72%)

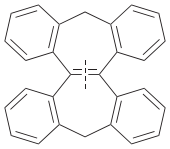


90 (13%)

The process has also been used to prepare the highly strained, unstable 7-membered cycloalkene **91**, which is transformed into the tricyclic diene **92** by a subsequent Cope rearrangement.[223] The transannular coupling also proceeds to give **93** if the two carbonyl groups are properly located.[224]



91 **92** (50%)

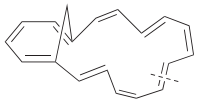


93 (81%)

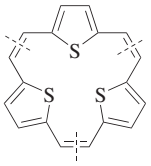
Another application of the McMurry coupling is the construction of cyclic conjugated polyenes. A variety of polyenes such as [12]-, [14]-, [18]-, [20]-, and [24]annulenes are obtained by intramolecular coupling. The bridged [14]annulene **94**[225] with a phenanthrene perimeter and [18]annulene **95**[226] are of interest in the context of aromaticity. Tandem cyclization is used for the preparation of sulfur-bridged [18]annulene **96**.[149]



94 (35–40%)



95 (12%)

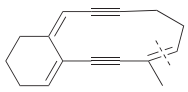


96 (38%)

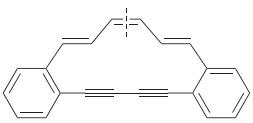
Strained cyclic enynes are analogously prepared from the corresponding dicarbonyl compounds. Thus, cyclo-1,3-dien-5-ynes **97** with ring sizes of 10–14 are synthesized by the deoxygenative cyclization of α,ω-dialdehydes.[227] These are transformed into benzocycloalkanes by thermal isomerization. The bicyclotriendiyne **98** is prepared as a model of a chromophore of the anti-tumor antibiotic neocarzinostatin by the cyclization of the dienediyne keto aldehyde.[228] The cyclotrienediyne **99** and its higher vinylogues, the bisdehydrodibenzo[16]-, [18]-, [20]-, and [22]annulenes, are similarly prepared; their yields decrease from 27 to 4% with increasing ring size.[229]



97 (5–44%) n = 4–8



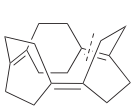
98 (47%)



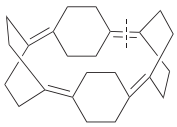
99 (27%)

Other ring compounds with novel structures include triene **100**[230] and tetraene **101**,[231] in which six-membered rings are connected with C–C double bonds at the C1 and C4 positions. These compounds are prepared from the corresponding diketones. Compound **101** acts as an eight-electron square-planar ligand to form a complex with Ag(I). $[6.8]_3$Cyclacene **102** is a hoop-shaped molecule consisting

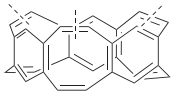
of annulated unsaturated rings and is synthesized by the 3-fold intramolecular ring closure of the hexaaldehyde.[232]



100 (24%)



101 (90%)

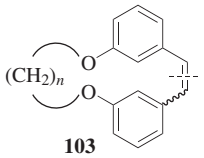


102 (8%)

Synthesis of Cyclophanes, Helicenes, and Related Compounds

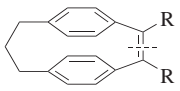
The low-valent titanium-promoted intramolecular cyclization of tethered bis(aromatic carbonyl compounds) is employed for the preparation of [2.*n*]cyclophan-1-enes in which each aromatic ring is connected to the other by an ethylene bridge. A variety of *o*-, *m*-, and *p*-cyclophan-1-enes are prepared from bis(arenecarbaldehydes) and bis(aryl ketones) having various aliphatic chain tethers such as oligo(methylene) and oligo(ethylene oxide). The geometry of the double bond formed is dependent on the length of the tethers. For example, the (*Z*)-isomer of metacyclophane **103** ($n = 3$) with a trimethylene chain predominates, whereas the (*E*)-isomer **103** ($n = 6$) with a hexamethylene chain is formed preferentially.[233] The highly strained paracyclophan-1-enes **104** can be synthesized by the intramolecular cyclization of trimethylene-tethered alkanophenones in good yields by slow addition of the diketones to a large excess of the titanium reagent.[234] The McMurry coupling of 4,13-dibenzoyl[2.2]paracyclophane provides 4,13-(α,α′-stilbeno)[2.2]paracyclophane (**105**), a triply bridged cyclophane, in good yield.[235]

Preparation of [2.*n*]cyclophan-1-enes with tethers containing aromatic rings is achieved by the intramolecular McMurry coupling of dicarbonyl compounds. Thus, the stilbenoprismand **106**, a new class of polyaromatic receptors with a Δ-shaped cavity, is prepared by the coupling of the corresponding diketone.[236] Bis(benzaldehydes) linked with an enantiomerically pure (*S*)-1,1′-bi-2-naphthol unit at the *ortho, meta*, and *para* positions are converted to the chiral receptors [2,n]cyclophan-1-ene **107** when subjected to the McMurry coupling.[237]



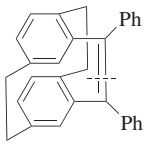
103

n	Yield (%)	(*E*)/(*Z*)
3	65	0:100
6	95	90:10

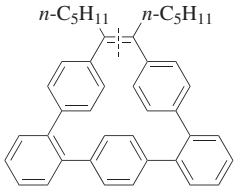


104

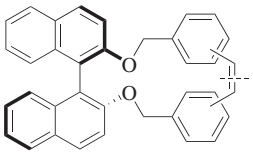
R	Yield (%)
Me	82
Et	60



105 (79%)



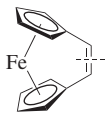
106 (93%)



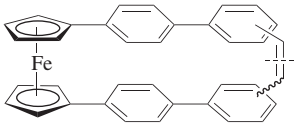
107

	Yield (%)
ortho	52
meta	62
para	15

The vinylene-bridged *ansa*-ferrocene **108** is prepared by slow addition of 1,1′-ferrocenedicarbaldehyde to the $TiCl_3$–Zn/Cu system.[238] The intramolecular reductive coupling of *o*-, *m*-, and *p*-benzaldehydes connected by a ferrocene-containing linker leads to the biphenylenevinylene-bridged ferrocenophanes **109**.[239] The (*E*)/(*Z*) ratios of the double bonds formed are dependent on the position of the formyl group.



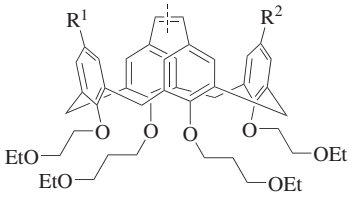
108 (44%)



109

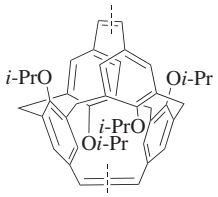
	Yield (%)	(*E*)/(*Z*)
ortho	59	34:35
meta	28	100:0
para	32	0:100

The intramolecular reductive coupling of bis(arenecarbaldeydes) described above can be applied to calix[4]arenes bearing formyl groups at the appropriate positions to produce intramolecularly double-bond-bridged calix[4]arenes. Thus, the ethylene-bridged calix[4]arenes **110** are obtained with (*E*)-stereoselectivity from the calix[4]arenes bearing two formyl substituents on the opposite benzene rings.[240] When the 1,3-alternate *p*-formylcalix[4]arene is employed, two-fold cyclization takes place between two formyl groups at the opposite side of the molecule to give the caged calix[4]arene **111**.[241] The reaction of calix[4]arenes having two benzaldehyde moieties connected by an ethylene oxide linker yields the stilbene-bridged calix[4]arenes **112**;[242] the configuration of the alkene is dependent on the substitution pattern of formyl groups.

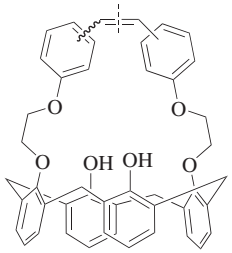


110

R^1, R^2 = H, Me, *t*-Bu (15–30%)



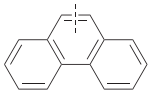
111 (25%)



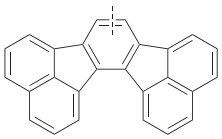
112

	Yield (%)	
	(*E*)-**112**	(*Z*)-**112**
ortho	15	62
meta	37	37
para	—	87

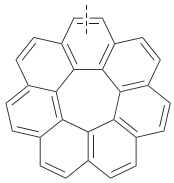
The intramolecular cyclization of 2,2′-diformylbiaryl derivatives and related compounds is employed for the preparation of various condensed polycyclic aromatic compounds. Phenanthrene (**113**)[243] and acenaphtho[1,2-j]fluoranthene (**114**)[243] are representative examples. The analogous compound, [7]circulene (**115**), in which seven benzene rings are circularly arranged in a strained saddle shape, is synthesized in a similar manner.[244] The aromatic ring construction by the intramolecular McMurry coupling has been also applied to the preparation of helicenes. Thus, the enantiomerically enriched [7]thiahelicenes **116**[245] are synthesized from the corresponding enantiomerically pure biaryl dialdehydes in good yields. This method is a good alternative to the oxidative photocyclization of a stilbene-type precursor. Similarly, the thiophene-based [7]helicene **117** is obtained from an axially chiral biaryl diketone.[246] In both cases, a stereochemical correlation between the (*R*) axial chirality of the biaryl dicarbonyl compounds and the (*M*) helical chirality of the helicenes is observed.



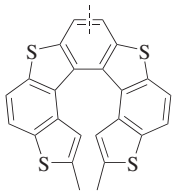
113 (67%)



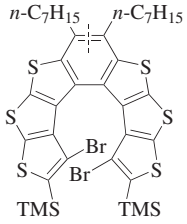
114 (56%)



115 (35%)



(*M*)-(–)-**116** (53%), er >99.5:0.5
(*P*)-(+)-**116** (52%), er >99.5:0.5



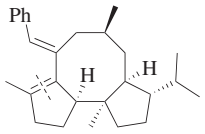
(*M*)-(–)-**117** (28%), er 87.0:13.0
(*P*)-(+)-**117** (17–63%), er 75:25 to 95:5

Total Synthesis of Natural Products

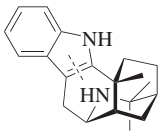
Many synthetic applications of the McMurry coupling in total syntheses of natural and related products have appeared as the process is efficient in constructing various macrocycles. Furthermore, the reaction can be carried out successfully in the presence of a variety of functional groups by the judicious choice of the reagents and reaction conditions.

The low-valent titanium-promoted intramolecular cyclization has been applied to the total synthesis of five-membered-ring natural products such as (±)-strigol[247], (±)-hirsutene[248], (±)-7,8-epoxy-4-basmen-6-one (**118**)[249] and (±)-araneosene.[250] (+)-Aristoteline (**119**), a naturally occurring indole alkaloid, can also be synthesized using this system.[7] Bicyclic six-membered-ring formation by the

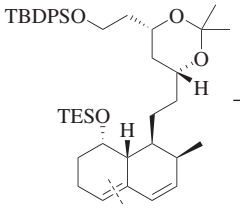
intramolecular coupling of dicarbonyl compounds is employed for the total synthesis of (+)-compactin (**120**)[251], (+)-mevinolin[251], and (+)-ipalbidine,[252] and the tricyclic ring formation leads to a hybrid analog of huperzine A and B.[253] A six-membered ring in spirocyclic (±)-α-chamigrene,[254] tricyclic (±)-isokhusimone (**121**),[255,256] and the steroid skeleton of 9(11)-dihydroestrone methyl ether (**122**)[257,258] are constructed by a similar cyclization. Seven-membered-ring formation is employed in the synthesis of bicyclic (±)-clavukerin A and isoclavukerin A.[259] The tetracyclic diterpene kempene-2 (**123**) is synthesized by the cyclization of a dialdehyde to form a seven-membered ring at the final stage.[260] A tricyclic system involving an eight-membered ring is constructed in the syntheses of the ABC system of taxol,[261] taxane triene **124**, which comprises the full and stereochemically correct carbon framework of natural taxusin,[262] and the ceroplastin nucleus.[263,264] The ten-membered-ring sesquiterpenes, bicyclogermacrene (**125**)[265] and its stereoisomer, lepidozene,[265,266] dihydrogermacrene,[267] and helminthogermacrene[268] are prepared through the low-valent titanium-promoted cyclization. Eleven-membered ring formation by the intramolecular coupling of keto aldehydes is involved in the syntheses of the tricyclic trinervitane skeleton **126**[269] and humulene (**127**).[270] Twelve-membered-ring formation is applied to the total synthesis of verticillene (**128**), a biogenetic precursor of taxane alkaloids.[271,272] The intramolecular cyclization of keto aldehydes for 14-membered-ring formation is used often in the synthesis of many cembrenoide diterpenes such as (±)-cembrene-A,[273] cembrene-C (**129**),[274–276] (+)-3,4-epoxycembrene-A,[277,278] (+)-11,12-epoxycembrene-C[279] and its 11,12-dehydro derivative,[280] (−)-[281] and (±)-[282] 13-hydroxyneocembrene (**130**), (−)-13-hydroxy-11,12-epoxy-neocembrene (**131**),[283] (±)-sarcophytols A and B,[284] (±)-sarcophytol A benzyl ether,[285] (±)-isosarcophytols A,[280] and (±)-crassin acetate methyl ether.[286] Synthesis of the marine cembranoid, (−)-1,3,11-cemratrien-6-ones,[287] preverecynarmin,[288] 14-deoxycrassin,[289] pseudoplexaural (**132**),[289] lepidozene,[267] and bicyclogermacrene[267] have been achieved via 14-membered-ring construction by the McMurry coupling. Syntheses of diterpene flexibilene (**133**),[290] sesterterpene terpestacin,[291] and its ring system[292] involve the formation of 15-membered rings. The macrocyclization of ansa-bridged benzofuranquinone (**134**) with an 18-membered ring is performed in the total synthesis of (±)-tridentoquinone.[293]



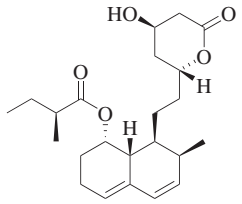
(±)-7,8-epoxy-4-basmen-6-one (**118**)
(73%)



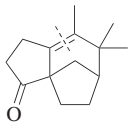
(+)-aristoteline (**119**)
(75%)



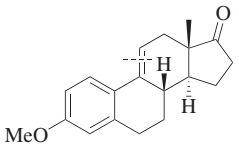
(85%)



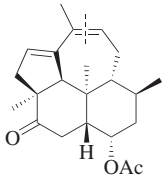
(+)-compactin (**120**)



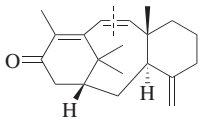
(±)-isokhusimone (**121**)
(57%)



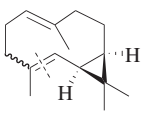
(+)-9(11)-dihydroestrone methyl ether (**122**)
(56%)



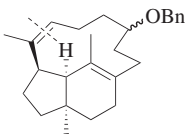
kempene-2 (**123**)
(32%)



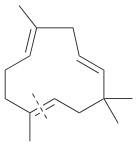
taxane triene (**124**)
(20%)



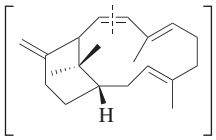
bicyclogermacrene (**125**)
(61%) (*E*)/(*Z*) = 80:20

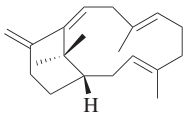


tricyclic trinervitane skeleton (**126**)
(11%)

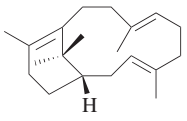


humulene (**127**)
(60%)

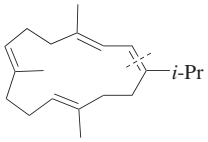




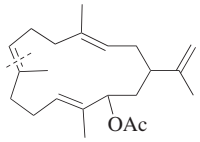
(23.5%)



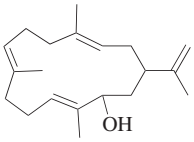
verticillene (**128**)



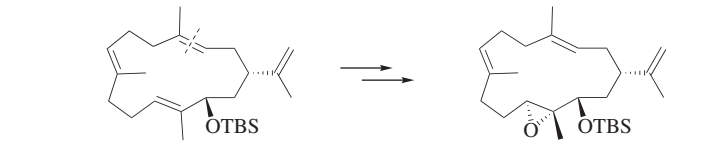
cembrene-C (**129**)
(72%)



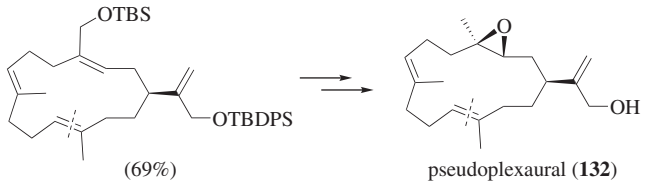
(38%)



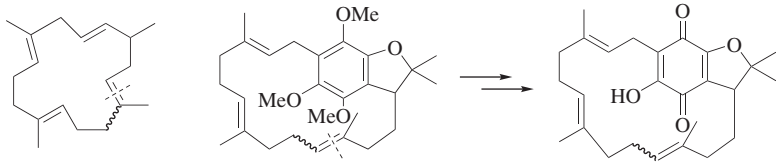
(±)-13-hydroxyneocembrene (**130**)



(81%) (–)-13-hydroxy-11,12-epoxy-neocembrene (**131**)



(69%) pseudoplexaural (**132**)



flexibilene (**133**) (79%) (*E*)/(*Z*) = 2:1 **134** (11%) (±)-tridentoquinone

COMPARISON WITH OTHER METHODS

The McMurry coupling suffers some drawbacks compared to other direct carbonyl olefination reactions described below. For example, it generally affords statistical mixtures of homo- and mixed-coupling products in the intermolecular coupling of two different carbonyl compounds and tends to result in the formation of stereoisomeric mixtures of alkenes. Although some of the following direct deoxygenative olefination procedures should be considered in such cases, the simplicity of the experimental procedure, without pre-formation of any organometallic reagents, is an attractive feature of the McMurry coupling.

Wittig and Related Reactions

The Wittig reaction is perhaps the most widely used method for the direct transformation of carbonyl compounds to alkenes (Scheme 22).[294] One of its advantages is that the configuration of the olefination products can be controlled by careful selection of the phosphorus reagent and reaction conditions, especially in the case of the preparation of 1,2-disubstituted ethenes. The Horner–Wadsworth–Emmons reaction using α-carbanions of phosphonates (Scheme 23)[295] and the Horner–Wittig reaction using phosphine oxide anions are also powerful methods for carbonyl olefination. These reactions using phosphorous-based reagents, however, still suffer several disadvantages. First, unlike the McMurry coupling, they are seriously affected by steric hindrance and the preparation of tetrasubstituted alkenes using phosphorus-based reagents is virtually impossible. Second, the Wittig-type reactions are generally not effective for the olefination of carboxylic acid derivatives.

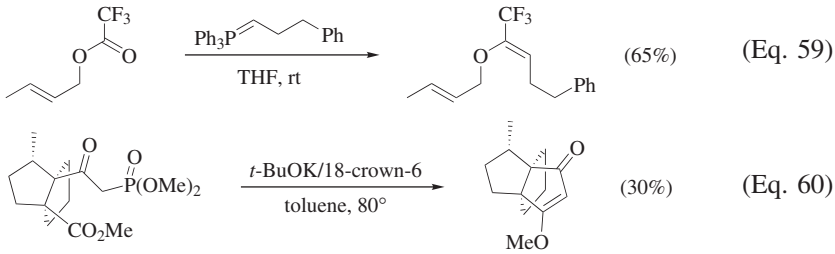
However, these so-called "non-classical Wittig reactions"[296] include the intermolecular olefination of electron-deficient esters and intramolecular olefination leading to the formation of certain cyclic compounds. Some examples are shown in Eqs. 59[297] and 60.[298]



Scheme 22



Scheme 23



(65%) (Eq. 59)

(30%) (Eq. 60)

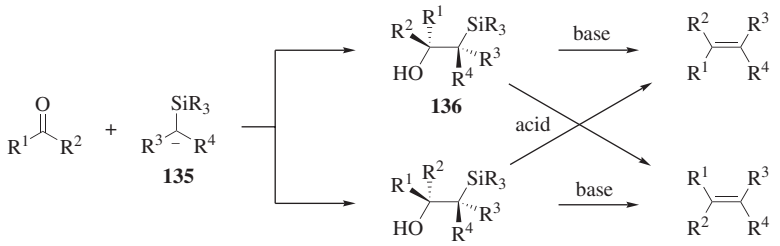
Peterson Olefination

The Peterson olefination consists of the addition of α-silyl carbanions **135** to carbonyl compounds and the subsequent elimination of silyloxide anions from the resulting β-hydroxyalkylsilanes **136** (Scheme 24).[299,300] The silanes **136** are usually isolated as mixtures of the two possible diastereomers by the protonation of the addition products when carbanions without an anion-stabilizing group are employed. The most striking feature of the Peterson olefination is that the two diastereomeric adducts **136** can be separated and the desired stereoisomers of alkenes can be obtained from either of the diastereomers depending on the reaction conditions employed for the elimination. Despite several characteristic features of the Peterson olefination, there remain some difficulties in terms of availability of adequate α-silyl carbanions and sensitivity to steric constraints.

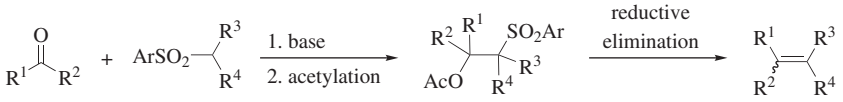
Julia–Lythgoe and Julia–Kocienski Reactions[301–305]

The Julia reaction (also known as the Julia–Lythgoe reaction) involves two separate steps: an addition of the α-carbanion of an aryl sulfone to a carbonyl compound and the reductive elimination of the resulting β-hydroxy sulfone (Scheme 25).[304]

The so-called modified Julia reaction (also known as the Julia–Kocienski reaction) is, in contrast, carried out in one pot and employed for the construction of a range of biologically active natural products as a tool for direct olefination

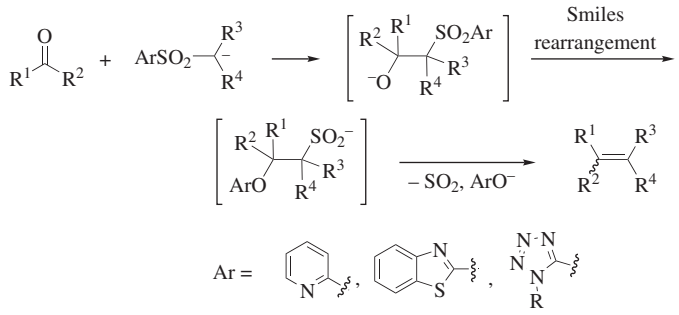


Scheme 24



Scheme 25

of aldehydes. The reaction consists of the addition of the α-anion of a heterocyclic sulfone to an aldehyde followed by Smiles rearrangement of the resulting β-alkoxysulfone and subsequent degradation of the sulfinate salt (Scheme 26).[304] The stereochemical course of the transformation is dependent on the nature of the heterocyclic moiety of the sulfone, the counter cation, and the reaction conditions. Generally (*E*)-alkenes predominate and high stereoselectivity is observed in certain cases. Excellent functional group compatibility is the synthetic advantage of the modified Julia reaction. Its major disadvantage over the McMurry coupling is its inapplicability to the preparation of highly sterically congested olefins.



Scheme 26

Carbonyl Olefination with Metal Carbene Complexes and Related Reactions

High-valent early transition-metal carbene complexes **137** possess ylide-like reactivity towards carbonyl compounds (Scheme 27).[167] Schrock first reported

that niobium and tantalum carbene complexes react with carbonyl compounds, including carboxylic acid derivatives, to produce the corresponding alkenes.[306] Shortly thereafter, synthetically useful Tebbe and related titanium-based reagents were developed for the generation of methylidenetitanocenes, which olefinate a variety of carbonyl compounds to give terminal olefins.[307] Although the olefination reactions of aldehydes, ketones, and carboxylic acid derivatives have been developed using alkylidenetitanocenes prepared from dialkyltitanocene,[308,309] inaccessibility of the carbene complexes bearing a β-hydrogen has limited their use. Development of the preparation of a range of titanium carbene complexes by the reductive titanation of thioacetals and related compounds with the titanocene(II) species $Cp_2Ti[P(OEt)_3]_2$, however, has enabled the wide use of titanium carbene complexes for carbonyl olefination (see "Scope and Limitations" section).



Scheme 27

Several dimetallic reagents are employed for the deoxygenative transformation of carbonyl compounds to alkenes. The *gem*-dizinc reagent, generated by the $PbCl_2$-catalyzed reduction of CH_2I_2 with Zn or the CH_2X_2–Zn–$TiCl_4$ system transforms aldehydes, ketones, and esters into olefins in the presence of appropriate additives.[159] The organometallic reagents generated from the $RCHBr_2$–Zn–$TiCl_4$–TMEDA system are employed for the olefination of various carboxylic acid derivatives (see "Scope and Limitations" section). A synthetic advantage of these reactions is their applicability to the olefination of carboxylic acid derivatives.

The organochromium reagents generated by the reaction of $RCHBr_2$ with $CrCl_2$ transforms aldehydes to (*E*)-1,2-disubstituted ethenes with high stereoselectivity.[310] A marked advantage of this carbonyl olefination over the McMurry coupling is that the chromium reagents show high chemoselectivity toward aldehydes, and can be carried out in the presence of keto and ester functionalities.

EXPERIMENTAL CONDITIONS

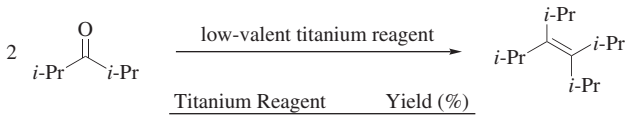
Preparation of Coupling Reagents: Stepwise vs One-pot Procedures

Since the first discovery of the deoxygenative coupling of carbonyl compounds, two types of procedures have been employed. A general procedure involving a stepwise sequence (formation of the reagent and then McMurry coupling) has been used in the coupling reaction using a variety of low-valent titanium species.[4,23] When highly reactive reducing agents, such as alkali metals or metal hydrides, are used for the generation of the low-valent titanium reagents, the stepwise procedure must be adopted. When the functional groups

present on the carbonyl compound are compatible with zinc as the reducing agent, a one-pot reaction involving the simple mixing of the titanium source, zinc, and the carbonyl compound can be performed.[3] This procedure can be used for the intramolecular coupling of oxo amides leading to the formation of indoles (so called "instant method").[7] The intramolecular McMurry coupling generally requires high-dilution conditions and slow addition of the substrate to avoid oligomerization. By contrast, the formation of heterocycles by the "instant method" does not require such special care. This protocol is also effectively employed for the intermolecular coupling of aldehydes.[241]

General Comments for the Preferred Conditions

Coupling Reagent. A variety of reagents have been developed for the McMurry coupling as described in the "Scope and Limitations" section. The choice of an appropriate reagent is crucial to obtain good yields of the desired products because different low-valent titanium species are formed depending on the particular titanium source, reducing agent, and conditions for its preparation. The $TiCl_3(DME)_{1.5}$–Zn/Cu system in DME seems to be the most versatile and reproducible reagent for both the inter- and intramolecular McMurry coupling (Scheme 28).[6,27] The $TiCl_4$–Zn–Py system and $TiCl_3$–C_8K system are also efficient for the coupling of a range of aldehydes and ketones.



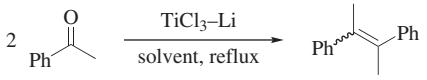
Titanium Reagent	Yield (%)
$TiCl_3$–$LiAlH_4$	12
$TiCl_3$–Zn/Cu	37
$TiCl_3$–K	37
$TiCL_3(DME)_{1.5}$–Zn/Cu	87

Scheme 28

Other reagents may be preferable depending on the carbonyl substrates. For example, the $TiCl_3$–$LiAlH_4$ system is employed for the oxo ester coupling, and the $TiCl_3$–Zn system is employed for the coupling of oxo amides through the "instant method."

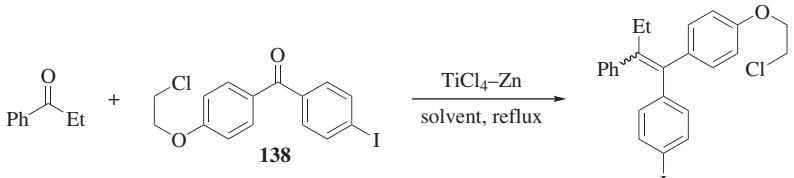
Solvent. Although the solvent-free McMurry coupling of benzophenone derivatives using the $TiCl_4$–Zn system has been reported,[311] the coupling is generally performed in ethereal solvents such as THF, DME, or 1,4-dioxane. The choice of a solvent is important to obtain good yields and selectivities. In several cases, THF and DME show different solvent effects. In the homocoupling of acetophenone with the $TiCl_3$–Li system, the reaction performed in DME preferentially furnishes the (*E*)-alkene whereas the (*Z*)-alkene predominates when THF is used (Scheme 29).[312] For the mixed-coupling of propiophenone

with benzophenone **138**, 1,4-dioxane is the solvent of choice to obtain the (*E*)-isomer in good yield (Scheme 30).[51] When 1,4-dioxane is replaced by THF, the (*Z*)-isomer slightly predominates.



Solvent	Yield (%)	(*E*)/(*Z*)
DME	92	83:9
THF	89	25:64

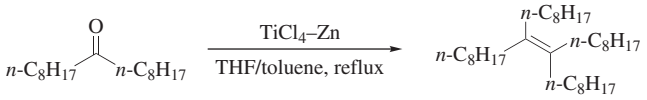
Scheme 29



Solvent	Yield (%)	(*E*)/(*Z*)
DME	35	1.3:1
THF	—	1:1.19
1,4-dioxane	56.5	3.9:1

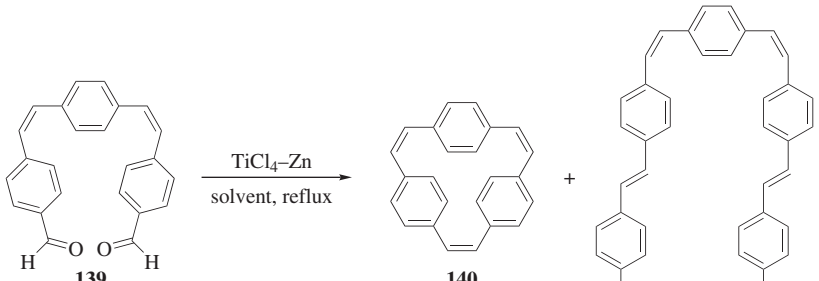
Scheme 30

Several reports describe the use of toluene as a co-solvent in the McMurry coupling. Although the preparation of 9,10-dioctyl-9-octadecene from dioctyl ketone could be achieved with difficulty and in low yields by the common variants of the McMurry coupling, the use of THF/toluene mixtures in the $TiCl_4$–Zn-promoted coupling affords the alkene in good yield (Eq. 61).[313] The combined use of toluene also affects the mode of intramolecular coupling. The deoxygenative cyclization of the dialdehyde **139** with the $TiCl_4$–Zn/Cu system carried out in DME produces the monomer **140** as a major product along with the dimer **141** as a mixture of stereoisomers (Scheme 31).[314] The dimer **141**, by contrast, is formed as a pure (*Z*,*Z*,*E*)-isomer by the reaction in a 1:1 mixture of DME and toluene.



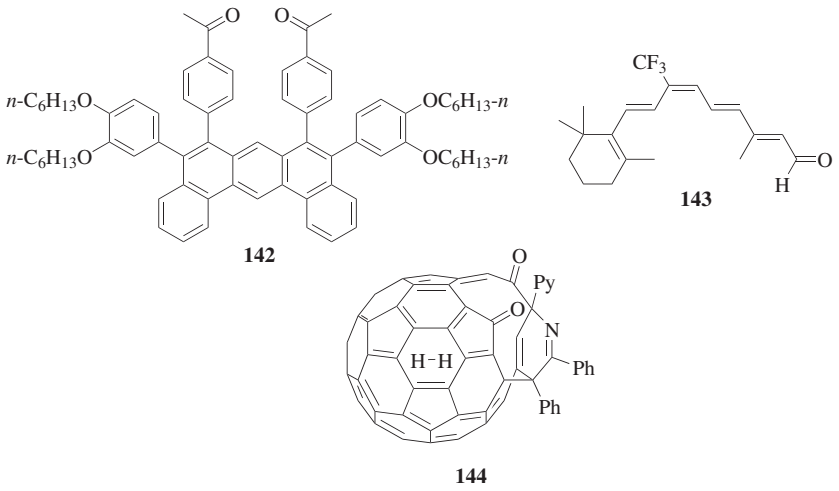
(Eq. 61)

Depending on the solubility of the substrates, the McMurry coupling may be carried out in mixed solvents. For example, THF/CH_2Cl_2 mixtures are employed for the $TiCl_4$–Zn promoted reaction of polyaromatic diketone **142**[315] and trifluoromethyl-substituted conjugated polyenal **143**.[122] THF/*o*-dichlorobenzene mixtures are employed for the intramolecular coupling of the fullerene derivative **144** encapsulating molecular hydrogen.[316]



Solvent	Yield (%) 140	141	
DME	34	12	(includes stereoisomers)
DME/toluene	3	53	

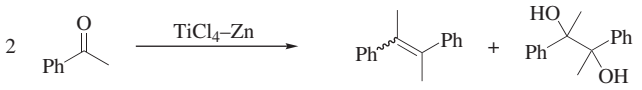
Scheme 31



In the intramolecular coupling of oxo amides leading to indoles by the "instant method" using the $TiCl_3$–Zn system, EtOAc, MeCN, and DMF are successfully employed in addition to ethereal solvents.[7]

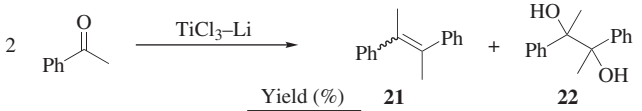
Temperature. Most of the McMurry coupling reactions are carried out at elevated temperatures, conveniently at reflux of the solvent. Since the McMurry coupling generally proceeds via the initial formation of titanium pinacolates followed by the reductive elimination to form alkenes, pinacols are typical by-products of the McMurry coupling reactions. Pinacols may be the major products when the reactions are performed at lower temperatures; the $TiCl_4$–Zn-promoted reaction of acetophenone carried out in dioxane at reflux affords dimethyldiphenylethylene (**21**) exclusively but pinacol **22** is exclusively obtained when the

reaction is run at ambient temperature in THF (Scheme 32).[3] A similar tendency is observed in the $TiCl_3$–Li-promoted reaction of acetophenone (Scheme 33).[312]



		Yield (%)		**21**	**22**
Solvent	Temp	**21**	**22**		
dioxane	reflux	92	0		
THF	rt	1	91		

Scheme 32



		Yield (%)		**21**	**22**
Solvent	Temp (°)	**21**	**22**		
THF	reflux	89	0		
THF	30	52	25		
DME	30	0	38		
THF[a]	30	87	0		
DME[a]	30	0	75		

[a] The reaction was carried out under ultrasonication.

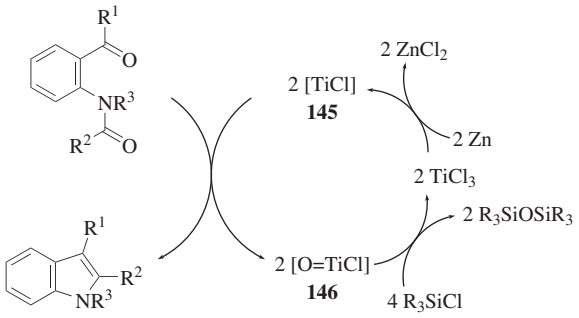
Scheme 33

Ultrasonication accelerates both the reduction of the titanium salts and formation of the alkenes in the above McMurry coupling; the reaction carried out in THF under irradiation of ultrasound proceeds at 30° and gives the same result as that carried out at reflux. Interestingly, however, the same reaction in DME results in the exclusive formation of the pinacol. The successful deoxygenative coupling of diferrocenyl ketone is achieved only under ultrasonication.[206] The McMurry coupling under microwave irradiation enjoys an advantage in that it is complete within a short period of time.[121,317]

High-Dilution Methods for Intramolecular Coupling. The intramolecular coupling of dicarbonyl compounds generally requires high-dilution conditions to obtain cyclic alkenes in good yields. Under the conditions suitable for intermolecular reactions, cycloalkenes are produced in rather low yield.[27] Therefore, the intramolecular coupling is typically performed by slow addition of the dicarbonyl compounds over several to dozens of hours by a motor-driven syringe pump to the refluxing solution of the coupling reagent. One of the exceptions is the intramolecular coupling of oxo amides leading to the formation of indoles. High dilution is neither necessary nor advantageous though the related formation

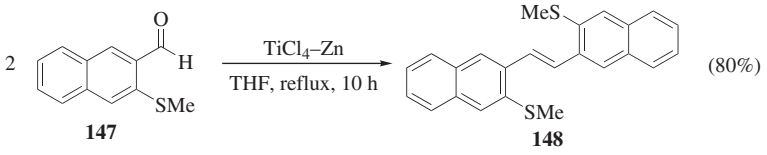
of benzofurans using the $TiCl_3-C_8K$ system requires high-dilution conditions.[79] The low-valent titanium reagent generated by the reduction of $TiCl_3$ with "high-surface sodium" (Na/Al_2O_3) is also recommended for the intramolecular coupling of dicarbonyl compounds to cycloalkenes since the reaction proceeds without using high-dilution techniques due to its pronounced template effect.[69] Because the second step of the tandem McMurry coupling of dicarbonyl compounds is an intramolecular cyclization, the high-dilution conditions are also employed in these reactions.

Catalytic McMurry Coupling. The preparation of indoles by the McMurry coupling with a catalytic amount of $TiCl_3$ has been realized by using trialkylchlorosilanes (Scheme 34).[83] In the catalytic cycle, the Ti(III) oxide **146** formed by the McMurry coupling of the oxo amides reacts with trialkylchlorosilanes to regenerate $TiCl_3$, which is then reduced with Zn to the low-valent titanium species **145** for further deoxygenative coupling. The procedure for the catalytic reaction is straightforward; heating a mixture of an oxo amide, $TiCl_3$, Zn dust, and a trialkylchlorosilane in MeCN furnishes the indole.



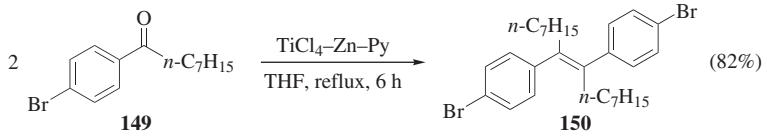
Scheme 34

EXPERIMENTAL PROCEDURES

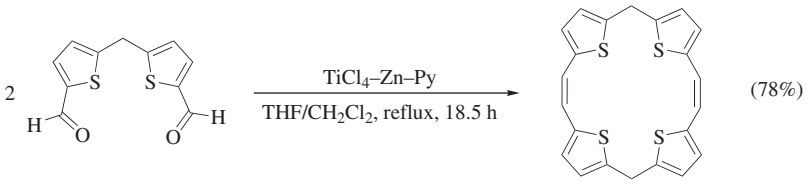


***trans*-1,2-bis(3-Methylthio-2-naphthyl)ethene (148) [Homocoupling with the $TiCl_4-Zn$ System].**[318] $TiCl_4$ (0.66 mL, 6.0 mmol) was slowly added to an

ice-cooled suspension of zinc powder (0.39 g, 6.0 mmol) in THF (10 mL), and the resulting mixture was heated to reflux for 1.5 h. After cooling to rt, a THF (10 mL) solution of **147** (0.405 g, 2.0 mmol) was slowly added and the mixture was heated to reflux for 10 h. After cooling to rt, the mixture was diluted with saturated aq. $NaHCO_3$ (30 mL) and CH_2Cl_2 (30 mL) and further stirred for 3.5 h. The mixture was filtered through a Celite pad, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2) to give **148** as yellow crystals (0.299 g, 80%). An analytical sample was obtained by recrystallization (CH_2Cl_2): mp 195.0–196.0°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 6H, S*Me*), 7.43 (ddd, $J = 7.5$, 7.5, 1.9 Hz, 2H, Ar*H*), 7.46 (ddd, $J = 7.5$, 7.5, 1.9 Hz, 2H, Ar*H*), 7.65 (s, 2H, Ar*H*), 7.67 (s, 2H, C*H* = C*H*), 7.76 (dd, $J = 7.5$, 1.9 Hz, 2H, Ar*H*), 7.86 (dd, $J = 7.5$, 1.9 Hz, 2H, Ar*H*), 8.10 (s, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 124.1, 125.2, 125.6, 126.4, 126.5, 127.9, 128.5, 131.5, 133.4, 134.9, 135.9. Anal. Calcd for $C_{24}H_{20}S_2$: C, 77.37; H, 5.41. Found: C, 77.07; H, 5.26.

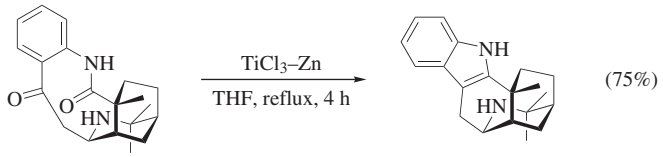


(*E*)-8,9-bis(4-Bromophenyl)-8-hexadecene (150) [Homocoupling with the $TiCl_4$–Zn–Py System].[319] $TiCl_4$ (19.0 g, 0.1 mol) was slowly added to anhydrous THF (400 mL) at −5 to 5° under N_2. To the resulting yellow solution, zinc (18.0 g, 0.27 mol) was added. Then pyridine (3 mL) was injected via syringe. The reaction mixture was heated to reflux before the ketone **149** (37.0 g, 0.13 mol) in THF (100 mL) was added over 1 h and the mixture was refluxed for an additional 5 h. After cooling, the solvent was removed under reduced pressure. The remaining dark solid was treated with a saturated aq. K_2CO_3 solution and was stirred overnight. The solid was removed by filtration, dried under reduced pressure at 70°, and subjected to a Soxhlet extraction with boiling light petroleum ether for three days. The extract was condensed and the residue was purified by silica gel chromatography (CH_2Cl_2). The pure product **150** crystallized on standing (28.4 g, 82%): colorless crystals, mp 103°; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.80 (t, 6H, C*H*), 1.10–1.38 (m, 20H, C*H*), 2.45 (m, 4H, α-CH_2), 6.77, 7.17 (AA'BB', 4H, Ar*H*); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.6, 23.6, 28.3, 29.1, 31.8, 34.2, 119.5, 137.9, 130.7, 131.3, 142.0. Anal. Calcd for $C_{28}H_{38}Br_2$: C, 62.93; H, 7.17; Br, 29.90. Found: C, 63.23; H, 7.38; Br 29.25.



151 **152**

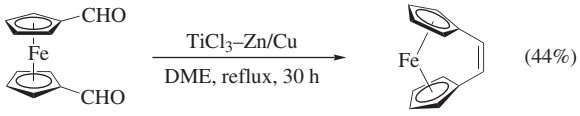
5,16-Dihydrotetrathia[22]annulene[2,1,2,1] (152) [Tandem Coupling with the $TiCl_4$–Zn–Py System].[149] A CH_2Cl_2 solution of $TiCl_4$ (1.0 M, 13.6 mL) was added to a THF (100 mL) suspension of zinc dust (1.76 g) under N_2 with stirring over 20 min. The reaction mixture was heated to reflux for 1 h, and then a THF (100 mL) solution of the dialdehyde **151** (310 mg, 1.31 mmol) and pyridine (1.76 mL) was added through a syringe over 30 min to the gently refluxing mixture. After refluxing for 18 h under N_2, the reaction was carefully quenched by addition of an aqueous solution of K_2CO_3 (10%, 24 mL). The reaction mixture was filtered, the filtrate was concentrated under reduced pressure, and the residue was extracted with CH_2C1_2 (150 mL). The extract was washed with water (2 × 50 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residue was subjected to silica gel column chromatography ($CHCl_3$) to give **152** (210 mg, 78%): mp 153.5–155.5°; ^{1}H NMR ($CDCl_3$) δ 6.52 (s, 4H), 6.77 (s, 4H), 6.78 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 31.6, 123.5, 124.8, 128.3, 138.5, 145.2; HRMS (m/z): M^+ calcd for $C_{22}H_{16}S_4$, 408.0135; found, 408.0137.



153 **119**

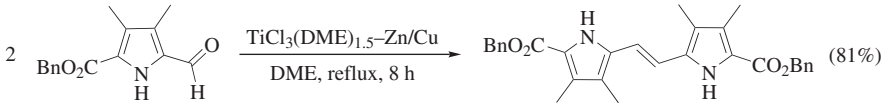
(+)-Aristoteline (119) [Intramolecular Coupling with the $TiCl_3$–Zn System by the "Instant Method"].[7] A suspension of the oxo amide **153** (24 mg, 0.074 mmol), $TiCl_3$ (45 mg, 0.29 mmol), and zinc (77 mg, 1.18 mmol) in THF (2 mL) was heated to reflux for 4 h. EDTA (430 mg, 1.47 mmol) was added, and the mixture was stirred for 1 h at rt, diluted with THF (20 mL), and filtered through a short plug of silica. The filtrate was condensed and the residue was purified by chromatography (hexane/EtOAc/Et_3N, 10:10:1) to afford **119** as colorless crystals (16.2 mg, 75%): mp 160–162.5°; $[\alpha]^{20}_D$ + 20.2 (*c* 0.3, $CDCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 3H), 1.31 (s, 3H), 1.53 (s, 3H), 1.20–1.71 (m, 5H), 1.90–1.93 (m, 1H), 1.95 and 2.05 (ddAB, J = 3.2, 14 Hz, 2H), 2.22–2.31 (m, 1H), 2.65 (d, J = 16.5 Hz, 1H), 3.07 (dd, J = 16.5, 5.8 Hz, 1H), 3.63 (dd, J = 1, 5.6 Hz, 1H), 7.05 (dt, J = 1.1, 7.2 Hz, 1H), 7.10 (dt, J = 1.1, 7.2 Hz, 1H), 7.29 (dd, J = 1, 8 Hz, 1H), 7.44 (dd, J = 1, 8 Hz, 1H), 7.77 (br s, 1H,

−N*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 25.5, 27.5, 27.8, 28.6, 29.1, 33.2, 35.7, 36.0, 39.4, 50.6, 53.6, 104.4, 110.5, 118.2, 119.2, 121.1, 128.2, 136.2, 142.5.



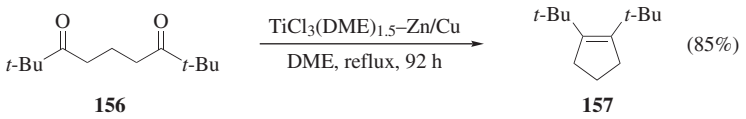
154 **108**

***ansa*-(Vinylene)ferrocene (108) [Intramolecular Coupling with the $TiCl_3$–Zn/Cu System].[238]** A 250-mL, round-bottomed Schlenk flask equipped with a magnetic stir bar was charged with $TiCl_3$ (3.50 g, 22.7 mmol), Zn/Cu (3.42 g, 5.16 mmol), and DME (∼80 mL). The resulting blue-green suspension was heated to reflux for 1.5 h to give a green-brown slurry. 1,1′-Ferrocenedicarbaldehyde (**154**) (0.50 g, 2.06 mmol) in DME (10 mL) was added under reflux through a septum at the top of the condenser over 20 h using a mechanical syringe pump under reflux. After completion of the addition, the reaction mixture was heated at reflux for an additional 10 h. The red-brown suspension was allowed to cool and was filtered through a pad of 200–400 mesh Florisil to give an orange-red solution. The DME was removed by vacuum transfer and the crude product was sublimed under reduced pressure at 45° to give **108** as a bright red crystalline powder (0.192 g, 44%): ^{1}H NMR (400 MHz, C_6D_6) δ 3.67 (t, J = 1.6 Hz, 4H), 4.66 (t, J = 1.6 Hz, 4H), 6.09 (s, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 67.9 (C_β), 75.3 (C_α), 89.5 (*ipso*), 135.9 (CH=CH). Anal. Calcd for $C_{12}H_{10}Fe$: C, 68.62; H, 4.80. Found: C, 68.16; H, 4.99.



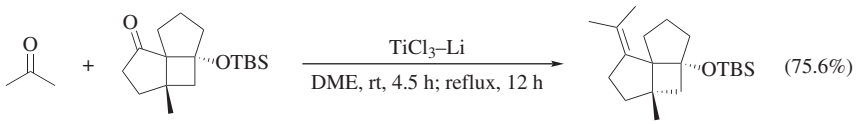
155 **77**

***trans*-1,2-bis(5-(Benzyloxycarbonyl)-3,4-dimethyl-2-pyrrolyl)ethene (77) [Homocoupling with the $TiCl_3(DME)_{1.5}$–Zn/Cu System].[210]** $TiCl_3(DME)_{1.5}$ (5.2 g, 17.9 mmol) and Zn/Cu (4.9 g, 69 mmol) were placed in a dry N_2-filled flask in a dry box. DME (100 mL) was added and the resulting mixture was heated to reflux for 2 h under N_2 to yield a black suspension. A solution of the formylpyrrole **155** (1.12 g, 4.36 mmol) in DME (10 mL) was added, and the mixture was heated to reflux for 8 h. After being cooled to rt, the reaction mixture was filtered through a glass bed of neutral alumina (CH_2Cl_2). The filtrate was condensed to afford **77** (0.853 g, 81%): mp 208–210°; ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 6H), 2.27 (s, 6H), 5.33 (s, 4H), 6.60 (s, 2H), 7.38 (m, 10H), 8.79 (bs, 2H); ^{13}C NMR ($CDCl_3$) δ 9.2, 10.6, 65.8, 114.3, 128.1, 128.6, 161.4; HRMS (m/z): M^+ calcd for $C_{30}H_{30}N_2O_4$, 482.2205; found, 482.2184. Anal. Calcd for $C_{30}H_{30}N_2O_4$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.64; H, 6.17; N, 5.71.



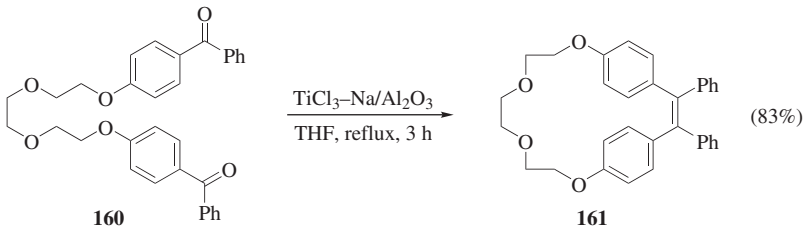
156 **157**

1,2-Di-*tert*-butylcyclopentene (157) [Intramolecular Coupling with the $TiCl_3(DME)_{1.5}$–Zn/Cu System].[320] DME (300 mL) was added to a mixture of $TiCl_3(DME)_{1.5}$ (21.59 g, 74.59 mmol) and Zn/Cu (17.0 g). After the mixture was heated to reflux for 1.5 h, 2,2,8,8-tetramethylnonane-3,7-dione (**156**) (10.00 g, 47.10 mmol) in DME (50 mL) was added via cannula. The mixture was heated to reflux for 92 h, cooled to rt, and hexane (200 mL) was added. The mixture was filtered through a glass frit in air and the solvent was removed. The residual murky oil was purified by silica gel column chromatography (hexane) to afford **157** as a colorless oil (7.20 g, 85%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 18H), 1.50 (q, $J = 7.69$ Hz, 2H), 2.49 (t, $J = 7.69$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 32.5, 33.8, 39.1, 141.4. Anal. Calcd for $C_{13}H_{24}$: C, 86.59; H, 13.41. Found: C, 85.75; H, 13.63.



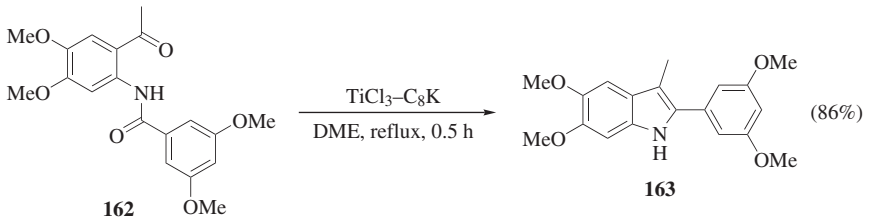
158 **159**

1-Isopropylidene-3a-methyl-4a-(*tert*-butyldimethylsiloxy)-2,3,3a,4,4a,5,6,7-octahydrocyclobuta[1,2:1,4]dicyclopentene (159) [Mixed-Coupling with the $TiCl_3$–Li System].[321] A slurry of lithium wire (0.90 g, 0.13 mol) and $TiCl_3$ (5.74 g, 0.15 mol) in DME (60 mL) was heated to reflux for 1 h under Ar. The mixture was cooled to rt and a solution of the cyclopentanone **158** (291.2 mg, 0.908 mmol) in anhydrous acetone (0.54 mL) was added over 4 h by a motor-driven syringe. After stirring for 30 min at rt, the mixture was heated to reflux for 12 h, cooled to rt, diluted with pentane (80 mL), and filtered through a pad of Florisil. The residue was washed with pentane (2 × 80 mL). Methanol was added slowly to the filtrate until gas evolution ceased to decompose any active Ti-species. The resulting black solution was passed through a pad of Florisil and the pad was washed with pentane. The combined filtrates were washed with water (200 mL) and then brine (200 mL), and dried. The solvent was evaporated and the residual pale-green oil was chromatographed on silica gel (pentane) to give **159** (239.8 mg, 75.6%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.02 (CH_3Si), 0.04 (CH_3Si), 0.86 (CH_3CSi), 0.93 (CH_3), 1.64 (d, $J = 1.5$ Hz, $CH_3C=$), 1.69 (d, $J = 1.6$ Hz, $CH_3C=$), 1.56–2.40 (m, 12H); ^{13}C NMR ($CDCl_3$) δ −2.9 (q), −2.5 (q), 17.9, 20.9 (q), 22.5 (q), 22.9 (q), 24.8 (t), 25.8 (3 x q), 30.9 (t), 32.3 (t), 40.9, 41.4 (t), 42.0 (t), 47.0 (t), 62.7, 82.3, 123.2, 139.1; HRMS (m/z): M^+ calcd for $C_{20}H_{36}OSi$, 320.2536; found, 320.2519.



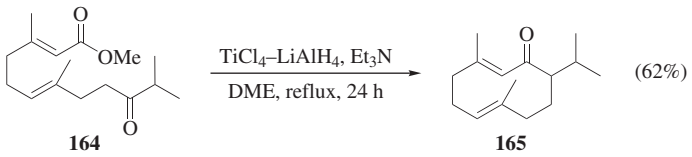
160 **161**

l5,16-Diphenyl-l,4,7,10-tetraoxa(10.2)[20]paracyclophan-15-ene (161) [Intramolecular Coupling with the $TiCl_3$–Na/Al_2O_3System].[85] $TiCl_3$ (1.05 g, 6.8 mmol) was added to a THF (50 mL) suspension of Na/Al_2O_3 (10%, 3.56 g, 13.6 mmol of sodium), and the mixture was heated to reflux for 1 h. A THF (20 ml) solution of diketone **160** (583 mg, 1.14 mmol) was then added dropwise over 2 h to the boiling mixture and reflux was continued for another 1 h. After being cooled to rt, the mixture was filtered and the insoluble materials were rinsed with THF (3 × 20 mL). The filtrate was evaporated and the residue was purified by column chromatography (hexane/EtOAc, 2:1) to afford **161** as colorless crystals (451 mg, 83%): mp 184.6°; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.56 (s, 4H), 3.70 (dd, J = 4.3, 4.7 Hz, 4H), 4.23 (dd, 4H), 6.69 and 6.85 (AB, J = 10 Hz, 8H), 7.10 (s, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.4, 70.5, 71.4, 115.1, 126.4, 127.6, 127.9, 131.2, 132.3, 137.3, 140.6, 142.9, 157.1. Anal. Calcd for $C_{32}H_{30}O_4$•H_2O: C, 74.70; H, 6.66. Found: C, 74.73; H; 6.50.



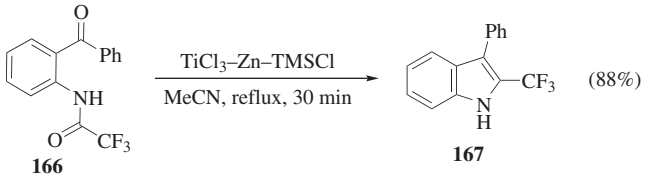
162 **163**

2-(3,5-Dimethoxyphenyl)-5,6-dimethoxy-3-methylindole (163) [Intramolecular Coupling with the $TiCl_3$–C_8K System].[82] $TiCl_3$ (1.58 g, 10.2 mmol) was added to a DME (50 mL) suspension of C_8K (4.2 g, 31 mmol), and the resulting suspension was heated to reflux for 1.5 h. The oxo amide **162** (310 mg, 0.9 mmol) in DME (15 mL) was added and heating was continued for 0.5 h. The suspension was filtered through a plug of silica gel, the graphite was washed with EtOAc (50 mL in several portions), the combined filtrates were concentrated, and the residue was purified by silica gel column chromatography to afford **163** as colorless crystals (240 mg, 86%): mp 141–142°; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 3H, CH_3), 3.84, 3.85, 3.88, 3.97 (s, 3H each, OCH_3), 6.45 (s, 1H, ArH), 6.71 (s, 2H, ArH), 6.84 (s, 1H, ArH), 7.02 (s, 1H, ArH), 8.06 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.1, 55.6, 56.4, 56.7, 94.7, 99.1, 101.2, 105.8, 109.0, 123.1, 130.4, 132.9, 135.7, 145.3, 147.7, 161.2. Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.65; H, 6.60; N, 4.20.



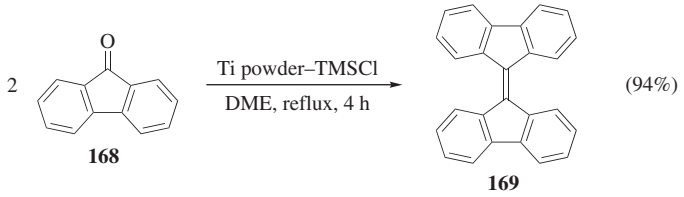
164 **165**

(±)-Acoragemacrone (165) [Intramolecular Coupling of a Keto Ester with the $TiCl_3$–$LiAlH_4$ System].[322] $LiAlH_4$ (80 mg, 2.06 mmol) was added to a suspension of $TiCl_3$ (640 mg, 4.16 mmol) in freshly distilled DME (25 mL) at 0° under Ar with stirring. After 5 min, anhydrous triethylamine (0.3 mL, 2.15 mmol) was added to the mixture and the slurry was heated to reflux for 2 h. A DME (20 mL) solution of the α,β-unsaturated oxo ester **164** (75 mg, 0.28 mmol) was slowly added by syringe over 20 h, the mixture was heated at reflux for an additional 4 h, cooled to 0°, diluted with Et_2O (15 mL), and quenched by addition of MeOH (5 mL) and water (5 mL). The mixture was passed through a short column of silica gel and the filtrate was washed with brine and dried. After removal of the solvent under reduced pressure, the residual oil was purified by flash column chromatography on silica gel (pentane/ether, 30:1) to give **165** as colorless oil (38 mg, 62%): ^{1}H NMR ($CDCl_3$) δ 0.87 (d, $J = 6.9$ Hz, 3H), 0.91 (d, $J = 6.9$ Hz, 3H), 1.24 (d, $J = 1.2$ Hz, 3H), 1.96 (d, $J = 1.1$ Hz, 3H), 1.50–2.40 (br m, 10H), 4.90–5.10 (br m, 1H), 5.71 (br s, 1H); EIMS (m/z): M^+ 220 (15), 205 (24), 177 (19), 149 (23), 121 (22), 107 (31), 81 (69), 69 (14), 43 (100).



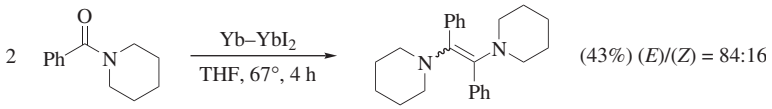
166 **167**

3-Phenyl-2-trifluoromethylindole (167) [Intramolecular Coupling with the Catalytic $TiCl_3$–Zn–TMSCl System].[83] TMSCl (2.29 g, 21.04 mmol) was added via syringe to a suspension of the oxo amide **166** (1.23 g, 4.19 mmol), $TiCl_3$ (65 mg, 10 mol %), and zinc dust (1.37 g, 21.04 mmol) in MeCN (18 mL). The mixture was heated at reflux for 30 min, cooled, diluted with EtOAc (25 mL), and filtered through a pad of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel (hexane/EtOAc, 10:1) to give **167** (961 mg, 88%) as pale yellow crystals: mp 63–64°; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.19 (td, $J = 7.5$, 1.3 Hz, 1H), 7.32–7.56 (m, 7H), 7.64 (d, $J = 8.0$ Hz, 1H), 8.45 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.7, 119.9, 121.1, 121.2 (q, $J = 37$ Hz), 121.3, 121.7 (q, $J = 167$ Hz), 125.1, 127.4, 127.6, 128.4, 130.0, 132.2, 135.0; MS (m/z): M^+ 261 (100), 240 (12), 222 (10), 221 (11).



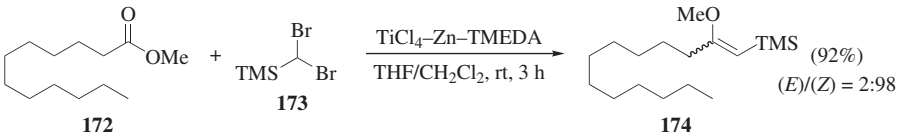
168 **169**

9,9-Bisfluorenylidene (169) [Homocoupling with the Commercial Titanium Powder–TMSCl System].[83] TMSCl (2.0 mL, 11.6 mmol) was added to a suspension of titanium powder (0.793 g, 16.55 mmol) in DME (10 mL). The mixture was heated at reflux for 67 h and then 9-fluorenone (**168**) (0.911 g, 5.06 mmol) was added to the boiling suspension in one portion. After being heated at reflux for 4 h, the mixture was cooled to rt and filtered through a short pad of silica gel. The insoluble residue was rinsed with THF in several portions (∼100 mL) and the combined filtrates were concentrated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc, 10:1) to give **169** (0.780 g, 94%) as orange-red crystals: mp 187−189°; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15−7.35 (m, 8H), 7.68 (dd, $J = 7$, 1 Hz, 4H), 8.37 (d, $J = 4$ Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 119.87, 126.71, 126.83, 129.13, 138.25, 141.00, 141.30; MS (m/z): M^+ 328 (100), 162 (23).



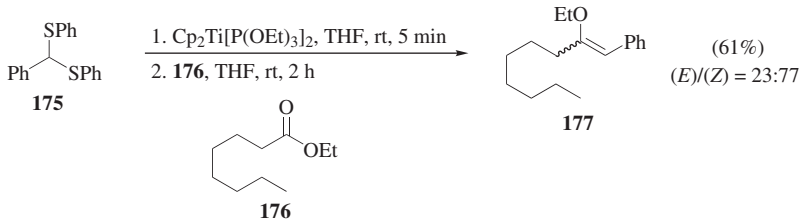
170 **171**

1,2-Dipiperidinostilbene (171) [Homocoupling with the Yb–YbI_2 System].[108] Ytterbium powder (0.7 mmol), 1,2-diiodoethane (0.3 mmol), and THF (3 mL) were placed in a 20-mL, two-necked flask equipped with a condenser under Ar. The mixture was heated to 67° for 1 h with stirring to generate the Yb–YbI_2 reagent. 1-Benzoylpiperidine (**170**) (0.5 mmol) was added, and the resulting mixture was stirred at 67° for 4 h. Saturated aq $NaHCO_3$ solution (40 mL) was added, and the products were extracted with Et_2O (3 × 20 mL). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by column chromatography (basic Al_2O_3, activity I, Merck Art. 02069 containing 15 wt % of water, hexane) to give **171** as a yellow solid (0.11 mmol, 43%, $(E)/(Z) = 84:16$): mp 112.0–112.5°; ^{1}H NMR (270 MHz, $CDCl_3$) [(E)-isomer] δ 1.27 (br s, 12H), 2.29 (br s, 8H), 7.05–7.19 (m, 2H), 7.19–7.35 (br d, 8H); [(Z)-isomer] δ 1.50 (br s, 12H), 2.91 (br s, 8H), 6.83–6.97 (m, 6H), 6.97–7.05 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) [(E)-isomer] δ 24.4, 27.2, 52.9, 126.2, 127.6, 129.7, 136.5, 142.4; [(Z)-isomer] δ 24.8, 27.0, 51.9, 125.4, 127.1, 131.3, 137.7, 140.6. Anal. Calcd for $C_{24}H_{30}N_2$: C, 83.19; H, 8.73; N, 8.08. Found: C, 82.99; H, 8.69; N, 8.02.



172 **173** **174**

2-Methoxy-1-(trimethylsilyl)tridec-1-ene (174) [Carbonyl Olefination with the CH_2X_2–Zn–$TiCl_4$ System].[162] A CH_2Cl_2 solution of $TiCl_4$ (2.0 M, 4.0 mmol) was added at 0° to a mixed solvent of THF (1.5 mL) and CH_2Cl_2 (6 mL) under Ar. TMEDA (8 mmol) was added to the yellow solution at rt and the mixture was stirred at rt for 15 min. Zinc dust (9.0 mmol) was added and the resulting mixture was stirred at rt for 30 min. The color of the suspension turned from brownish-yellow to dark greenish-blue in a slightly exothermic process. The ester **172** (1.0 mmol) and $TMSCHBr_2$ (**173**) (2.2 mmol) in CH_2Cl_2 (1 mL) were added to the mixture. The color of the mixture gradually turned dark reddish-brown. After being stirred at rt for 3 h, THF (10 mL) was added. The mixture was cooled to 0° and a saturated aq. K_2CO_3 solution (2.0 mL) was added. After being stirred at 0° for another 1 h, the mixture was diluted with ether/Et_3N (200:1, 10 mL) and then passed rapidly through a short column of basic alumina (activity III). The solution was concentrated and the resulting white solid was removed by filtration with the aid of Hyflo Super-Cel^R using hexane/Et_3N 200:1, (50 mL) as an eluent. The filtrate was concentrated and the crude product was purified by column chromatography on basic alumina (activity III, hexane/Et_3N, 200:1) to give **174** (92%, $(E)/(Z) = 2:98$): bp 60° (bath temp, 1.0 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9H), 0.88 (t, $J = 7$ Hz, 3H), 1.20–1.70 (m, 18H), 2.16 (t, $J = 7$ Hz, 2H), 3.48 (s, 3H (E)), 3.51 (s, 3H (Z)), 4.00 (s, 1H (E)), 4.30 (s, 1H (Z)). Anal. Calcd for $C_{17}H_{36}OSi$: C, 71.75; H, 12.75. Found: C, 71.72; H, 13.01.



175 **176** **177**

2-Ethoxy-1-phenylnon-1-ene (177) [Carbonyl Olefination with the $RCH(SPh)_2$–$Cp_2Ti[P(OEt)_3]_2$ System].[170] To a flask charged with finely powdered 4 Å molecular sieves (200 mg), Mg turnings (58 mg, 2.4 mmol), and Cp_2TiCl_2 (498 mg, 2 mmol) were added THF (4 mL) and $P(OEt)_3$ (0.68 mL, 4 mmol) with stirring at rt under Ar. After 3 h, a solution of α,α-bis(phenylthio) toluene (**175**) (170 mg, 0.55 mmol) in THF (1 mL) was added to the THF solution of the resulting $Cp_2Ti[P(OEt)_3]_2$ and the reaction mixture was further stirred for 5 min. Then a solution of ethyl caprylate (**176**) (86 mg, 0.5 mmol) in THF

(2.5 mL) was added dropwise over 10 min. After stirring the reaction mixture for 2 h, the reaction was quenched by the addition of 1 M aqueous NaOH solution (30 mL) and the insoluble materials were removed by filtration through celite. The filtrate was extracted with Et_2O and the extract was dried (K_2CO_3). After removal of the solvent, the residue was purified by column chromatography (Merck aluminum oxide 90, Brockmann III, hexane) to give **177** (75 mg, 61%, $(E)/(Z) = 23:77$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83–0.94 (m, 3H), 1.21–1.41 (m, 1H), 1.49–1.62 (m, 2H), 2.27 (t, $J = 7.6$ Hz, 1.54H), 2.30 (t, $J = 7.8$ Hz, 0.46H), 3.83 (q, $J = 6.8$ Hz, 0.46H), 3.90 (q, $J = 6.8$ Hz, 1.54H), 5.40 (s, 0.77H), 5.54 (s, 0.23H), 7.05–7.31 (m, 3.46H), 7.65 (m, 1.54H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.7, 15.5, 22.7, 27.7, 27.8, 29.1, 29.2, 29.3, 29.4, 31.0, 31.8, 32.8, 62.4, 63.4, 99.6, 108.3, 125.0, 125.3, 128.0, 128.1, 128.7, 136.8, 138.1, 156.9, 159.5; HRMS (m/z): M^+ calcd for $C_{17}H_{26}O$, 246.1984; found, 246.1990.

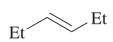
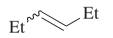
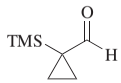
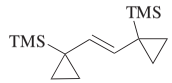
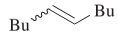
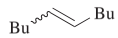
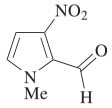
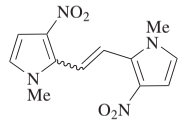
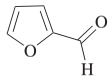
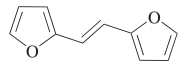
TABULAR SURVEY

The tables are organized by type of reaction (homocoupling, mixed-coupling, intramolecular coupling, and tandem coupling) and by carbonyl compounds (aldehydes, ketones, or carboxylic acid derivatives). Within each table, entries are listed in the order of increasing number of carbons of the carbonyl compounds. In the case of mixed-couplings between aldehydes and ketones, entries are ordered based on the number of the carbons of the aldehydes. In all tables, reaction condition 1 denotes the source of low-valent metal reagent, reducing agent, solvent, and the conditions for the generation of the low-valent metal reagent. In Tables 1A, 1B, 1C, 2A, 2B, and 2C, conditions 2 indicate conditions for the coupling of the carbonyl compounds. In Tables 2D, 3A, 3B, 3C, 3D, 4A, and 4B, conditions 2 indicate the reaction conditions for addition of the carbonyl compounds and conditions 3 represent conditions for the coupling of the carbonyl compounds. An em-dash (—) in the "Conditions" column means that reaction conditions were not given and an em-dash (—) in the "Product(s) and Yield(s) (%)" column means that yields were not reported. The computerized literature survey was conducted using SciFinder, Web of Science, PubMed, and ScienceDirect with several search headings, and the literature coverage is from 1973 to mid 2010. Coupling reactions reported in patents are not included in the tables. Our apologies are extended to the authors whose work has been inadvertently omitted.

The following abbreviations (not included in *The Journal of Organic Chemistry* Standard Abbreviations and Acronymns) are used in the Tabular Survey:

DPMS	diphenylmethylsilyl
Np	naphthyl
PGC	process gas chromatography
SCE	saturated calomel electrode
TES	triethysilyl
TBDPS	*tert*-butyldiphenylsilyl
Tol	tolyl

TABLE 1A. HOMOCOUPLING OF ALDEHYDES

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3			
	1. $TiCl_3(THF)_3$, Mg, THF, 40°, 1 h 2. 40°, 1.5 h	 (30) +  (30)	4
	WCl_5, $LiAlH_4$, THF, rt, 6 h	 (18)	45
C_4			
	1. $TiCl_3$, Li, DME, reflux, 16 h 2. rt, 2 h; then reflux, 20 h	 (38)	43
C_5			
	1. $TiCl_3$, K, THF, reflux, 40 min 2. Reflux, 16 h	 (77), (*E*)/(*Z*) = 70:30	27, 62
	$InCl_3$, Zn, MeCN, reflux, 9 h	 (70), (*E*)/(*Z*) = 70:30	104
	$TiCl_4$, Zn, THF, py, reflux 1.5 h	 (7)[a]	125
	$TiCl_2(THF)_2$, THF, reflux, 24 h	 (95)	34

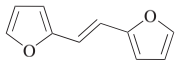
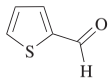
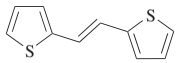
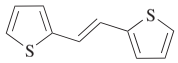
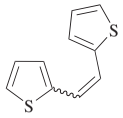
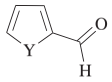
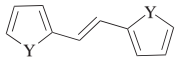
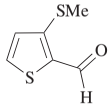
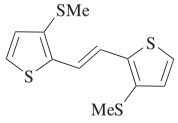
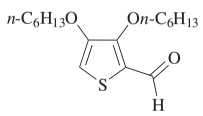
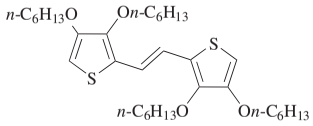
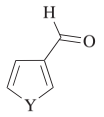
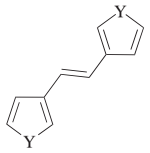
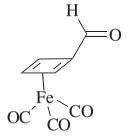
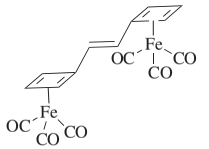
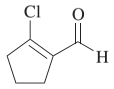
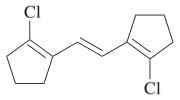
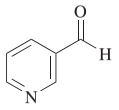
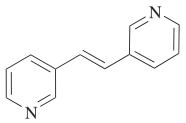
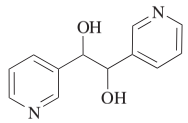
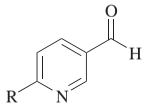
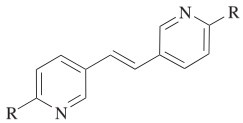
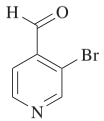
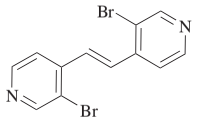
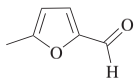
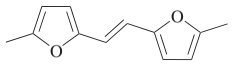
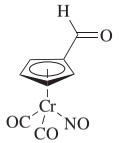
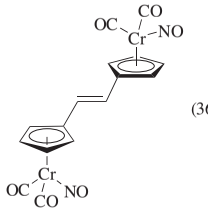
	$TiCl_4$, Zn		(—)	323
	$TiCl_4$, Zn, THF, reflux		Time (h) 4 (71) 3.5 (98)	324 325, 326
	—		(—)	327
	$Ti(Oi\text{-}Pr)_4$, Mg, TMSCl, Et_3N, THF, 40°, 72 h		(53), (*E*)/(*Z*) = 10:90	87
	1. $TiCl_3$, Li, DME, reflux, 2 h 2. Reflux, 15 h		Y S (91) EtO_2CN (30) MeO_2CN (50)	124
	1. $TiCl_4$, Zn, py, THF, reflux, 1.5 h 2. Reflux, 5 h		(55)	328

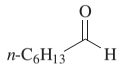
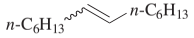
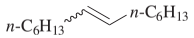
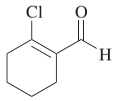
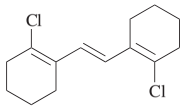
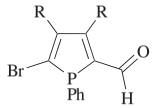
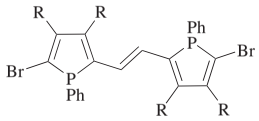
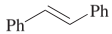
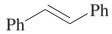
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	1. $TiCl_4$, Zn, THF, reflux, 30 min 2. Py, reflux, 2 h	 (76)	329
	1. $TiCl_3$, Li, DME, reflux, 2 h 2. Reflux, 15 h	 Y: S (93); O (45)	124
	1. $TiCl_3$, $LiAlH_4$, THF, rt, 10 min 2. Reflux, 4 h	 (56)	207
C_6			
	1. $TiCl_4$, Zn, DME, reflux, 2 h 2. 0–5°, 1 h; then rt, 4 h; then reflux, 2 h	 (50)	44

	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1 h 2. Reflux, 15 h	 (28) +  (24)	124
	1. $TiCl_4$, Zn, py, dioxane, 80°, 2 h 2. 80°, 12 h		212
	1. $TiCl_3$, Li, DME, reflux, 2 h 2. Reflux, 15 h	 (30)	124
	$TiCl_3$, $LiAlH_4$, THF, reflux	 (52)	330
	1. $TiCl_4$, $LiAlH_4$, THF, 90°, 12 h 2. 55°, 16 h	 (36)	205

R	
MeO	(40)
MeS	(30)

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 18 h	 (52)	114
	1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. rt, 5.5 h	 (47)	67
	1. $TiCl_4$, Zn, DME, reflux, 2 h 2. 0–5°, 30 min; then reflux, 3 h	 (70)	44
C_{7-17}			
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 3 h		126
C_7			
	1. Ti powder, TMSCl, DME, reflux, 67 h 2. Reflux, 77 h	 (90)	83
	$TiCl_2(THF)_2$, THF, reflux, 24 h	 (98)	34

R		dr
Me	(47)	—
Ph	(71)	90:10

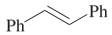
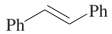
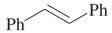
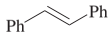
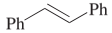
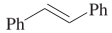
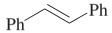
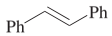
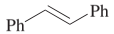
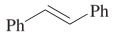
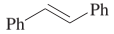
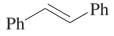
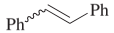
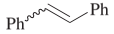
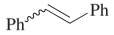
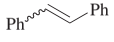
1. $TiCl_3$, Li, DME, reflux, 1 h 2. Reflux, 16 h		(97)	27
1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. rt, 2 h		(72)	67
1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 3 h		(95)	73, 74
$TiCl_3$, Zn, DME, reflux, 1 h		(78)	7
1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h		(85)	5
1. $TiCl_4$, C_8K, THF, reflux, 30 min 2. Reflux, 1 h		(95)	73
$TiCl_4$, Zn, dioxane, reflux, 4 h		(98), (*E*)/(*Z*) >99:1	3
1. $TiCl_4$, Zn, py, dioxane, –10 to –5°, 30 min 2. Microwave irradiation, 7 min		(92)	121

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. $TiCl_4$, $LiAlH_4$, THF, reflux, 20 min 2. Tertiary amine, reflux, 3 h	 Tertiary amine *n*-Bu_3N (92) Proton Ssponge[b] (92)	110
	1. $TiCl_4$, Hg/Mg, THF 2. 0°, 2 h; then reflux, 24 h	 (>95)	331
	1. $NbCl_5$, MeLi, DME, 80°, 24 h 2. Reflux, 8 h	 (100)	96
	$W_2(OCH_2CMe_3)_6(Py)_2$, hexane, 22°, 2–24 h	 (34)	99
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 2 h	 (85), (*E*)/(*Z*) = 90:10	114
	1. $TiCl_3$, Li, THF, ultrasonication, 30°, 1 h 2. Ultrasonication, 30°, 45 min	 (83)	312
	1. $TiCl_3$, Na/Al_2O_3, THF, reflux, 1 h 2. Reflux, 30 min	 (82) dr 95:5	69
	1. $TiCl_3$, $LiAlH_4$, THF, 0°, 30 min; then reflux, 10 min 2. Reflux, 20 h	 (88)	120

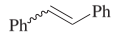
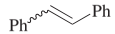
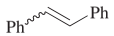
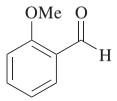
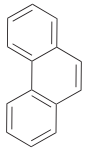
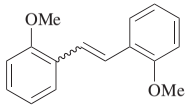
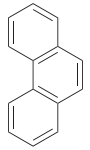
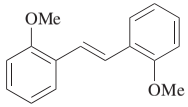
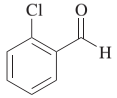
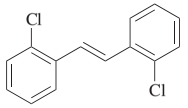
1. $TiCl_3(THF)_3$, Mg, THF, 40°, 1 h 2. 40°, 1.5 h		(—)	4
$AlCl_3$, Zn, MeCN, reflux, 10 h		(92), (*E*)/(*Z*) = 99:1	88
$Mo(CO)_6$, rt, 24 h		Solvent CH_2Cl_2 (5) THF (10) ether (39) dioxane (13) benzene (39) pentane (41) cyclohexane (38)	45
W(0), CH_2Cl_2, rt, 24 h		W(0) (42) (*E*)/(*Z*) $W(CO)_6$ 21:21 $W(CO)_5PPh_3$ (18) 9:9 $W(CO)_5NH_2C_6H_{11}$ (15) 8:7 $[W(CO)_5Cl]NEt_4$ (31) 27:4 $W(CO)_5$=C(OMe)Ph (32) 19:13	45
WCl_5, [Reagent], rt, 6 h		[Reagent] Solvent (78) (*E*)/(*Z*) $LiAlH_4$ THF 73:5 $LiAlH_4$ ether (23) — $LiAlH_4$ dioxane (13) — $NaAlH_4$ THF (69) — Zn THF (16) —	45

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	WCl_6, electroreduction,[c] THF, 4 h	 (96), (*E*)/(*Z*) = 91:9	103
	$TiCl_3$, Li, THF	 (25)[d]	332
	1. $TiCl_3$, Li, THF, reflux, 3 h 2. Additive, reflux, 16 h	 +  **I** **II**	Additive **I** **II** Fullerene (35) (47) — (0) (25) 333
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 12 h 3. I_2, heptane, reflux[e]	 (10)	334
	1. $TiCl_4$, Zn, DME, reflux, 2 h 2. 0–5°, 30 min; then reflux, 3 h	 (85)	44

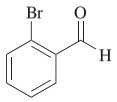
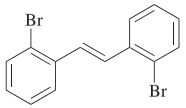
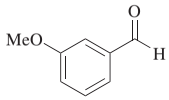
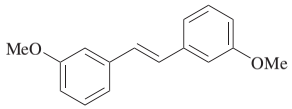
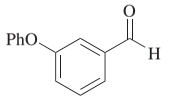
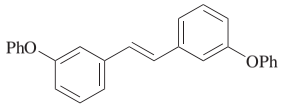
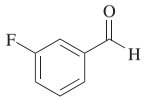
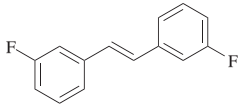
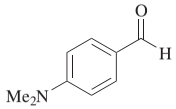
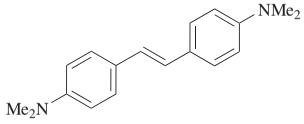
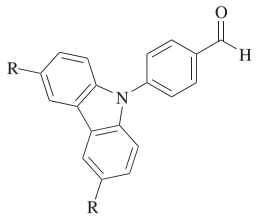
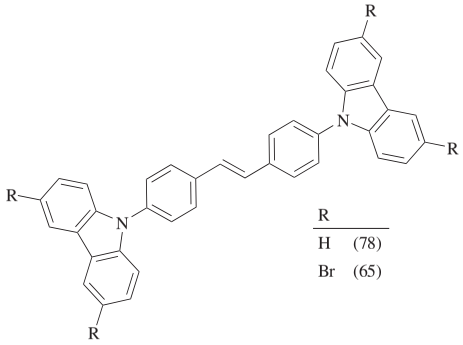
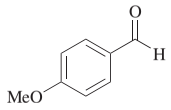
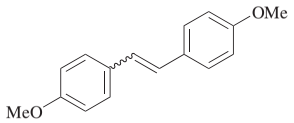
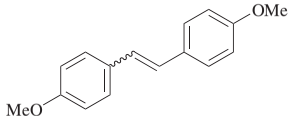
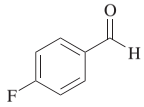
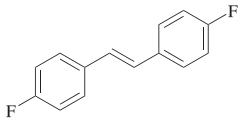
	$TiCl_3$, Li, DME, reflux, 6 h		(71)	335
	1. $TiCl_4$, Zn, THF, –10° 2. Reflux, 5 h		(88)	233
	1. $TiCl_4$, Zn, py, dioxane, –10 to –5°, 30 min 2. Microwave irradiation, 10 min		(80)	121
	$TiCl_3$, Li, DME, reflux, 18 h		(95), (*E*)/(*Z*) = 99.92:0.08	336
	$TiCl_4$, Zn, THF, reflux, 2 h		(—)	337

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	$TiCl_4$, Zn, dioxane	 R: H (78); Br (65)	338
	1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. rt, 3 h	 (68), (*E*)/(*Z*) = 60:40	67
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 14 h	 (64), (*E*)/(*Z*) = 85:15	114
	1. $TiCl_3(DME)_{1.5}$, Li, DME, reflux, 1.5 h 2. Reflux, 20 h	 (58)	339

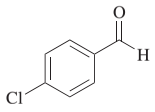
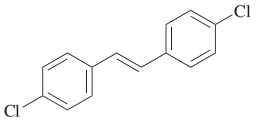
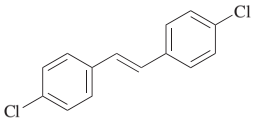
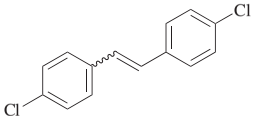
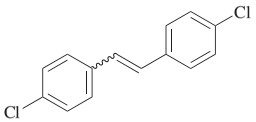
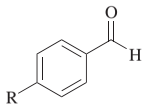
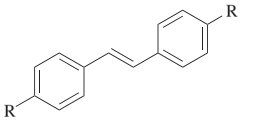
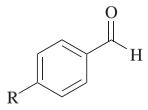
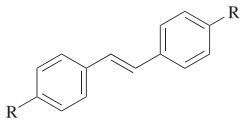
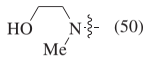
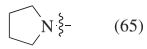
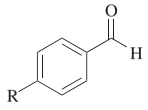
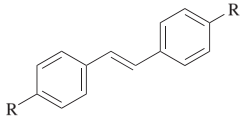
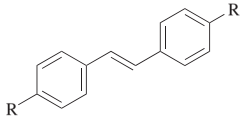
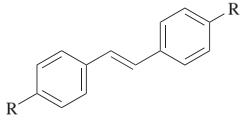
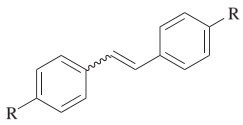
	1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. rt, 2 h		(70)	67
	1. $TiCl_4$, Zn, py, dioxane, –10 to –5°, 30 min 2. Microwave irradiation, 5 min		(80)	121
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 2.5 h		(65), (*E*)/(*Z*) = 92:8	114
	$AlCl_3$, Zn, MeCN, reflux, 18 h		(72), (*E*)/(*Z*) = 80:20	88
	1. $TiCl_3$, Li, THF, reflux, 3 h; then I_2, 5 min 2. 0–5°, time		R Time (h) H 3 (85) Cl 2.5 (82) MeO 3.5 (62)	115

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. $TiCl_4$, Zn, Na, THF, reflux, 1 h 2. Reflux, 20 h		340
		R: Et_2N (54);  (50);  (65)	
C_{7-8}			
	$TiCl_4$, Zn, THF, 110°, microwave irradiation, 10 min		317
		R: H (93); *t*-BuS (87); Me (91)	
	Zn amalgam, $ClMe_2Si(CH_2)_2SiMe_2Cl$, THF, rt, overnight		341
		R: H (69); MeO (79); Cl (26); Me (86)	
	1. $ZrCl_4$, Li, DME, rt, 1 h 2. Reflux, 5 h		93
		R: H (86); Me (78)	

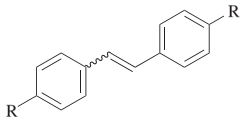
$Cp_2Ti(CO)_2$, THF, reflux, 10 h



R		
H	(98)	
Cl	(88)	
Me	(99)	

86

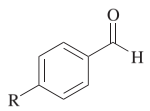
$InCl_3$, Zn, MeCN, reflux



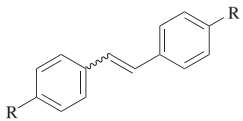
R	Time (h)		(*E*)/(*Z*)
H	8	(93)	98:2
Cl	9	(90)	86:14
Br	8	(75)	80:20
O_2N	9	(70)	70:30
Me	7	(88)	90:10
MeO	8	(80)	75:25

104

C_7



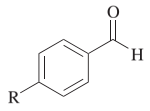
1. $NbCl_5$, $NaAlH_4$, THF/benzene, 0°, 10 min
2. Reflux, time



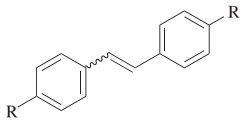
R	Time (h)		(*E*)/(*Z*)
H	1	(70)	>20:1
Cl	3	(95)	>20:1
MeO	3	(56)	>20:1

95

C_{7-8}



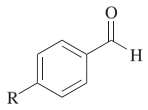
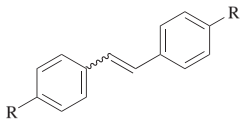
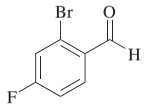
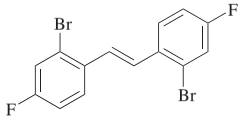
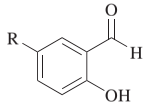
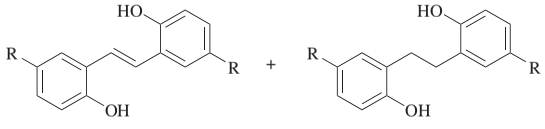
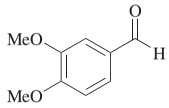
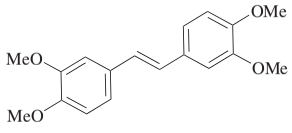
WCl_5, $LiAlH_4$, THF, rt, 6 h



R		(*E*)/(*Z*)
Cl	(65)	63:2
Me	(60)	57:3
MeO	(82)	76:6

45

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 	$W(CO)_6$, CH_2Cl_2, rt, 24 h	 R = Cl (62%) 36:26; R = Me (43%) 29:14; R = MeO (63%) 39:24	45
C_7 	1. $TiCl_4$, Zn, THF, heat, 1 h 2. Reflux, 6 h	 (76)	342
C_{7-13} 	1. $TiCl_4$, Zn, dioxane, reflux, 3 h 2. Reflux, 2 h	 **I** + **II** R = Br: **I** (83%), **II** (<1) R = Me: **I** (53%), **II** (30) R = *t*-Bu: **I** (50%), **II** (29) R = Ph: **I** (88%), **II** (2)	343
C_7 	1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. –10 to 0°, 5.5 h	 (65)	67

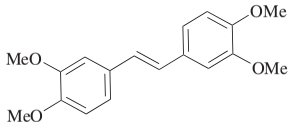
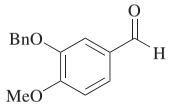
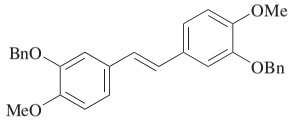
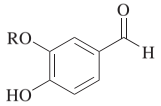
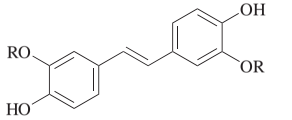
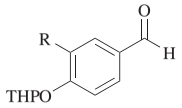
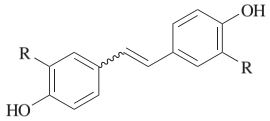
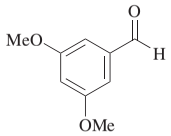
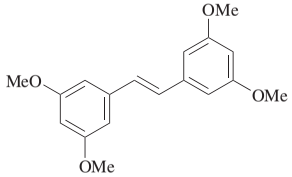
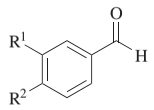
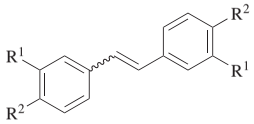
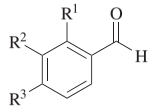
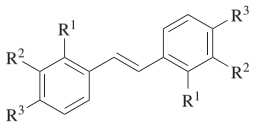
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 12 h		(65)	114
	$TiCl_4$, Zn, py, THF, reflux, 2 h		(93)	344
	1. $TiCl_4$, Zn, THF, reflux, 40 min 2. Reflux, 3–5 h		R H (—) Me (—)	345
	1. $TiCl_3$, Zn, THF, reflux, 3 h 2. Reflux		R H (65) MeO (68)	346
	$TiCl_4$, Zn, THF, heat		(—)	347

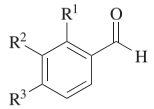
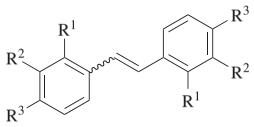
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 	1. WCl_6, BuLi, THF, –78° to rt, 20 min 2. rt, 6 h		2

R^1	R^2	
H	H	(76)
H	MeO	(47)
H	Cl	(57)
Cl	H	(28)
H	NC	(20)

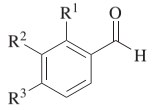
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	1. $TiCl_3$, Li, DME, reflux, 1.5 h 2. Reflux, 18 h		348

R^1	R^2	R^3	
Br	H	H	(71)
H	F	H	(95)
H	MeO	H	(81)
H	$–OCH_2O–$		(73)

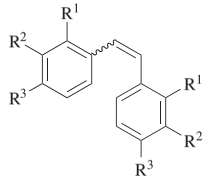
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 	1. $TiCl_3$, Zn/Cu, solvent, reflux, 1 h 2. Reflux, time		349

R^1	R^2	R^3	Solvent	Time (h)	
H	AcO	MeO	DME	16	(97)
H	AcO	H	DME	16	(87)
H	H	AcO	THF	17	(94)
H	MeO	AcO	THF	16	(87)
H	MeO_2C	MeO	THF	13	(74)
H	$MeO_2C(CH_2)_2O_2C$	MeO	DME	16	(60)
H	4-TsO	MeO	THF	16	(80)
4-TsO	MeO	H	THF	16	(92)

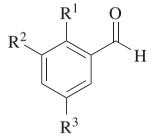
C_7



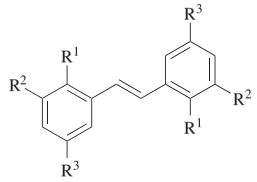
[bmim]Cl($AlCl_3$),[e] Zn, rt



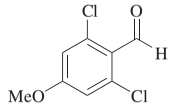
R^1	R^2	R^3	Time (min)		(*E*)/(*Z*)	
H	H	H	15	(81)	12:88	
H	HO	H	30	(79)	9:91	
H	H	HO	15	(85)	0:100	46
H	H	MeO	15	(72)	5:95	
HO	H	H	15	(79)	13:87	
Cl	H	H	15	(83)	7:93	
O_2N	H	H	15	(80)	15:85	



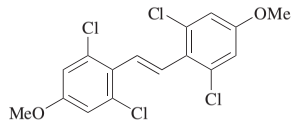
$TiCl_4$, Zn, dioxane, reflux, 3–5 h



R^1	R^2	R^3		
MeO	H	H	(71)	
H	MeO	H	(57)	350
H	MeO	MeO	(42)	

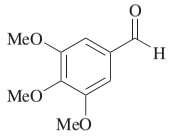
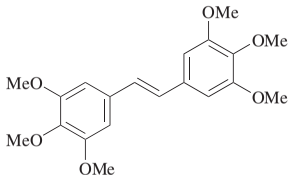
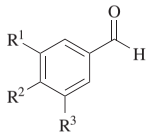
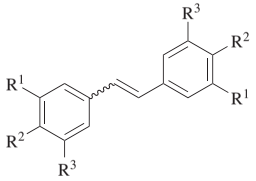
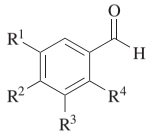
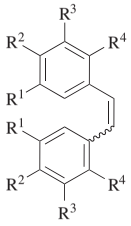


$TiCl_4$, Zn, dioxane, reflux



(55) 351

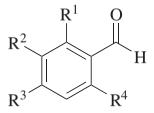
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. $TiCl_4$, Zn, py, dioxane, –10 to –5°, 30 min 2. Microwave irradiation, 8 min	 (95)	121
	$TiCl_3$, Zn, THF		352
	1. $TiCl_3$, Zn, THF, reflux, 3 h 2. Reflux, 22 h		346

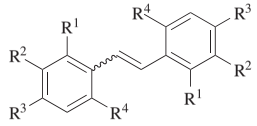
R^1	R^2	R^3	
H	HO	H	(—)
MeO	HO	H	(—)
HO	HO	H	(—)
HO	H	HO	(—)

R^1	R^2	R^3	R^4		(*E*)/(*Z*)
H	HO	H	H	(38)	30:70
MeO	HO	H	H	(36)	40:60
MeO	MeO	H	H	(72)	50:50
MeO	H	MeO	H	(70)	50:50
MeO	MeO	H	MeO	(74)	50:50

C_{7-10}



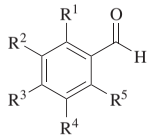
$Ti(Oi\text{-}Pr)_4$, Mg, Et_3N, TMSCl, 40°



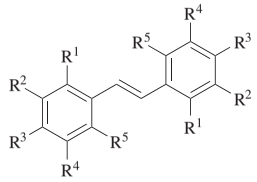
87

R^1	R^2	R^3	R^4	Time (h)		$(E)/(Z)$
H	H	H	H	48	(77)	87:13
MeO	H	H	H	72	(51)	91:9
H	H	MeO	H	24	(95)	99:1
H	H	Cl	H	72	(58)	61:39
H	MeO	MeO	H	48	(65)	94:6
H	H	Me	H	48	(85)	99:1
Me	H	Me	Me	24	(76)	90:10

C_{7-9}



1. $TiCl_4$, Zn/Cu (or Zn), THF
2. Reflux
3. Catalytic I_2, *o*-xylene, reflux[f]

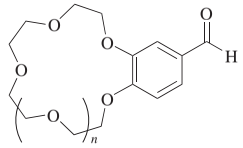
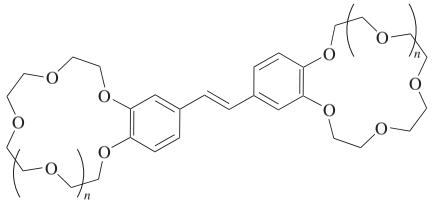
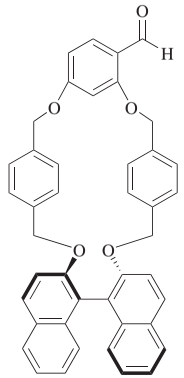
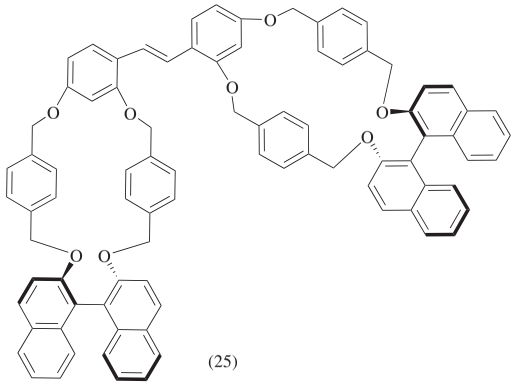


(56-76)

R^1	R^2	R^3	R^4	R^5
H	H	Cl	H	H
H	H	F	H	H
F	F	F	F	F
CF_3	H	H	H	H
H	H	NC	H	H
H	CF_3	H	CF_3	H

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TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. $TiCl_4$, Zn, py, THF, reflux, 30 min 2. Proton Sponge,[b] reflux, 5 h	 *n*: 1 (26); 2 (31)	354
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 12 h	 (25)	237

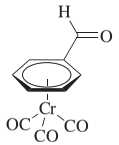
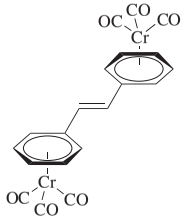
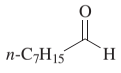
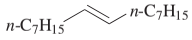
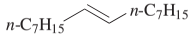
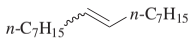
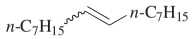
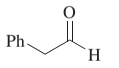
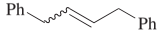
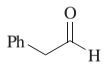
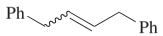
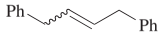
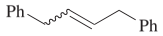
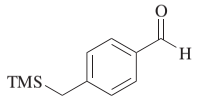
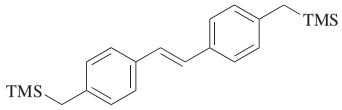
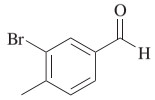
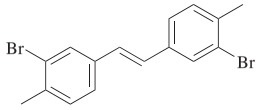
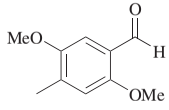
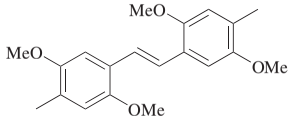
		$NbCl_3$(DME), THF, rt, 8 h		(78)	97
C_8					
		1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 3 h		(96)	73, 74
		1. $TiCl_4$, Hg/Mg, THF 2. 0°, 2 h; then reflux, 24 h		(72)	331
		1. $TiCl_3$, Li, THF, reflux, 3 h; then I_2, 5 min 2. rt, 8 h		(80)	115
		$InCl_3$, Zn, MeCN, reflux, 9 h		(72), (*E*)/(*Z*) = 70:30	104
		1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. rt, 4 h		(75)	67

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 6 h	 (76)	114
	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 16 h	 (23), (*E*)/(*Z*) = 90:10	355
	1. $TiCl_3$, Li, THF, reflux, 3 h; then, I_2, 5 min 2. rt, 4 h	 (79)	115
	1. $TiCl_4$, Zn, DME, reflux, 1 h 2. Reflux, 20 h	 (10.7)	356
	$TiCl_4$, Zn, THF, reflux, 4 h	 (58)	357
	1. $TiCl_3$, Li, DME, reflux, 2 h 2. Reflux, 16 h	 (34)	358

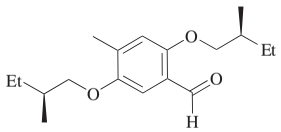
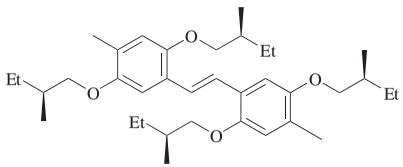
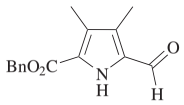
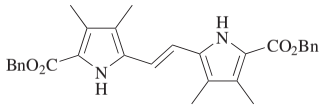
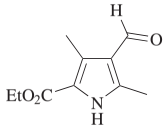
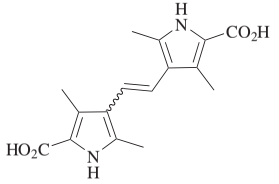
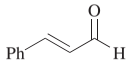
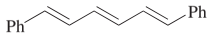
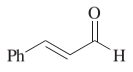
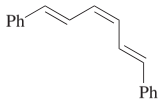
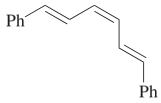
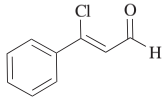
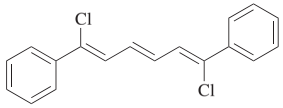
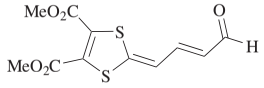
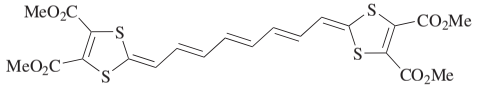
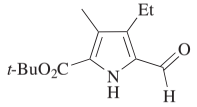
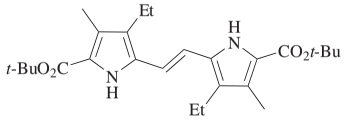
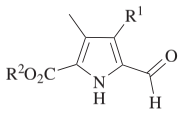
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 16 h		(31)	359
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 8 h		(81)	210
	$TiCl_4$, Zn, THF		(10)	211
C_9				
	1. $TiCl_4$, Zn, py, dioxane, –10 to –5°, 30 min 2. Microwave irradiation, 5 min		(83)	121

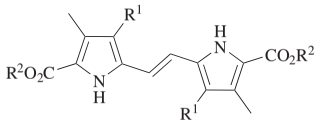
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	1. $NbCl_5$, MeLi, DME, 80°, 24 h 2. Reflux, 72 h	 (26)	96
	1. $NbCl_5$, K, DME, 80°, 30 min 2. Reflux, 1 h	 (55)	96
	1. $TiCl_4$, Zn, DME, reflux, 2 h 2. 0–5°, 30 min; then reflux, 3 h	 (79)	44
	1. $TiCl_3$, $LiAlH_4$, THF 2. Py, reflux, 2 h	 (20)	199
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 8 h	 (21.7)	210

C_{9-10}

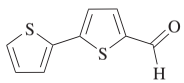


1. $TiCl_4$, Zn, THF, reflux, 30 min
2. Reflux, overnight

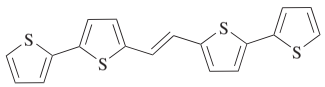


R^1	R^2		
Et	Et	(66)	
$EtO_2C(CH_2)_2$	Me	(75)	209
$EtO_2C(CH_2)_2$	Et	(68)	
$EtO_2C(CH_2)_2$	Bn	(74)	

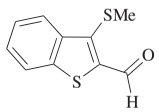
C_9



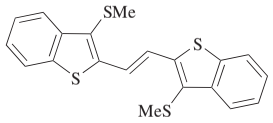
$TiCl_4$, Zn, THF, reflux, 4 h



(63) 324

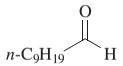


1. $TiCl_4$, Zn, py, THF, reflux, 1.5 h
2. Reflux, 9.5 h



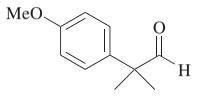
(95) 328

C_{10}

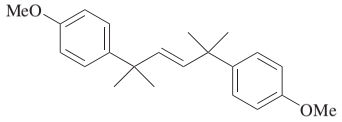


1. $TiCl_3$, K, THF, reflux, 40 min
2. Reflux, 16 h

(60) 27

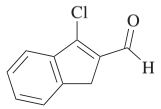
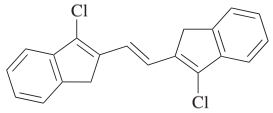
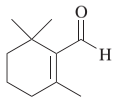
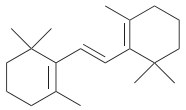
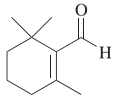
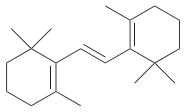
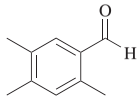
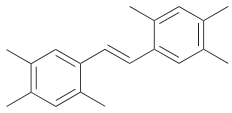
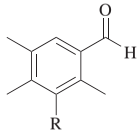
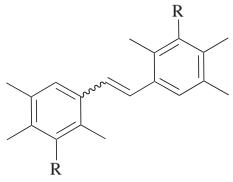


1. $TiCl_4$, Zn, THF, py, reflux, 1 h
2. Reflux, 2 h; then addition of aldehyde; then reflux, 40 h

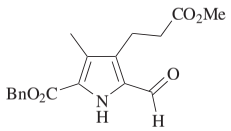


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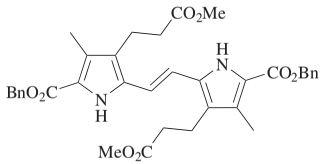
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. $TiCl_4$, Zn, DME, reflux, 2 h 2. 0–5°, 1 h; then rt, 2 h; then reflux, 2 h	 (60)	44
	1. $TiCl_4$, $LiAlH_4$, THF, reflux, 20 min 2. Tertiary amine, reflux, 3 h	 Tertiary amine: n-Bu_3N (90); Proton Sponge[b] (94)	110
	1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h	 (90)	361
	$TiCl_4$, Zn, THF, reflux, 16 h	 (74)	362
C_{10-11}			
	$TiCl_4$, Zn	 R: H (—); Me (—)	363

C_{10}

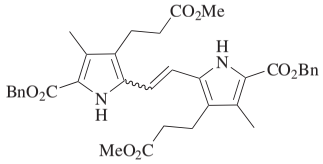


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 8 h



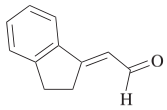
(45.8) 210

$TiCl_4$, Zn, THF

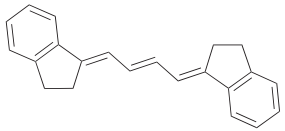


(86), (*E*)/(*Z*) = 4:1 211

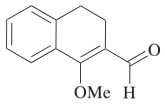
C_{11}



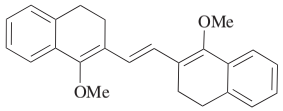
1. $TiCl_3$, $LiAlH_4$, THF, rt, 40 min
2. Reflux, 4.5 h



(45) 364

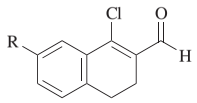
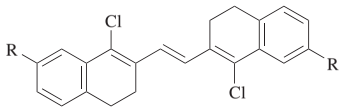
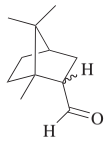
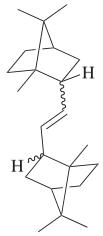
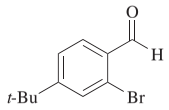
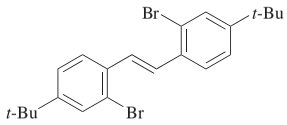
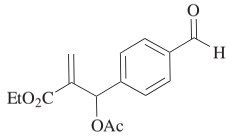
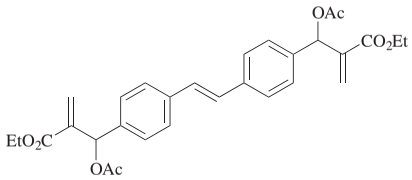


$TiCl_4$, Zn, DME



(—) 365

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	1. $TiCl_4$, Zn, DME, reflux, 2 h 2. 0–5°, 30 min; then reflux, 4 h	 R: H (92); Br (84)	44
	$TiCl_3$, Li, THF, reflux, 40 h	 (79) ~90:10[g]	366
	$TiCl_4$, Zn, THF, reflux, 4 h	 (97)	367
	$TiCl_4$, Zn, THF, –10° to reflux, 4 h	 (86)	123

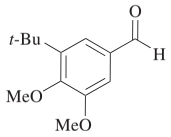
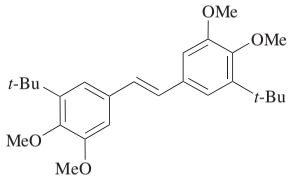
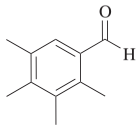
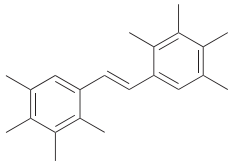
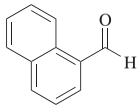
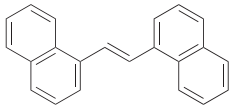
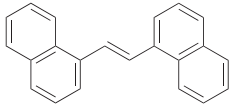
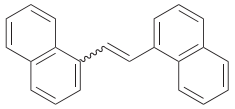
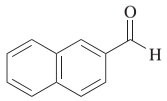
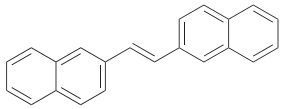
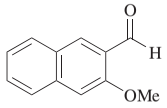
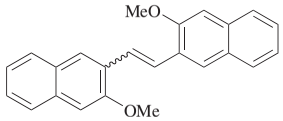
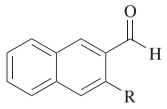
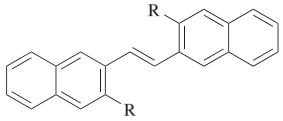
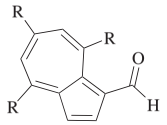
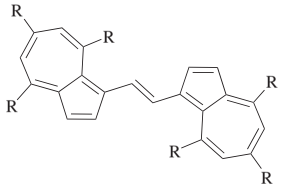
	1. $TiCl_4$, Zn, THF, reflux 2. Reflux, 24 h		(58)	368
	$TiCl_4$, Zn, THF, reflux, 16 h		(64)	362
	1. $TiCl_3$, Li, DME, reflux, 3 h 2. Reflux, 3 h		(21)	197
	1. $TiCl_4$, Zn/Cu, THF 2. Reflux, 3 h		(90)	369
	1. $TiCl_3(THF)_3$, Na/Al_2O_3, THF, reflux, 1 h 2. Reflux, 30 min		(60) dr 95:5	69

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	1. $TiCl_3$, Li, DME, reflux, 3 h 2. Reflux, 3 h	 (33)	197
	$Ti(Oi\text{-}Pr)_4$, Mg, TMSCl, Et_3N, THF, 40°, 48 h	 (49), (*E*)/(*Z*) = 65:35	87
	1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Reflux, 10 h	 R: MeS (80); MeSe (77)	318
C_{11-14}			
	1. $TiCl_3$, Li, DME, reflux, 3 h 2. Reflux, 3 h	 R: H (68); Me (40)	197

C_{11}

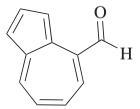
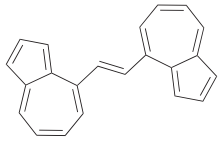
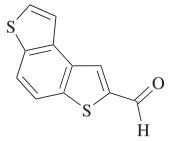
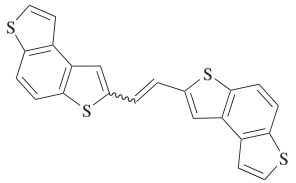
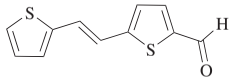
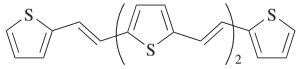
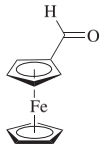
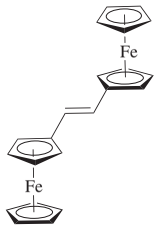
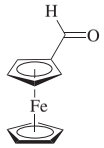
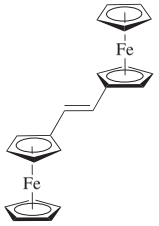
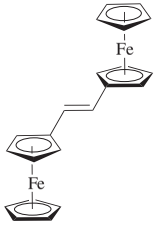
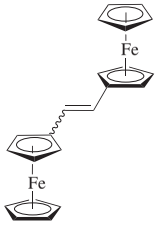
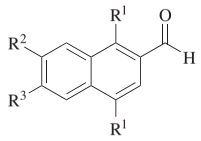
	1. $TiCl_3$, Li, DME, reflux, 3 h 2. Reflux, 3 h		(61)	197
	1. $TiCl_4(THF)_2$, Zn, THF, reflux, 2 h; then py, 30 min 2. Reflux, 7 h		(97)	370
	$TiCl_4$, Zn, THF, reflux, 4 h		(97)	326
	$TiCl_4$, Zn, THF, reflux, 4 h		(76)	371

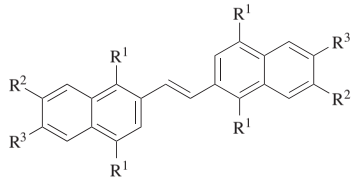
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	$TiCl_4$, Zn	 (40)	47
	Zn, TMSCl, THF, 0°, 2 h	 (75)	92
	1. $TiCl_3$, $LiAlH_4$, THF, 0°, 0.5 h 2. rt, 3 h	 (25), (*E*)/(*Z*) = 3.5:1	205

C_{12-13}

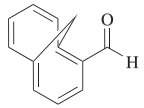


$TiCl_3$, $LiAlH_4$, THF

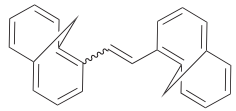


R^1	R^2	R^3		
H	Me	H	(—)	140
H	H	Me	(—)	
Me	H	H	(—)	

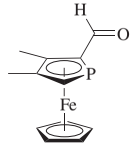
C_{12}



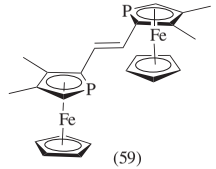
$TiCl_4$, Zn, py, THF, reflux, 20 min



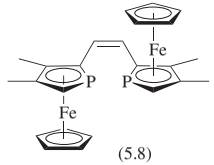
(83) 372



$TiCl_3(DME)_{1.5}$, Zn/Cu, py, DME, reflux 30 min

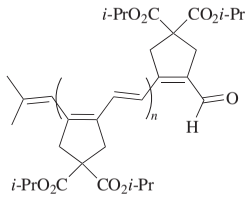
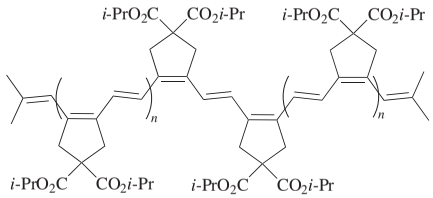


(59) +



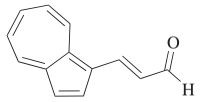
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TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

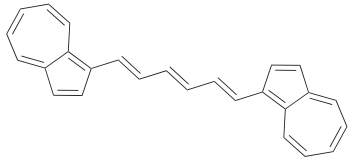
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-30} 	1. $TiCl_4$, Zn, DME, reflux, 2 h 2. rt, 12 h; then reflux, 1 h		198

n	
0	(61)
1	(82)
2	(25)

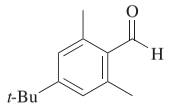
C_{13}



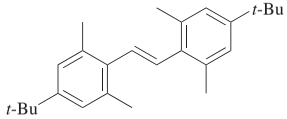
1. $TiCl_3$, Li, DME, reflux, 3 h
2. Reflux, 3 h



(33) 197



1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h;
2. Reflux, 6 h



(75) 374

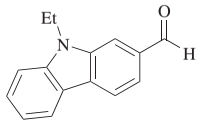
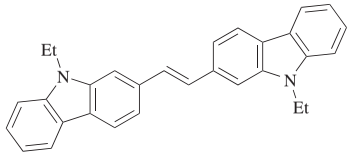
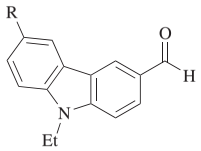
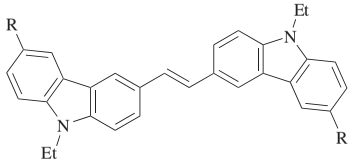
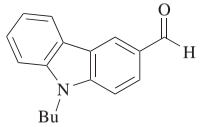
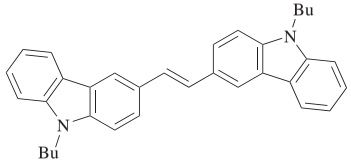
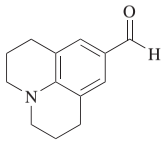
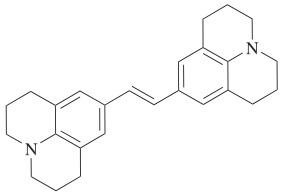
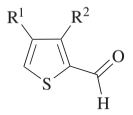
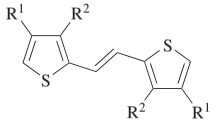
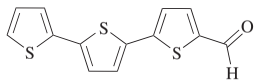
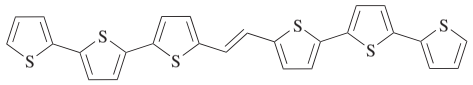
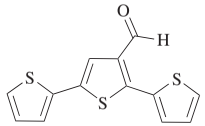
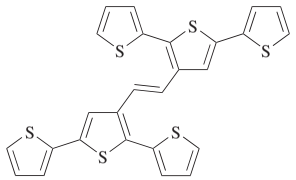
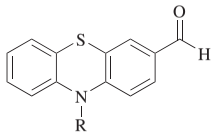
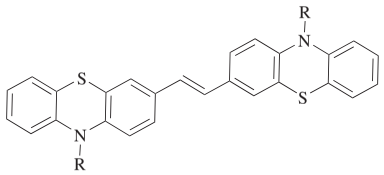
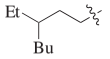
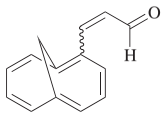
	1. $TiCl_4$, Zn, THF, 1 h 2. Reflux, 4 h		(88)	375
	$TiCl_4$, Zn, THF, reflux, 4 h		R H (90) Br (85)	376
	1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 1 h 2. Py, reflux, 10 h		(58)	377
	$TiCl_4$, Zn, THF, reflux, 2 h		(—)	337

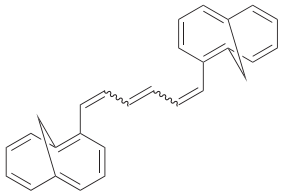
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	1. $TiCl_4$, Zn, THF 2. Reflux, 2 h	 R^1 R^2 H n-C_8H_{17} (89) n-C_4H_9 n-C_4H_9 (67)	218 378
	$TiCl_4$, Zn, THF, reflux, 6 h	 (68)	324
	1. $TiCl_4$, Zn, THF, reflux, 15 min 2. Reflux, 17 h	 (66)	216
	1. $TiCl_4$, Zn, THF, 1 h 2. Reflux, 4 h	 R 4-$MeOC_6H_4$ (45)  (34)	375

C_{14}

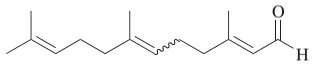


$TiCl_4$, Zn, py, THF, reflux, 20 min

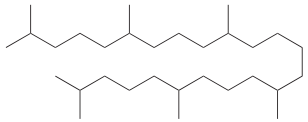


(52) 372

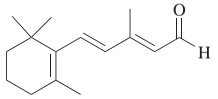
C_{15}



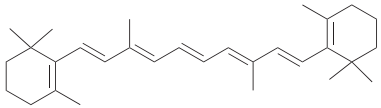
1. Pd/C, H_2, EtOH
2. $TiCl_4$, Mg/Hg, THF, rt, 12 h
3. H_2, Pd/C, EtOH



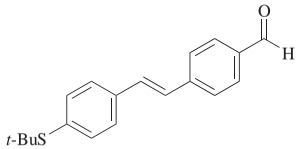
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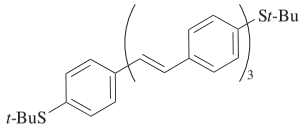
1. $TiCl_4$, Zn, CH_2Cl_2, rt, 30 min
2. rt



(33) 202

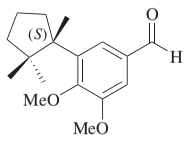
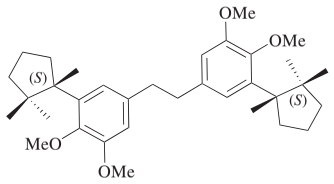
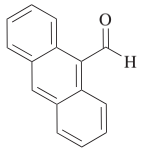
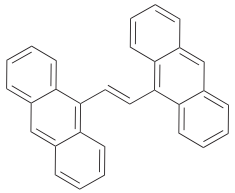
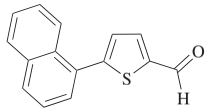
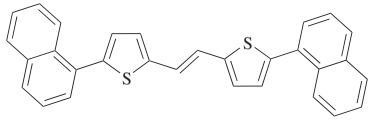
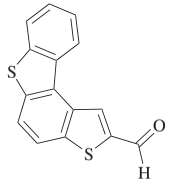
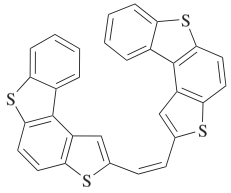


1. $TiCl_4$, Zn, THF, 0°
2. Reflux, 6 h

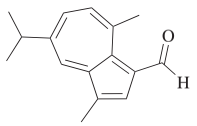


(48) 380

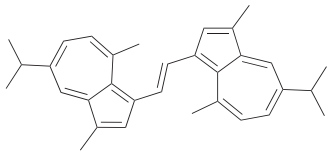
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	1. $TiCl_4$, Zn, THF, reflux 2. Reflux, 24 h 3. H_2, Pd/C, EtOH	 (67)[h]	368
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 30 min 2. Reflux, 20 h	 (53)	381
	$TiCl_4$, Zn, THF, –18°, 1 h; then reflux, 4 h	 (60)	382
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Py, reflux, overnight	 (quant)	383

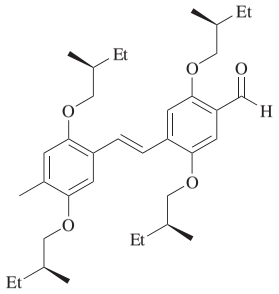
C_{16}



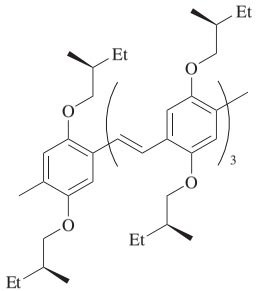
1. $TiCl_3$, Li, DME, reflux, 3 h
2. Reflux, 3 h



(70) 197

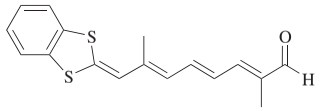


1. $TiCl_4$, Zn, THF, reflux, 1 h
2. THF/DMF, reflux, 16 h

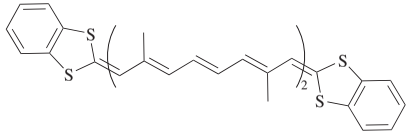


(41) 359

C_{17}



1. $TiCl_4$, Zn/Cu, THF, reflux, 45 min
2. Reflux, 30 min; then addition of aldehyde; then reflux, 2 h

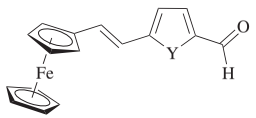


(4) 384

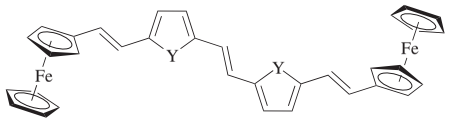
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17-35}	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Py, reflux, time		
		m *n* Time (h) 0 0 12 (74) 0 0 overnight (83) 1 2 12 (86) 1 2 overnight (70)	385, 384 387 385, 386 387
C_{17}	1. $TiCl_4$, Zn, THF 2. Reflux, 2 h	(41)	218
	$TiCl_4$, Zn, dioxane, reflux, 2 h	(40)	326
C_{17-29}	$TiCl_4$, Zn, THF, 65°, 1.5 h	*n* 1 (47) 2 (37.5)	388

C_{17}

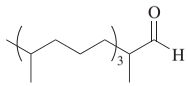


$TiCl_4$, Zn, THF, reflux, 3 h

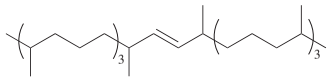


Y		
O	(86)	389
S	(92)	

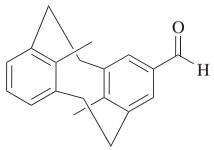
C_{19}



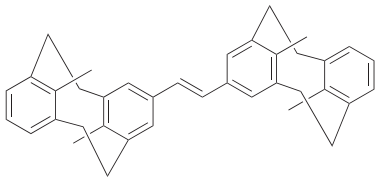
1. $TiCl_3$, Li, DME, reflux, 1 h
2. Reflux, 24 h



(59) 390

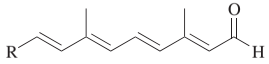


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h
2. rt

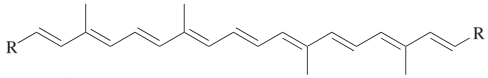


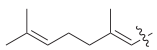
(45) 391

C_{20}



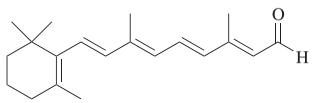
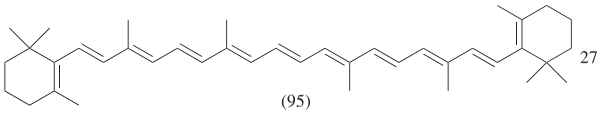
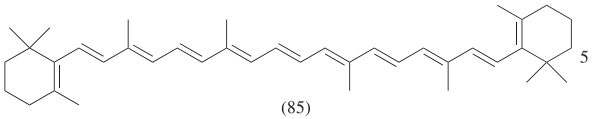
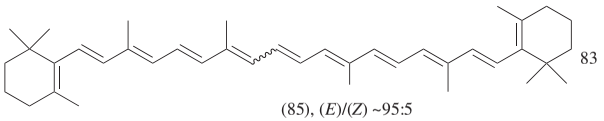
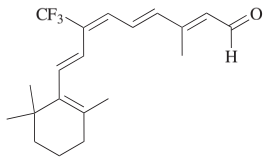
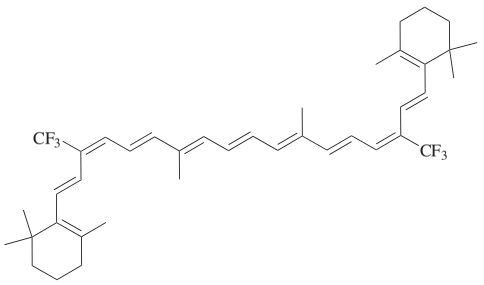
1. $TiCl_3$, $LiAlH_4$, THF, rt, 2 h
2. rt, overnight

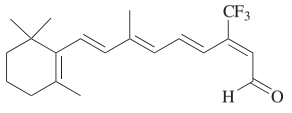


R	
	(75)
	(84)

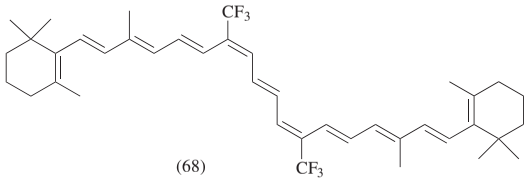
201

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	1. $TiCl_3$, Li, DME, reflux, 1 h 2. Reflux, 16 h	 (95)	27
	1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h	 (85)	5
	1. Ti powder, TMSCl, DME, reflux, 67 h 2. Reflux, 45 min	 (85), (*E*)/(*Z*) ~95:5	83
	$TiCl_4$, Zn, THF/CH_2Cl_2, 2 h	 (95)	122

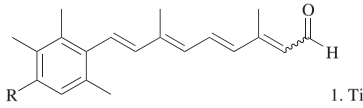


$TiCl_4$, Zn, THF/CH_2Cl_2, 2 h

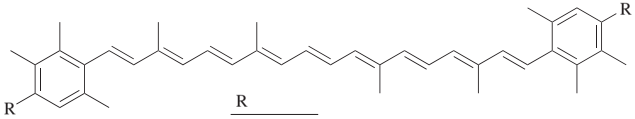


(68)

122



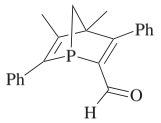
1. $TiCl_3$, $LiAlH_4$, THF, rt, 2 h
2. rt, overnight



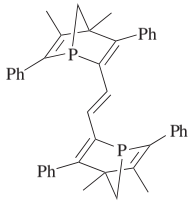
R	
H	(85)
MeO	(75)

203

C_{21}



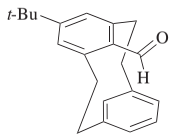
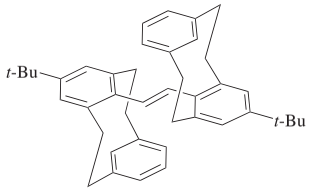
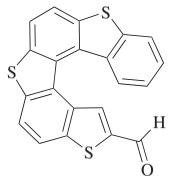
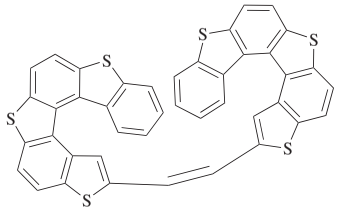
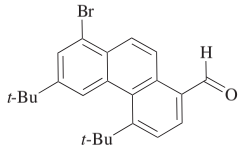
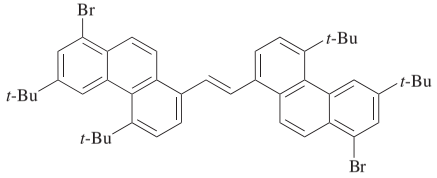
1. $TiCl_4$, Zn, THF, reflux, 1.5 h
2. Reflux, 1 h

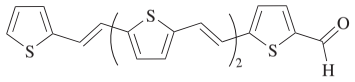


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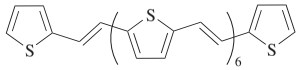
392

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

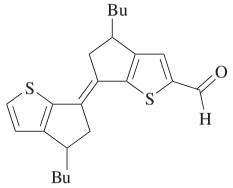
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2h 2. Reflux, 6 h	 (78)	374
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Py, reflux, overnight	 (quant)	383
C_{23}			
	1. $TiCl_4$, Zn, THF, 0° 2. Reflux, 8 h	 (78)	367



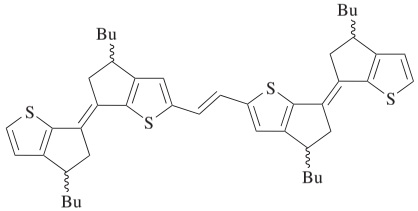
$TiCl_4$, Zn, dioxane



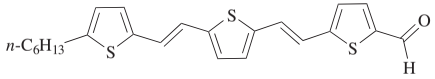
(5) 326



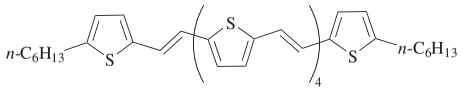
1. $TiCl_4$, Zn, THF, reflux, 30 min
2. Reflux, 1.5 h



(69) 393

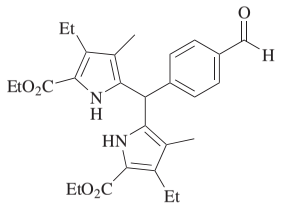
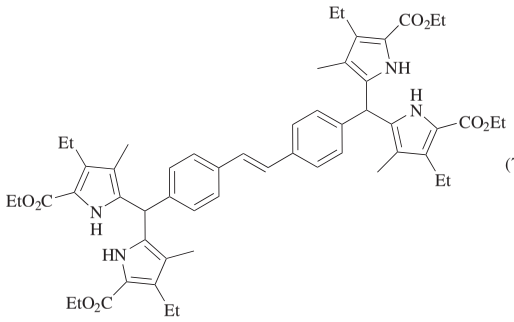
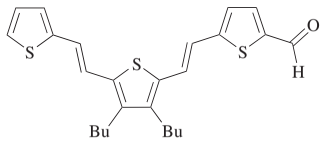
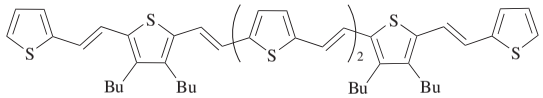
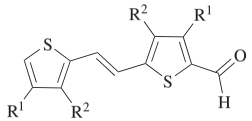
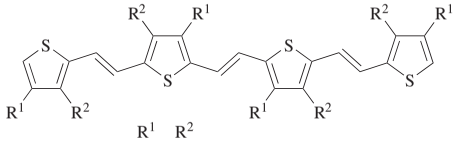


1. $TiCl_4$, Zn, THF
2. Reflux, 2 h



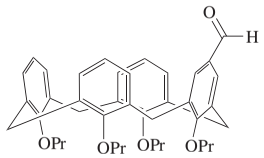
(21) 218

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

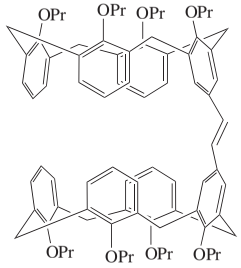
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 1 h	 (76)	394, 395
C_{25} 	1. $TiCl_4$, Zn, THF 2. Reflux, 2 h	 (25)	218
C_{27} 	1. $TiCl_4$, Zn, THF 2. Reflux, 2 h		

R^1	R^2		
H	n-C_8H_{17}	(71)	218
Bu	Bu	(78)	378

C_{29}

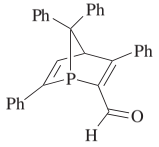


1. $TiCl_3$, Zn, THF
2. Reflux, addition of aldehyde over 2 h; then reflux, 15 h

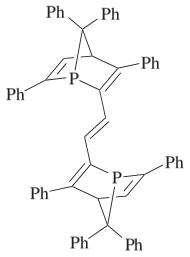


(35) 241

C_{31}

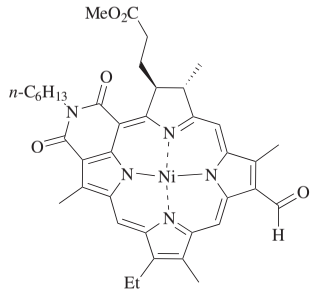
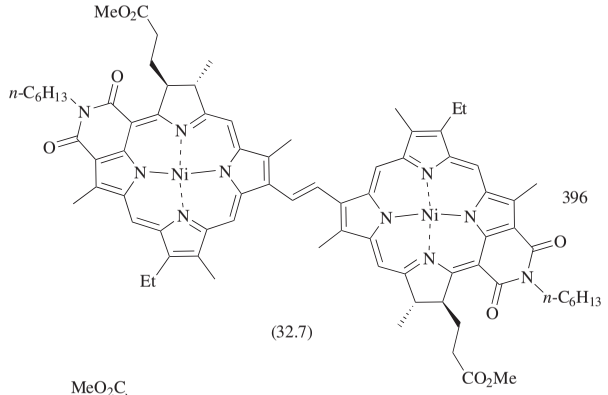
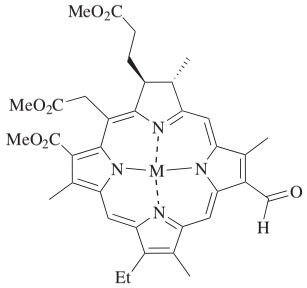
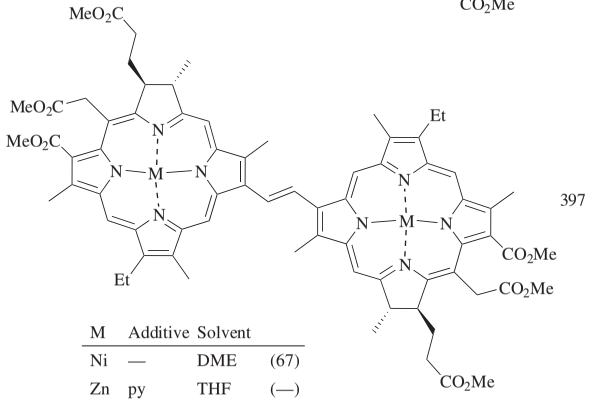


$TiCl_4$, Zn, THF, rt



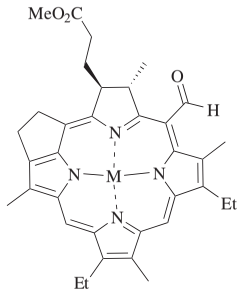
(—) 392

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

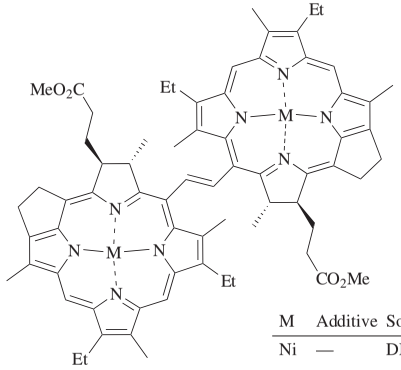
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{32} 	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 45 min	 (32.7)	396
C_{33} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, additive, solvent, reflux, 2 h 2. Reflux, 3 h		397

M	Additive	Solvent	
Ni	—	DME	(67)
Zn	py	THF	(—)

C_{34}

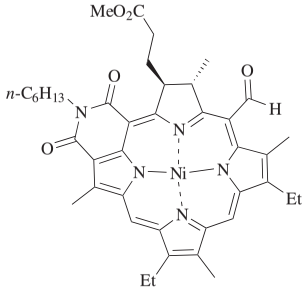


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, additive, solvent, reflux, 2 h
2. Reflux, 3 h

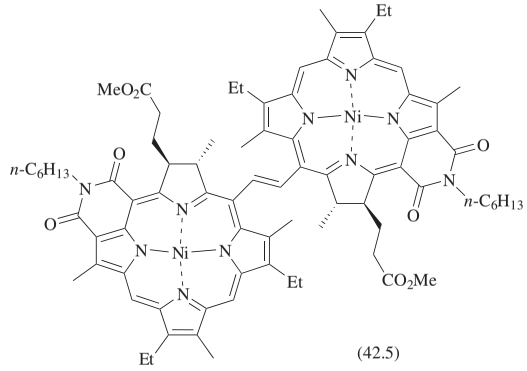


M	Additive	Solvent	
Ni	—	DME	(72)
Zn	py	THF	(—)

397



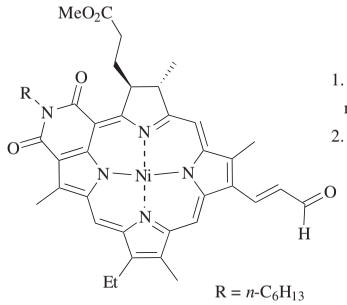
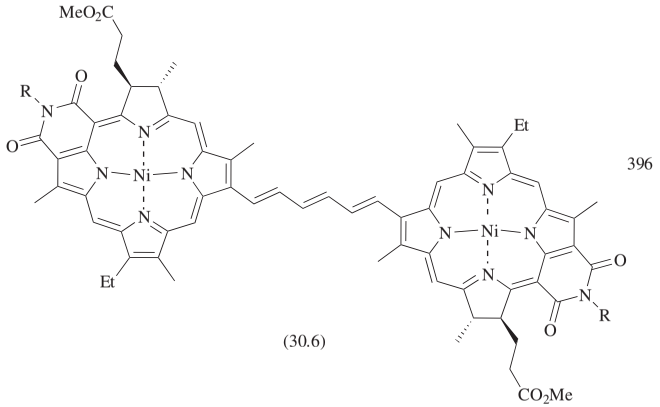
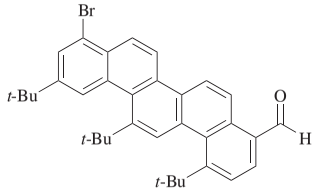
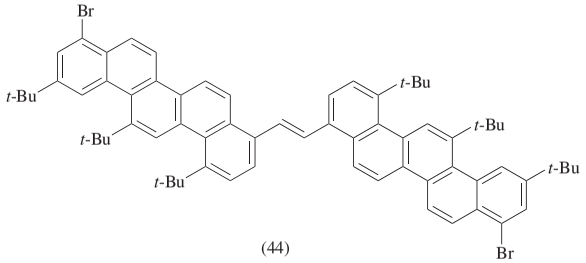
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 45 min

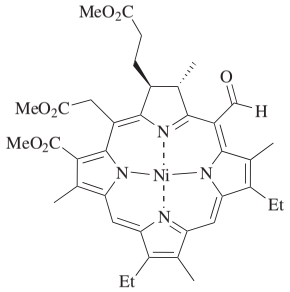


(42.5)

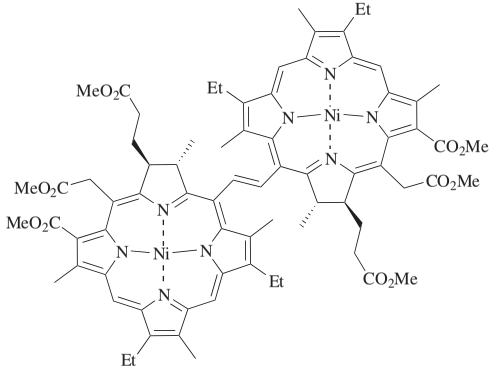
396

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{34}  R = *n*-C_6H_{13}	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 30–45 min	 (30.6)	396
C_{35} 	1. $TiCl_4$, Zn, THF, 0° 2. Reflux, 8 h	 (44)	367

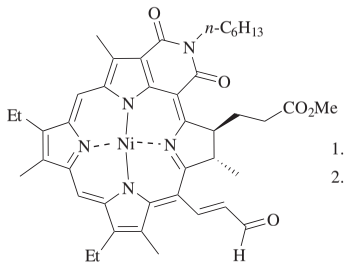
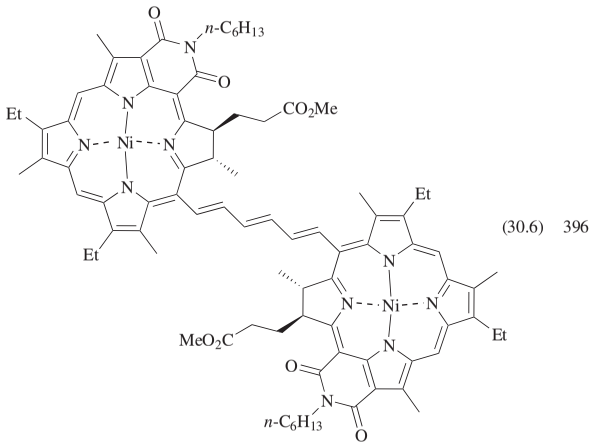


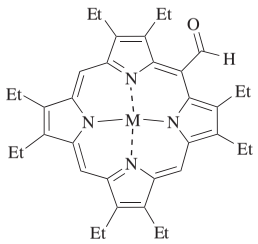
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 3 h



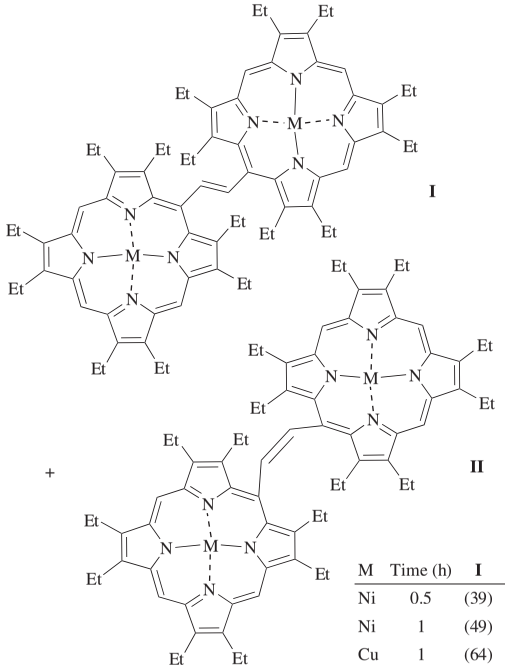
(52) 397

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{36} 	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 45 min	 (30.6)	396



1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h
2. Reflux, time



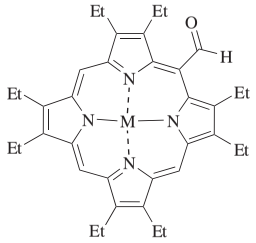
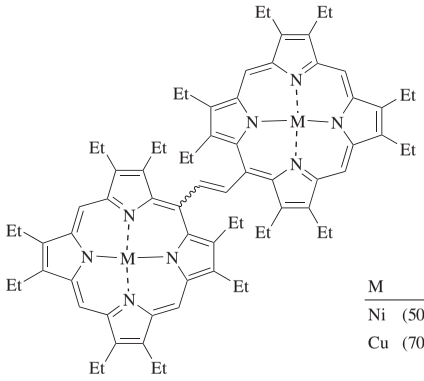
I

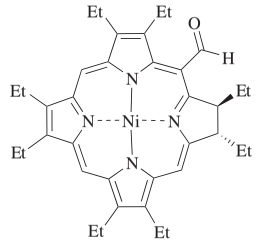
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II

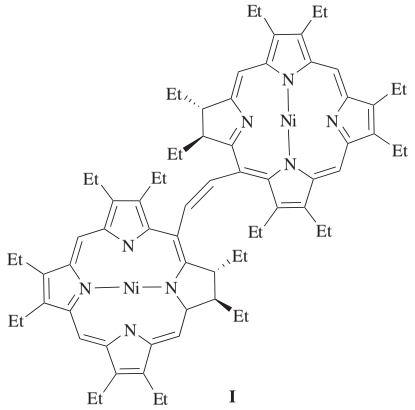
M	Time (h)	**I**	**II**	
Ni	0.5	(39)	(33)	214
Ni	1	(49)	(0)	215
Cu	1	(64)	(0)	215

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{37} 	—	 M (50) (*E*)/(*Z*) = Ni —; Cu 0:100	49



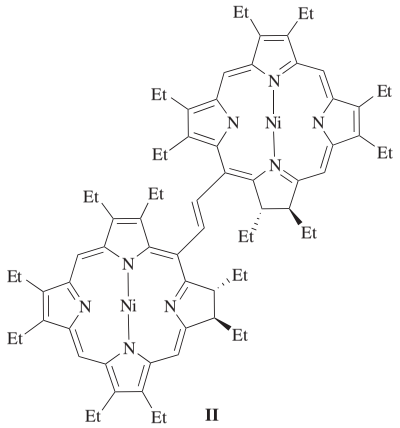
"low-valent titanium-induced coupling"



I

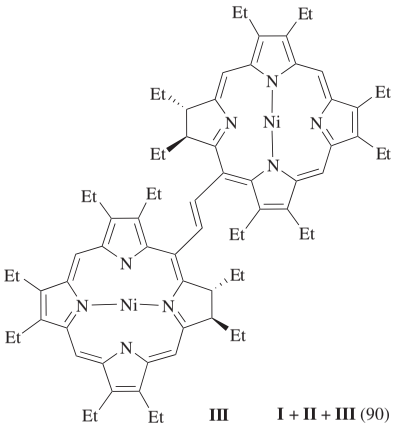
398

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II

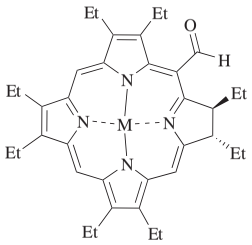
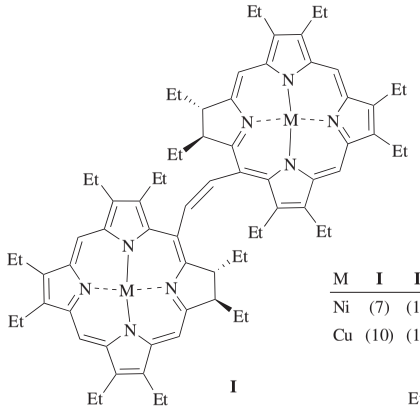
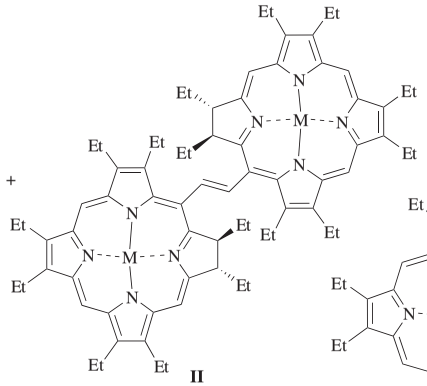
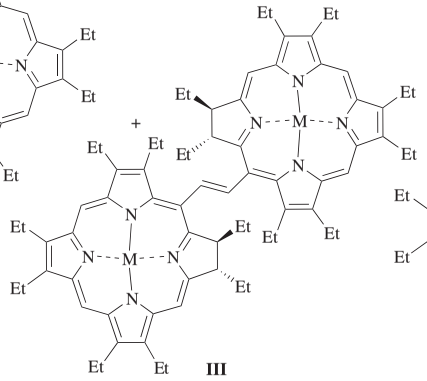
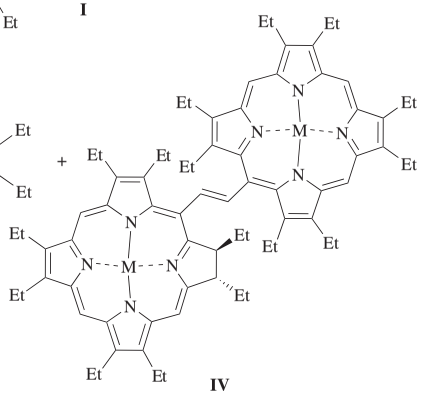
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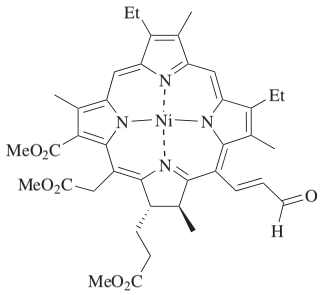


III

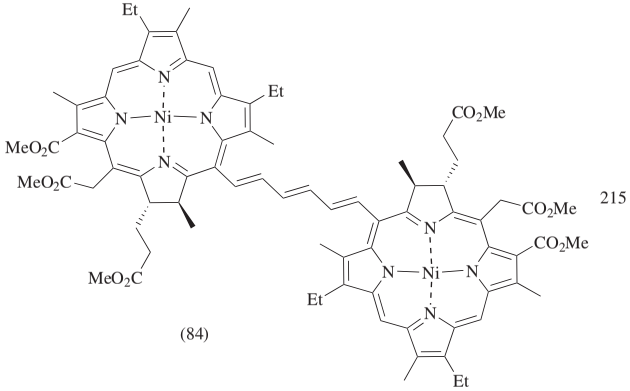
I + **II** + **III** (90)

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{37} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 30 min	 **I** +  **II** +  **III** +  **IV** **M** **I** **II** **III** **IV** Ni (7) (11) (52) (11) Cu (10) (10) (8) (0)	50



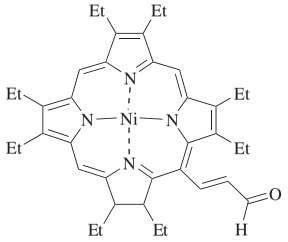
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 45 min



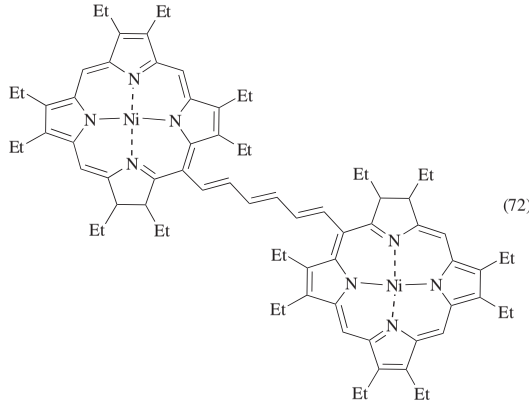
(84)

215

C_{39}



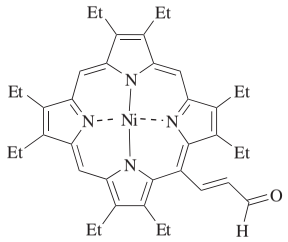
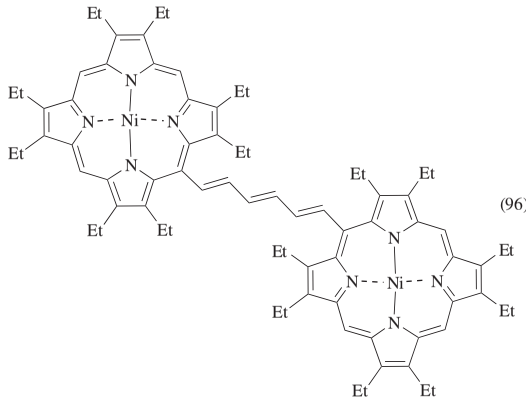
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 1 h

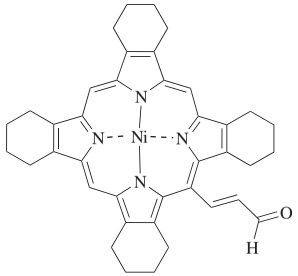


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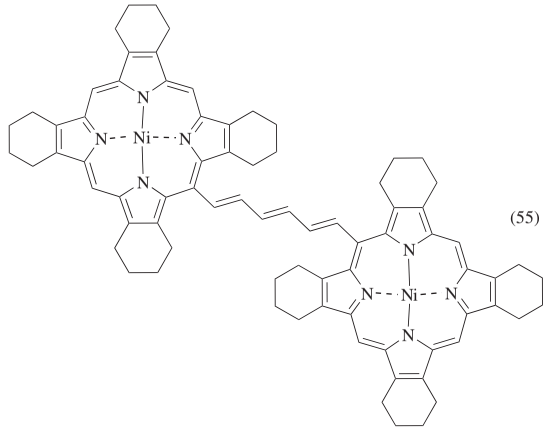
215

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{39} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 45 min	 (96)	215, 215a

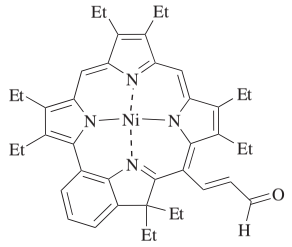
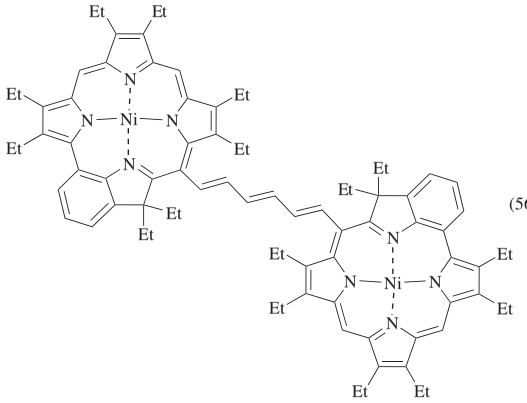


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 1 h

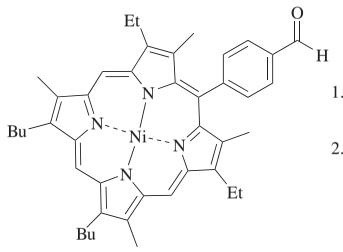


(55) 215

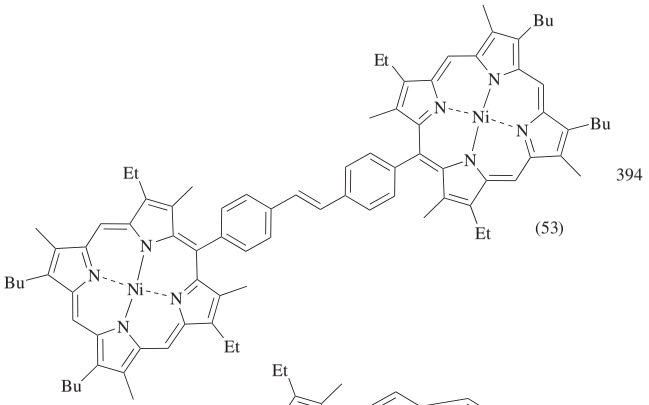
TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{42} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 1 h	 (56)	215

C_{43}



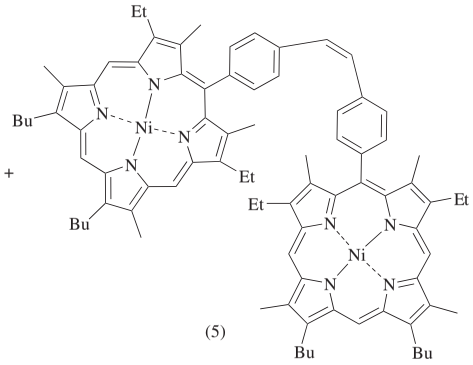
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 3 h



394

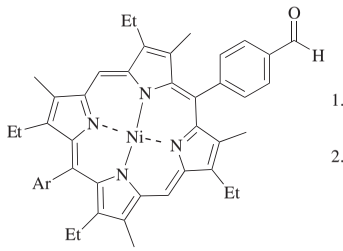
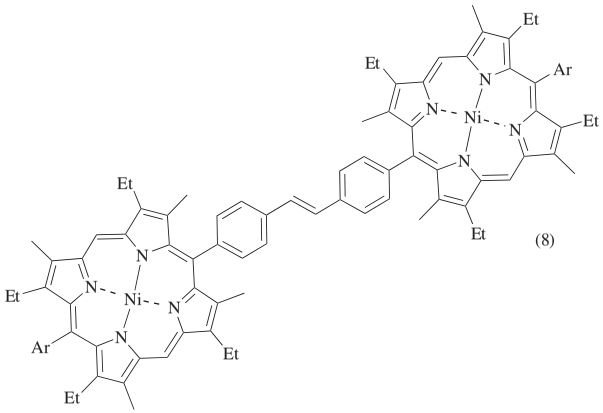
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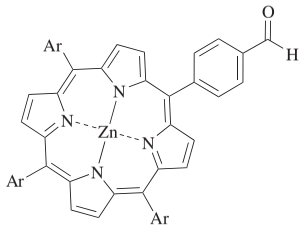


(5)

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

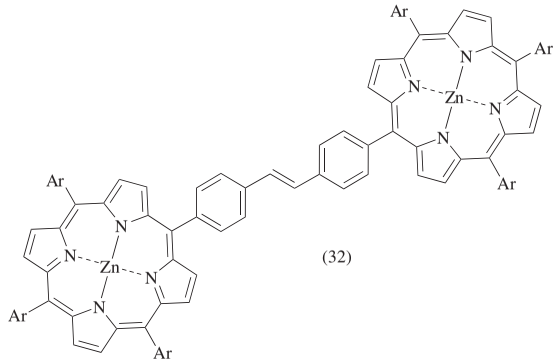
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{45}  Ar = 2,5-$(MeO)_2C_6H_3$	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 3 h	 (8)	394

C_{48}



Ar = 4-MeC_6H_4

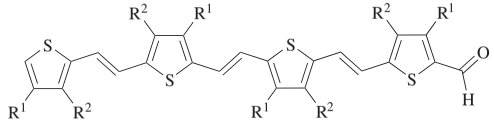
$TiCl_4$, Zn, THF, 0°



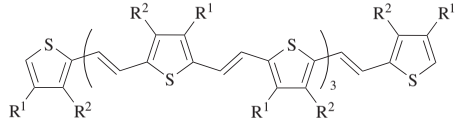
(32)

399

C_{55}



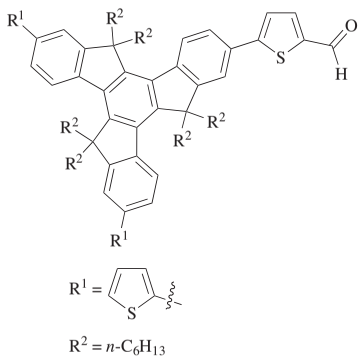
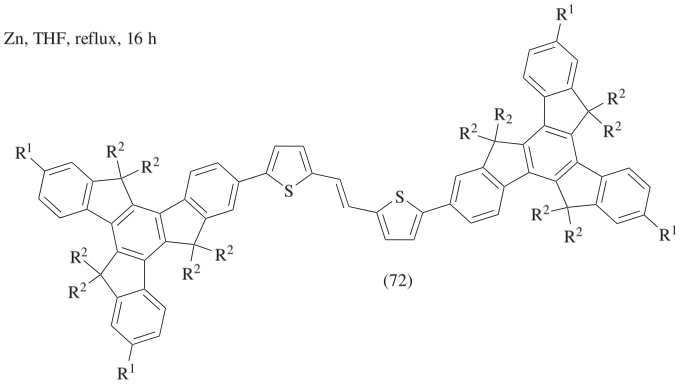
1. $TiCl_4$, Zn, THF
2. Reflux, time



218

R^1	R^2	Time (h)	
H	*n*-C_8H_{17}	2	(25)
Bu	Bu	12	(52)

TABLE 1A. HOMOCOUPLING OF ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{76}  R^1 = $R^2 = n\text{-}C_6H_{13}$	$TiCl_4$, Zn, THF, reflux, 16 h	 (72)	400

[a] The yield is after hydrogenation of the double bond.

[b] The Proton Sponge is *N,N,N,N*-tetramethyl-1,8-diaminonaphthalene.

[c] The electroreduction was carried out at V ≤ –1900 mV/SCE.

[d] The McMurry coupling product is an intermediate along the path to this product.

[e] [bmim]Cl($AlCl_3$) is 1-butyl-3-methylimidazolium chloroaluminate.

[f] The *Z*-isomer was isomerized to the *E*-isomer.

[g] The ratio of the *endo-endo* (*E*)-isomer to other isomers is given.

[h] Optically active starting material was employed.

TABLE 1B. HOMOCOUPLING OF KETONES

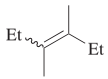
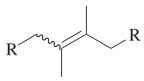
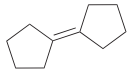
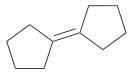
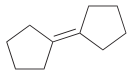
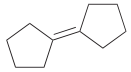
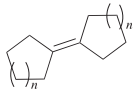
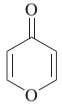
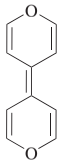
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3			
	1. $TiCl_3(THF)_3$, Mg, THF, 40°, 1 h 2. 40°, 1.5 h	 (98)	4
$C_{4–7}$			
	$TiCl_4$, Zn	 R = Et (65), 1.1:1 (*E*)/(*Z*) Pr (61), 1.4:1 *i*-Pr (46), 1.5:1 *t*-$BuCH_2$ (48), 4:1	47
C_4			
	1. WCl_6, BuLi, THF, –78° to rt, 20 min 2. rt, 6 h	 (10)	2
$C_{5–7}$			
	1. $TiCl_4$, Zn, py, solvent, 0° 2. Reflux, 20 h	 R = Et, dioxane (61), ~1:3 dr *t*-Bu, THF (48), 4:1	111
$C_{5–15}$			
	1. $TiCl_4$, Zn, py, THF, 0° 2. Reflux, 20 h	 R = Et (62) Bn (80)	111

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 2 h	 (68)	114
	1. $TiCl_3$, K, THF, reflux, 40 min 2. Reflux, 16 h	 (40)	27, 62
	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 10 h	 (83)	74
	$TiCl_4$, Hg/Mg, THF, 0°, 2 h; then reflux, 24 h	 (80)	331
C_{5-6}			
	1. $TiCl_3$, Li, THF, reflux, 3 h; then I_2, 5 min 2. rt, time		115

n	Time (h)	
1	6	(71)
2	5	(88)

C_5			
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux, 4 h	 (69)	200

C_6

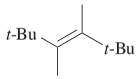
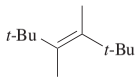
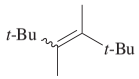
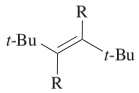
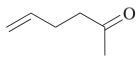
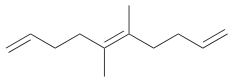
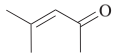
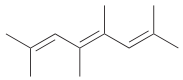
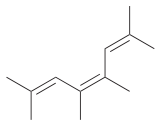
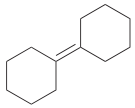
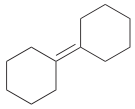
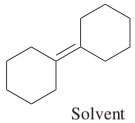
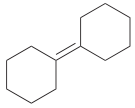
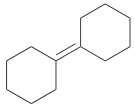
	$TiCl_4$, Zn		(62)	47
	$TiCl_3$, Zn, THF, reflux, 30 h		(65)	181
	1. $TiCl_3$, $LiAlH_4$, THF, –78 to 0° 2. Reflux, 24 h		(62), (*E*)/(*Z*) = 1:1	401
	$TiCl_3$, $LiAlH_4$		R: Me (—); CD_3 (—)	402
	$W_2(OCH_2CMe_3)_6(py)_2$, hexane, 22°, 2–24 h		(21)	99, 100
	1. $TiCl_4$, Mg, –60° to rt, 3–4 h; then rt, 20 h 2. Reflux, 10 h		(60) +  (25)	129

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	1. $TiCl_3$, M, solvent, reflux, time 2. Reflux, 16 h	 M Solvent Time Li DME 1 h (79) K THF 40 min (85)	27 27, 62
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 2 h	 (70)	114
	1. $TiCl_3$, C_8K, solvent, temp 1, time 1 2. Temp 2, time 2	 Solvent Temp 1 Time 1 (h) Temp 2 Time 2 (h) THF 70–75° 3 70–75° 12 (79) THF reflux 1.5 reflux 10 (83) DME reflux 2 reflux 12 (58)	72 73 84
	$TiCl_3$, Zn, DME, reflux, 21 h	 (57)	7
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 8 h	 (97)	6

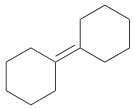
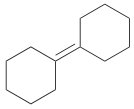
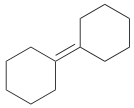
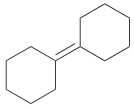
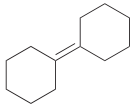
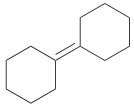
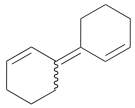
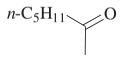
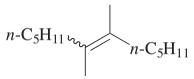
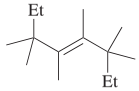
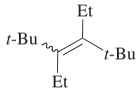
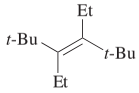
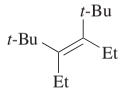
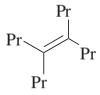
1. $ZrCl_4$, Li, DME, rt, 1 h 2. Reflux, 10 h		(43)	93
1. $TiCl_4$, C_8K, THF, reflux, 1.5 h 2. Py, reflux, 10 h		(75)	73
1. $TiCl_4$, Zn, py, dioxane, –10 to –5° 2. Microwave irradiation, 10 min		(52)	121
$TiCl_4$, Hg/Mg, THF, 0°, 2 h; then reflux, 24 h		(70)	331
$AlCl_3$, Zn, MeCN, reflux, 17 h		(86)	88
WCl_5, $LiAlH_4$, THF, rt, 6 h		(55)	45

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	1. $TiCl_4$, Zn, py, THF 2. Reflux, 30 min	 (65), (*E*)/(*Z*) = 57:43	403
C_7			
	1. $NbCl_5$, $NaAlH_4$, THF/benzene, 0°, 10 min 2. Reflux, 3 h	 (33)	95
	$TiCl_4$, Zn	 (12)	47
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1 h 2. Reflux, 45 h	 (47), (*E*)/(*Z*) = 12:1[a]	182
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1 h 2. Reflux, 66 h	 (8.7) +  (0.4)	404
	1. $TiCl_3$, Li, THF, reflux, 3 h; then I_2 2. rt, 8 h	 (59)	115

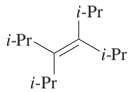
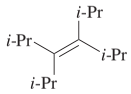
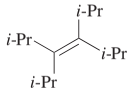
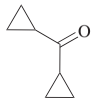
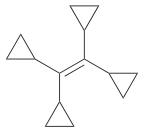
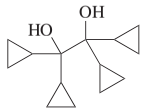
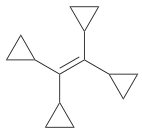
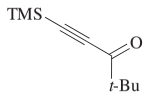
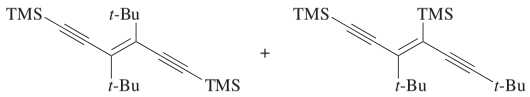
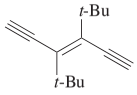
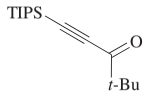
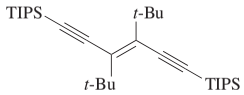
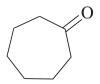
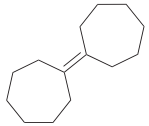
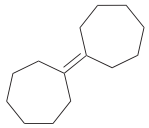
	1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. rt, 8 h		(59)		67
	1. $TiCl_3$, K, THF, reflux, 40 min 2. Reflux, 16 h		(37)		27, 62
	$TiCl_3(DME)_{1.5}$, Zn/Cu		(87)		6
	1. $TiCl_3/LiAlH_4$,[b] THF, 0°, 1.5 h 2. 0°, addition of ketone over 2 h; then 45°, 2 d		(15)	+ 	(7) 183
	1. $TiCl_4$, Zn, py, THF, 0° 2. Reflux, 20 h		(25)		111

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	$TiCl_4$, Zn	 **I** + **II** **I** + **II** (15–20), **I/II** = 2:1	405
	1. $TiCl_4$, Zn, py, THF 2. Reflux, 10 h	 (15)	406
	$TiCl_4$, Zn, py, THF, 0°, 30 min; then rt, 2h	 (62)	405
	1. $TiCl_3$, M, solvent, reflux, time 2. Reflux, 16 h		27

M	Solvent	Time	
Li	DME	1 h	(85)
K	THF	40 min	(86)

	1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h	 (95)	5

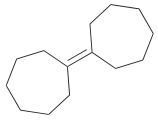
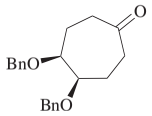
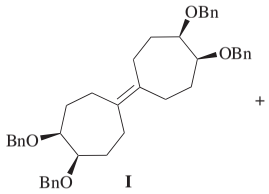
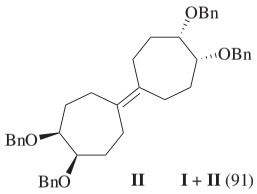
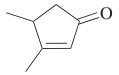
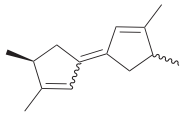
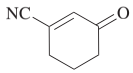
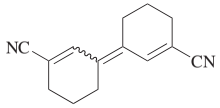
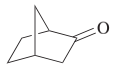
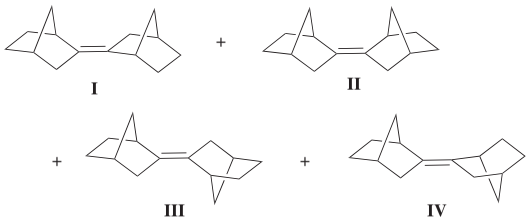
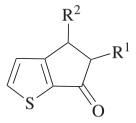
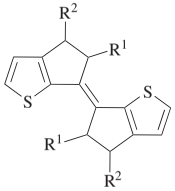
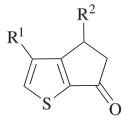
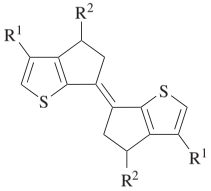
	1. $NbCl_5$, K, DME, 80°, 30 min 2. Reflux, 24 h		(82)	96
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 30 min 2. Reflux, 48 h	 **I** +  **II**	**I** + **II** (91)	407
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 14 h 2. rt, 3 h		(93) dr 9:7	408
	1. $TiCl_4$, Zn, py, THF 2. Reflux, 30 min		(—)	409

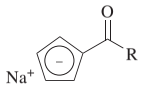
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. $TiCl_3$, Li, THF, reflux, 1 h 2. Reflux, 10 h	 **I** + **II** + **III** + **IV** (20)	410
C_{7-11}			
	1. $TiCl_4$, Zn, THF, reflux, 0.5 h 2. Reflux, 4 h		411
	$TiCl_4$, Zn, THF		393

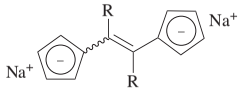
R^1	R^2	
H	H	(86)
Me	H	(37)
H	Me	(83)
H	Bu	(50)

R^1	R^2	
H	H	(—)
H	Bu	(—)

C_{7-12}



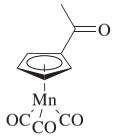
1. $TiCl_3(THF)_3$, C_8K, THF, reflux, 1.5 h
2. Reflux, 12 h



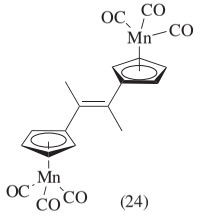
R	R	
Me	(—)	
Ph	(60)[d]	

76

C_7

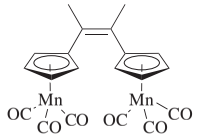


1. $TiCl_3$, C_8K, THF, reflux, 2.5 h
2. Reflux, 6 h



(24)

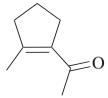
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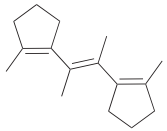
(57)

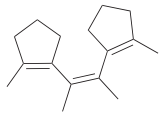
77

C_8



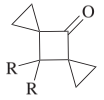
1. $TiCl_4$, Mg, –60° to rt, 3–4 h; then rt, 20 h
2. Reflux, 12 h



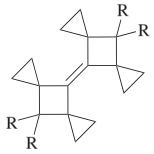
(65) +  (15)

129

C_{8-10}



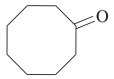
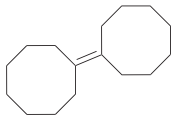
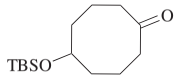
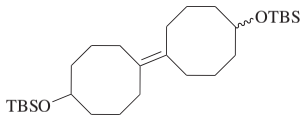
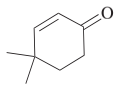
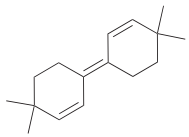
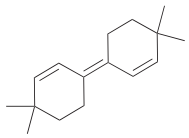
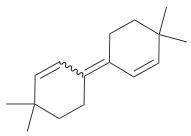
1. $TiCl_3$, $LiAlH_4$, THF, 65°, 2 h
2. 55°, 2 d



R	R	
H	H	(22)
$-(CH_2)_2-$		(28)

186

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. $TiCl_3$, K, THF, reflux, 40 min 2. Reflux, 16 h	 (70)	27, 62
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 4 h 2. Reflux, 3 h	 (65) *syn/anti* ~1:1	412
	Zn, TMSCl, THF	 (23)	91
	Zn amalgam, $ClMe_2Si(CH_2)_2SiMe_2Cl$, THF, rt, overnight	 (76)	341
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux, 4 h	 (34)	200

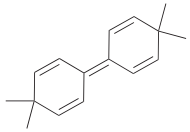
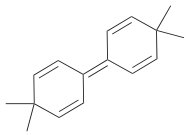
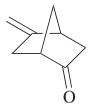
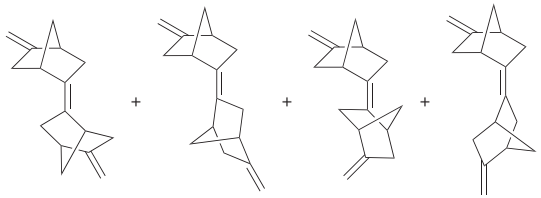
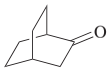
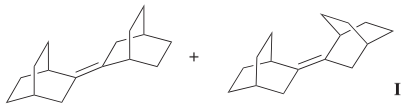
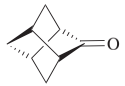
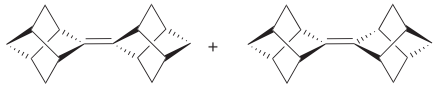
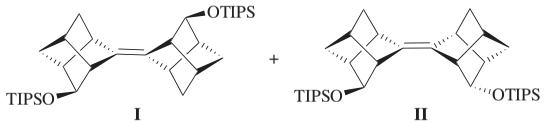
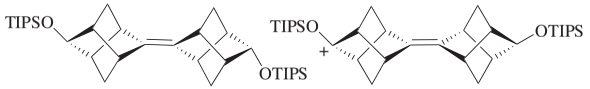
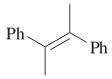
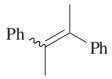
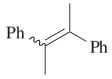
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux, 4 h		(97)	200
	Zn, HCl, THF, reflux, 10 h		(—)	90
	1. $TiCl_4$, Zn, py, dioxane, reflux, 1 h 2. Reflux, 15 h	 **I** + **II** + **III** + **IV**	**I** + **II** + **III** + **IV** (14) dr 1:1.2:1.3:1.2	413
	1. $TiCl_3$, Li, THF, reflux, 1 h 2. Reflux, 20 h	 **I** + **II**	**I** + **II** (25), **I/II** = 2:1	410

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	$TiCl_3(DME)_{1.5}$, Zn/Cu, DME, 40°, 19 h	 **I** + **II** (30)	194
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 3 h 2. 44°, 18 h	 **I** + **II** (40.1), **I**/**II** = 1:1	195
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 3 h 2. 40°, 19 h	 **I** + **II** (59)	195, 194
	$TiCl_2(THF)_2$, THF, reflux, 24 h	 (88)	34
	1. $TiCl_3$, Li, DME, reflux, 1 h 2. Reflux, 16 h	 (94), (*E*)/(*Z*) = 90:10	27
	$TiCl_3$, Li, reflux, 16 h		312

Solvent		(*E*)/(*Z*)
DME	(92)	83:9
THF	(89)	25:64

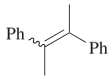
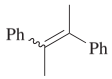
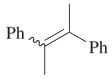
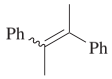
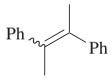
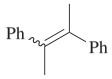
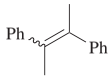
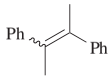
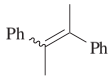
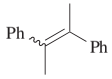
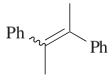
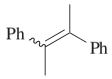
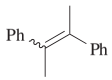
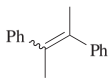
1. $TiCl_3$, Li, THF, ultrasonication, 30°, 1 h 2. Ultrasonication, 30°, 45 min		(87), (*E*)/(*Z*) = 21:66	312
1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 2 h		(82), (*E*)/(*Z*) = 85:15	114
1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. Reflux, 1.5 h		(89), (*E*)/(*Z*) = 56:44	67
1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 10 h		(86), (*E*)/(*Z*) = 20:1	73
1. $TiCl_3$, C_8K, THF, 70–75°, 3 h 2. 70–75°, 12 h		(84), (*E*)/(*Z*) = 2:1	72
$TiCl_3(DME)_{1.5}$, Zn/Cu		(—), (*E*)/(*Z*) = 8:92	414
$TiCl_4$, Zn, additive, solvent reflux		Additive / Solvent / Time (h) / (*E*)/(*Z*) — / dioxane / 4 (92) / 18:81 py / THF / 20 (87) / 1:4	3 415

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. $TiCl_4$, Zn, py, dioxane, −10 to −5° 2. Microwave irradiation, 8 min	 (90), (*E*)/(*Z*) = 7:3	121
	$Ti(Oi\text{-}Pr)_4$, Mg, TMSCl, Et_3N, THF, 40°, 24 h	 (88), (*E*)/(*Z*) = 47:53	87
	$AlCl_3$, Zn, MeCN, reflux, 12 h	 (78), (*E*)/(*Z*) = 88:12	88
	1. $ZrCl_4$, Li, DME, rt, 1 h 2. Reflux, 6 h	 (92), (*E*)/(*Z*) = 81:11	93
	1. $NbCl_5$, $NaAlH_4$, THF/benzene, 0°, 10 min 2. Reflux, 2 h	 (73), (*E*)/(*Z*) = 1:9	95
	1. $NbCl_5$, MeLi, DME, 80°, 24 h 2. Reflux, 72 h	 (54), (*E*)/(*Z*) = 33:67	96
	$InCl_3$, Zn, MeCN, reflux, 9 h	 (60), (*E*)/(*Z*) = 80:20	104

C_{8-13}



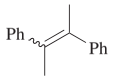
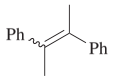
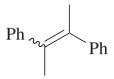
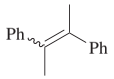
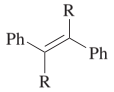
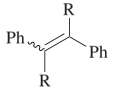
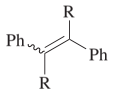
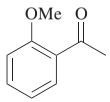
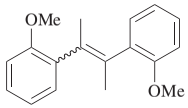
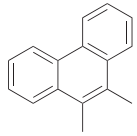
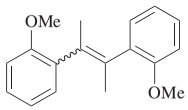
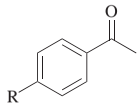
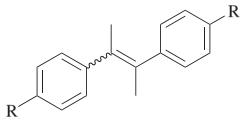
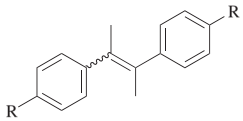
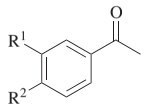
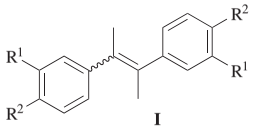
WCl_5, $LiAlH_4$, THF, rt, 6 h		(33), (*E*)/(*Z*) = 20:13	45
$W(CO)_6$, CH_2Cl_2, rt, 24 h		(7), (*E*)/(*Z*) = 3:4	45
WCl_6, electroreduction[e], THF, 4 h		(46), (*E*)/(*Z*) = 30:16	103
1. WCl_6, BuLi, THF, –78° to rt, 20 min 2. rt, 6 h		(44), (*E*)/(*Z*) = 60:40	2
1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, time		R Time (h) Me 10 (86) Ph 2 (87)	74
1. $TiCl_3$, Li, THF, reflux, 3 h; then I_2 2. Temp, time		R Temp Time (h) (*E*)/(*Z*) Me 0–5° 8 (90) 80:20 $Cl(CH_2)_2$ 0–5° 5 (69) — Ph rt 5 (95) —	115
1. $TiCl_3(THF)_3$, Mg, THF, 40°, 1 h 2. 40°, 1.5 h		R (*E*) (*Z*) Me (—) (42) (29) Ph (67) (—) (—)	4

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. $TiCl_3$, Li, THF, reflux, 3 h 2. Py, reflux, 16 h	 (50) +  (41)	416
	$TiCl_n$, M	 n M Solvent 3 Li DME (79) 3 Mg THF (85) 4 Zn THF (89) 4 Mg THF (90)	332
	1. $TiCl_3$, M, solvent, reflux, time 1 2. Reflux, time 2	 R M Solvent Time 1 (h) Time 2 (h) (*E*)/(*Z*) HO Zn THF 3 6 (65) 35:65 Br Li DME 1 27 (67) — Br $LiAlH_4$ THF 1 20 (51) —	346 417 418
	[bmim]Cl($AlCl_3$),[f] Zn, rt, 30 min	 R (*E*)/(*Z*) H (75) 3:97 MeO (82) 15:85	46

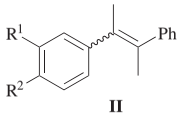


$TiCl_3$, Li



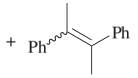
I

+



II

+

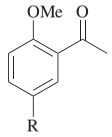


III

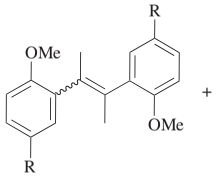
R^1	R^2	Solvent	**I**	**II**	**III**
MeO	H	THF	(53)	(18)	(10)
H	MeO	DME	(78)	(—)	(—)

332

$C_{8–9}$

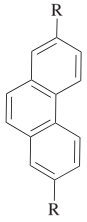


1. $TiCl_3$, Li, reflux, 3 h
2. Additive, reflux, 16 h



I

+

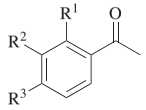


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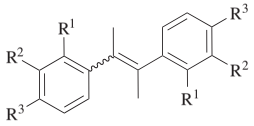
R	Additive	**I**	**II**
H	Fullerene	(17)	(58)
H	—	(0)	(36)
Me	Fullerene	(12)	(49)
Me	—	(0)	(36)

333

C_8



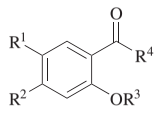
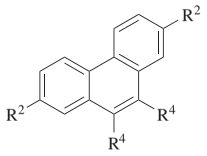
1. $TiCl_3$, Zn/Cu, solvent, reflux, 1 h
2. Reflux, 16 h



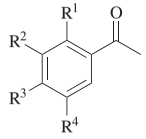
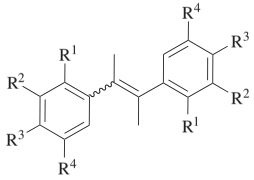
R^1	R^2	R^3	Solvent	
H	AcO	H	DME	(75)
H	H	AcO	DME	(64)
TsO	H	H	THF	(64)

349

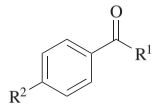
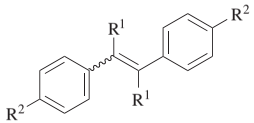
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 	$TiCl_3$, Li, THF, heat		332

R^1	R^2	R^3	R^4	
H	H	Me	Me	(36)
H	Me	Me	Me	(38)
H	H	Et	Me	(38)
MeO	H	Me	Me	(32)
H	H	Me	Et	(35)

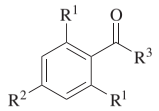
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	$TiCl_4$, Zn, dioxane, reflux, 5 h		419

R^1	R^2	R^3	R^4	
AcO	H	H	H	(12)
HO	H	H	Br	(13)
H	HO	H	H	(55)
H	H	HO	H	(62)

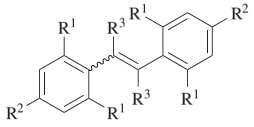
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-13} 	$TiCl_4$, Zn, py, THF, reflux, 20 h		48

R^1	R^2		$(E)/(Z)$
Me	H	(81)	26:74
Me	MeO	(50)	16:84
Et	H	(59)	27:73
Et	HO	(35)	22:78
Et	MeO	(44)	25:75
Pr	H	(55)	11:89
i-Pr	H	(25)	88:12
t-Bu	H	(3)	100:0
4-$MeOC_6H_4$	MeO	(45)	—

C_{8-16}

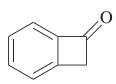


1. $TiCl_3$, $LiAlH_4$, THF, reflux, 30 min
2. Reflux, 8 h

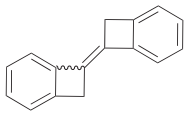


R^1	R^2	R^3		$(E)/(Z)$	
H	H	Me	(70)	1:4.5	
MeO	MeO	Me	(42)	1:1.8	420
Me	Me	Me	(22.5)	1:1.2	
H	Me	Ph	(70)	1:1	
Me	Me	Ph	(18)	1:0.45	

C_8

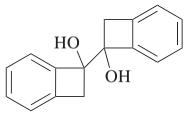


1. $TiCl_4$, Zn, THF
2. Reflux, 21 h



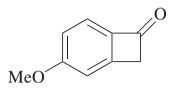
(22), $(E)/(Z)$ = 1:1

+

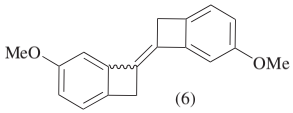


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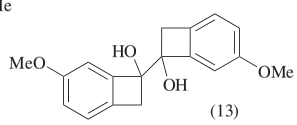


$TiCl_4$, Zn, THF, reflux, 15 h



(6)

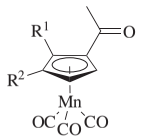
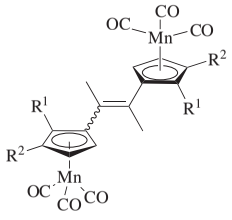
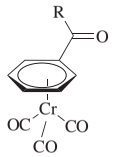
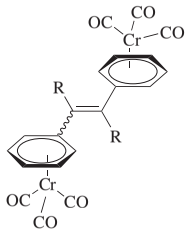
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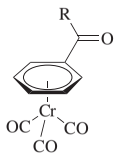
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188

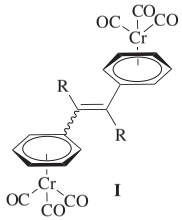
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 2.5 h 2. Reflux, 4 h	 R^1 R^2 Me H (44)[c] H Me (59)[c]	77
C_{8-11}			
	1. $TiCl_3$, Li, DME, reflux, 1 h 2. Reflux, 4 h	 (*E*)/(*Z*) ~3:1 R Me (80) Et (85) Pr (75) Bu (79)	422

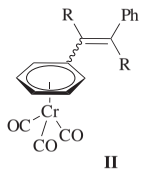
C_{8-13}



$NbCl_3$, THF, rt, 24 h



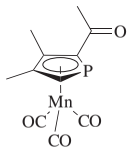
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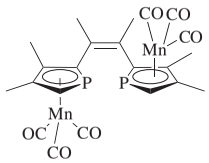
97

R	**I**	(*E*)/(*Z*)	**II**	(*E*)/(*Z*)
Me	(39)	7:3	(37)	2:1
Ph	(38)	(—)	(48)	(—)

C_8

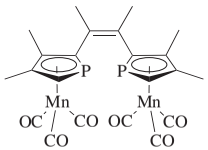


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 18 h



(45)

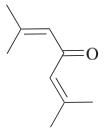
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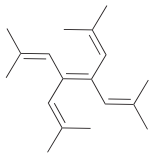
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C_9



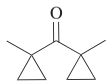
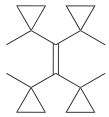
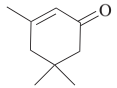
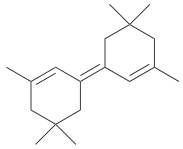
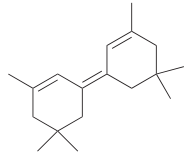
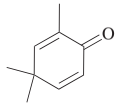
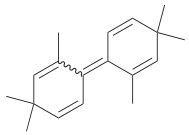
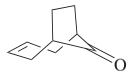
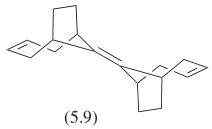
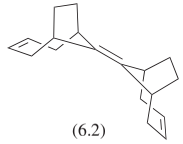
1. $TiCl_4$, Mg, –60° to rt, 3–4 h; then rt, 20 h
2. *t*-BuOH, reflux, 10 h



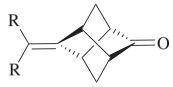
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129

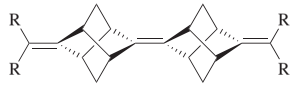
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	1. $TiCl_3/LiAlH_4$,[b] $LiAlH_4$, THF, reflux, 1 h 2. 50°, 2 d	 (13)	184
	1. $TiCl_4$, Mg, –60° to rt, 3–4 h; then rt, 20 h 2. *t*-BuOH, reflux, 3 h	 (40) +  (35)	129
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux, 4 h	 (73) dr 1:3	200
	1. $TiCl_3$, K, DME, reflux, 1 h 2. Reflux, 16 h	 (5.9) +  (6.2)	423

C_{9-11}

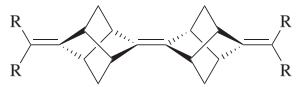


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, time 1
2. Temp, time 2



I

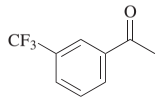
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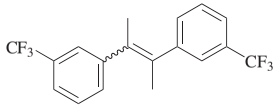
II

R	Time 1 (h)	Temp (°)	Time 2 (h)	**I + II**	**I/II**	
H	6	40	19	(12)	98:2	195, 194
Me	3	45–50	16.5	(1.3)	98:2	195

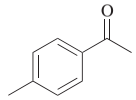
C_9



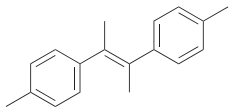
1. $TiCl_3$, Li, DME, reflux, 1 h
2. Reflux, 27 h



(60) 417

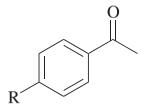


$W_2(OCH_2CMe_3)_6(Py)_2$, hexane, 22°, 2–24 h

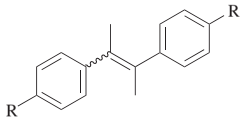


(51) 99, 100

C_{9-12}

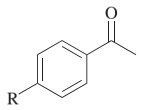
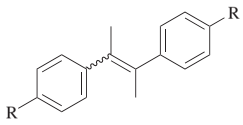
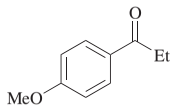
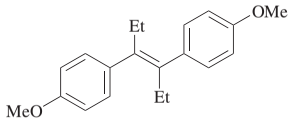
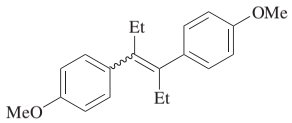
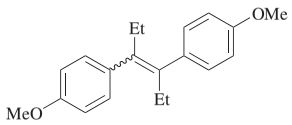
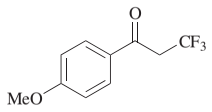
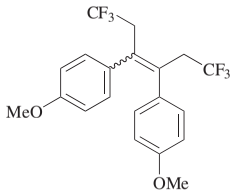


1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h
2. rt, time

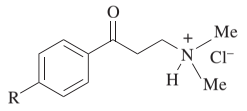


R	Time (h)		(*E*)/(*Z*)	
Me	2.5	(72)	78:22	67
t-Bu	3	(64)	76:24	

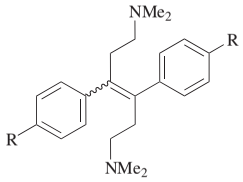
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-12} 	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, time	 R = Me, time = 3 h, (82), (*E*)/(*Z*) = 65:35; R = *t*-Bu, time = 10 h, (78), (*E*)/(*Z*) = 75:25	114
C_9 	1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h	 (85)	5
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 30 min 2. Reflux, 21 h	 (73), (*E*)/(*Z*) = 5:95	424
	$InCl_3$, Zn, MeCN, reflux, 14 h	 (80), (*E*)/(*Z*) = 95:5	104
	$TiCl_3$, Zn/Cu, THF	 (75), (*E*)/(*Z*) = 1:4	425

C_{9-10}

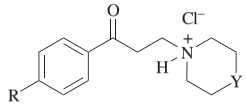


1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Reflux, 2 d
3. 10% aq K_2CO_3

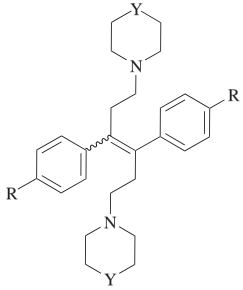


R	
H	(71)
Br	(45)
Me	(38)

426



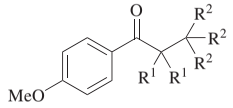
1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Reflux, 2 d
3. 10% aq K_2CO_3



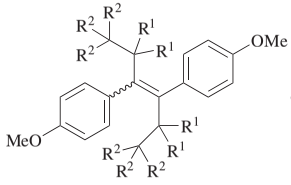
R	Y	
H	CH_2	(81)
Br	CH_2	(51)
MeO	CH_2	(33)
Me	CH_2	(66)
H	O	(57)

426

C_9



1. $TiCl_3$, Li, DME, reflux, 3 h
2. Reflux, 16 h

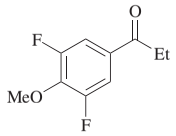
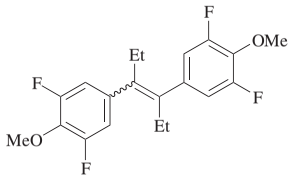
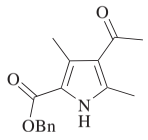
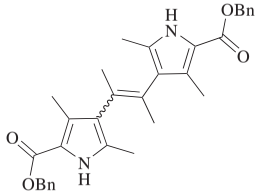
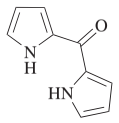
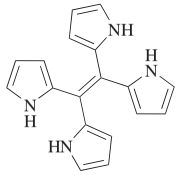
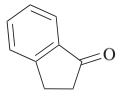
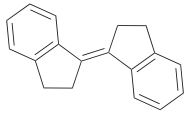


(*E*)/(*Z*) = 5:95

R^1	R^2	
D	H	(58)
H	D	(—)

427

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	1. $TiCl_3$, Zn/Cu, THF, reflux, 1 h 2. Reflux, addition of ketone over 1 h; then reflux, 16 h	 (96)	428
	$TiCl_4$, Zn, THF	 (—)	211
	—	 (56)	429
	1. $TiCl_4$, Zn, THF 2. Reflux, 16 h	 (69)	430

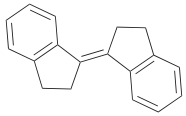
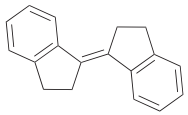
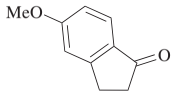
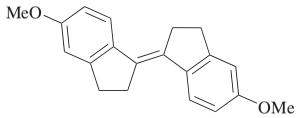
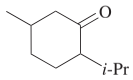
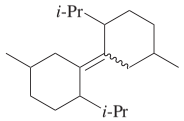
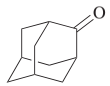
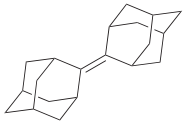
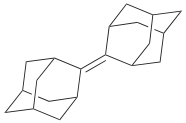
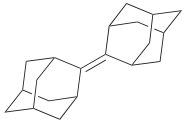
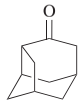
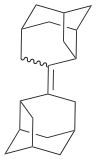
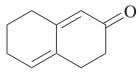
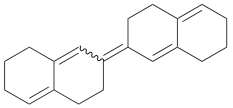
	1. $TiCl_4$, Zn, py, dioxane, –10 to –5° 2. Microwave irradiation, 5 min		(74)	121
	—		(70–80)	431
	1. $TiCl_4$, Zn, 0°, 10 min 2. Reflux, 20 h		(53)	432
C_{10}				
	1. $TiCl_4$, Zn, py, THF, 0° 2. Reflux, 20 h		(51) dr 3:1	111

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. $TiCl_3$, M, solvent, reflux, time 2. Reflux, 16 h	 M Solvent Time Li DME 1 h (82) K THF 40 min (91)	27 27, 62
	1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h	 (85)	5
	$TiCl_4$, Zn, py, THF, reflux, 46 h	 (98.2)	433
	1. $TiCl_4$, Zn, py, THF, 0° 2. Reflux, 18 h	 (45)	111
	1. $TiCl_4$, Zn, py, THF 2. rt, 15 min	 (54), (*E*)/(*Z*) = 82:18	434

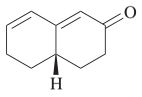
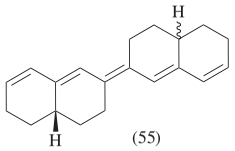
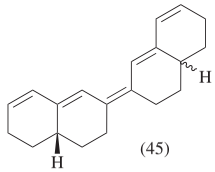
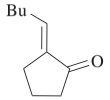
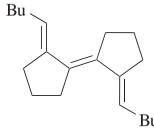
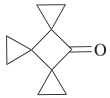
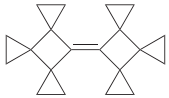
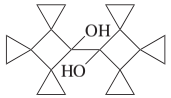
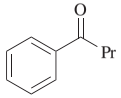
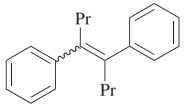
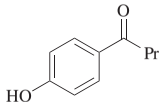
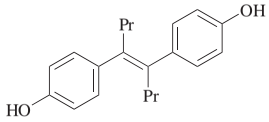
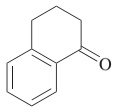
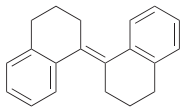
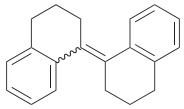
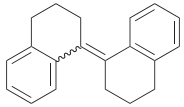
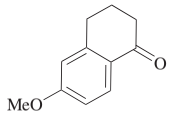
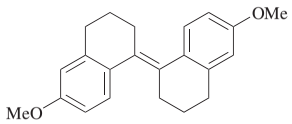
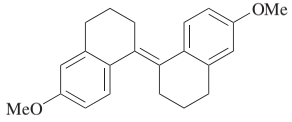
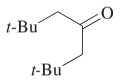
	1. $TiCl_4$, Zn, py, THF 2. Reflux, 5 min	 (55) +  (45)	403
	Zn amalgam, $ClMe_2Si(CH_2)_2SiMe_2Cl$, THF, rt, overnight	 (72)	341
	$TiCl_3$, $LiAlH_4$, THF, rt, 3 d	 (8) +  (—)	435
	$TiCl_4$, Zn, THF, 110°, microwave irradiation, 10 min	 (93), (*E*)/(*Z*) = 9:1	317
	$TiCl_3$, $LiAlH_4$, THF	 (42)	436

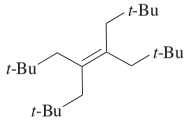
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. $TiCl_4$, Zn, py, dioxane, –10 to –5° 2. Microwave irradiation, 5 min	 (89)	121
	1. $TiCl_4$, Zn, 0°, 10 min 2. Reflux, 20 h	 (53), (*E*)/(*Z*) = 7:3	432
	$AlCl_3$, Zn, MeCN, reflux, 18 h	 (88), (*E*)/(*Z*) = 99:1	88
	$AlCl_3$, Zn, MeCN, reflux, 12 h	 (85)	88
	1. $TiCl_4$, Zn, THF 2. Reflux, 20 h	 (41)	187

C_{11}

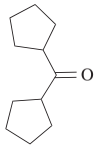


1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1 h
2. Reflux, 8 h

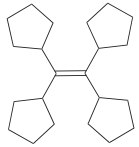


(38)

437

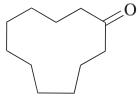


1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h
2. rt, 8 h

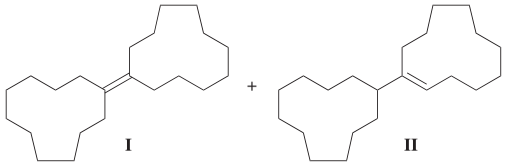


(72)

67

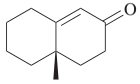


$TiCl_4$, Zn, dioxane, −10° to reflux, 21 h

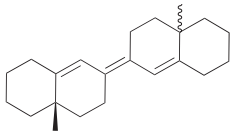


I + **II** (100), **I**/**II** = 88:12

438



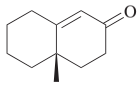
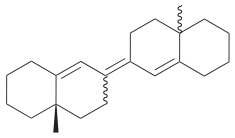
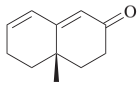
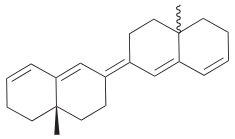
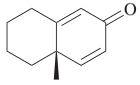
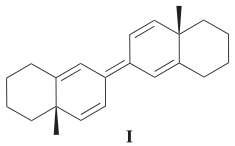
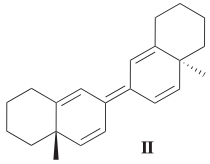
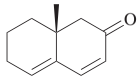
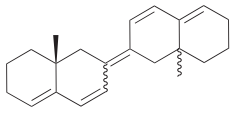
Zn, TMSCl, THF

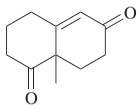


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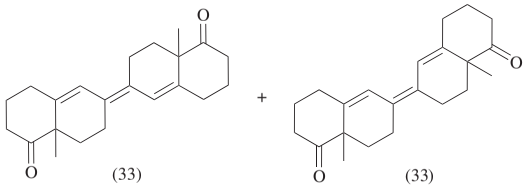
91

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	1. $TiCl_4$, Zn, py, THF 2. —	 (39) dr 20:15:42:23[g]	439
	1. $TiCl_4$, Zn, py, THF, reflux, 1 h 2. rt, 1 h	 (80)	439
	1. $TiCl_4$, Zn, py, THF, 0° 2. 0°, 30 min	 **I** +  **II** **I** + **II** (91), **I**/**II** = 50:50	440
	1. $TiCl_4$, Zn, py, THF, reflux, 1 h 2. rt, 1 h	 (38)	439

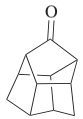


1. $TiCl_4$, Mg, –60° to rt, 3–4 h; then rt, 20 h
2. 20°, 12 h

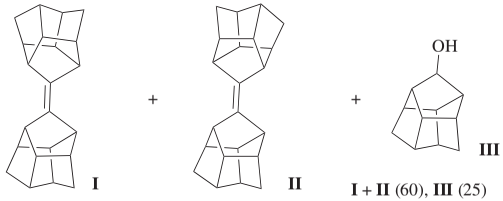


(33) + (33)

129



1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Py, reflux, 24 h



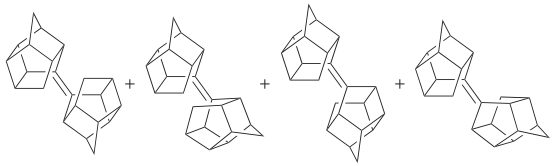
I + **II** + **III**

I + **II** (60), **III** (25)

190



$TiCl_4$, Zn, py, THF, reflux, 3 d

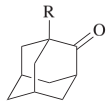
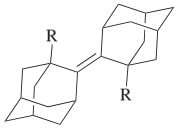
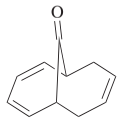
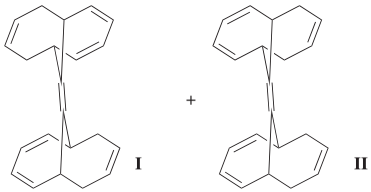
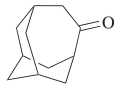
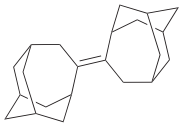
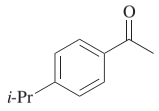
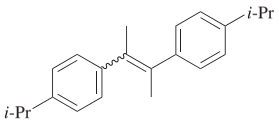


I + **II** + **III** + **IV**

I + **II** + **III** + **IV** (44)

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TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12}			
	$TiCl_3$, K	 R = Me (52), Et (40)	47
C_{11}			
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 30 min 2. Reflux, 4 h	 **I** + **II** (3.1)	441, 442
	1. $TiCl_3$, $LiAlH_4$, THF, 30 min 2. Reflux, 8 h	 (40)	443
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 10 h	 (75), (*E*)/(*Z*) = 80:20	114

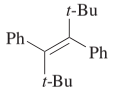
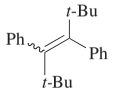
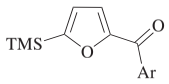
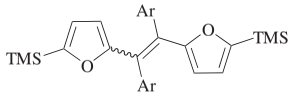
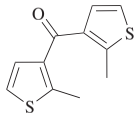
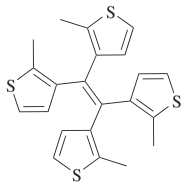
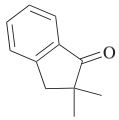
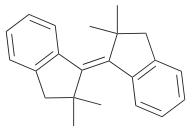
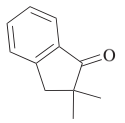
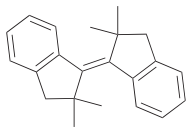
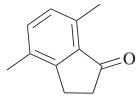
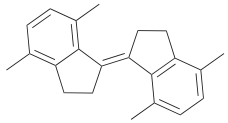
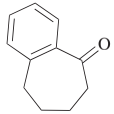
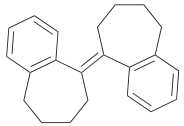
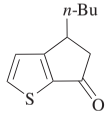
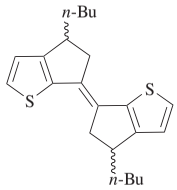
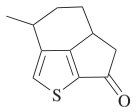
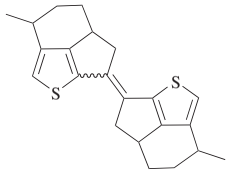
	$TiCl_4$, Zn		(48)	47
	$AlCl_3$, Zn, MeCN, reflux, 11 h		(82), (*E*)/(*Z*) = 90:10	88
 Ar = 4-$MeOC_6H_4$	1. $TiCl_4$, Zn, THF, reflux, 3 h 2. Reflux, 40 min		(72), (*E*)/(*Z*) = 3:1	444
	$TiCl_4$, Zn, py, THF		(59)	445
	$TiCl_4$, Zn, THF, reflux		(52)	446

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	1. $TiCl_4$, Zn, THF 2. Reflux, 16 h	 (42)	430
	1. $TiCl_4$, Zn, 0°, 10 min 2. Reflux, 18 h	 (95)	432
	1. $TiCl_4$, Zn, THF 2. Reflux, 22 h	 (27)	187
	1. $TiCl_4$, Zn, THF, reflux, 30 min 2. Reflux, 4 h	 (50)	411

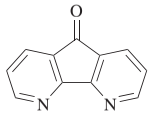


1. $TiCl_4$, Zn, THF, reflux, 30 min
2. Reflux, 4 h

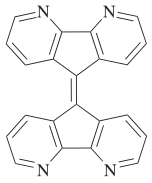


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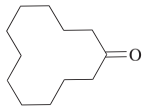
$TiCl_3$, $LiAlH_4$, THF, reflux, 12 h



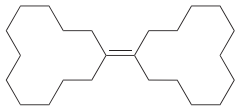
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C_{12}

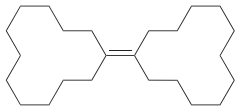


1. $TiCl_3$, M, solvent, reflux, time
2. Reflux, 16 h



M	Solvent	Time (h)		
Li	DME	1	(65)	27
K	THF	0.75	(90)	27, 62

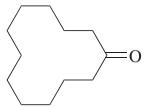
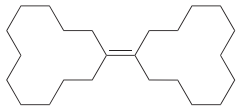
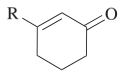
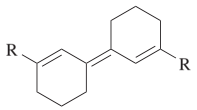
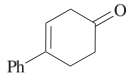
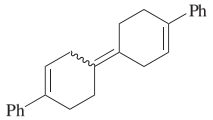
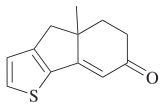
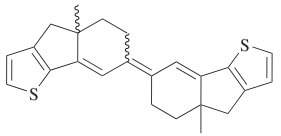
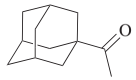
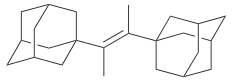
1. $TiCl_3$, C_8K, DME, reflux, 2 h
2. Reflux, 12 h

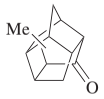


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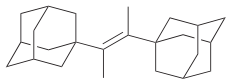
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TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h	 (80)	5
C_{12-16} 	$TiCl_4$, Zn, dioxane	 R: Ph (—), 2-Np (—)	448
C_{12} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 2.5 h 2. Reflux, 12 h	 (31) dr 43:54	449
	1. $TiCl_4$, Zn, THF, reflux, 30 min 2. Reflux, 30 min	 (84)	450, 451
	$TiCl_4$, Zn	 (15)	47

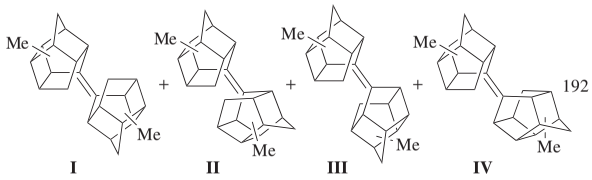


1. $TiCl_4$, Zn, py, THF, 0°
2. Reflux, 3 d



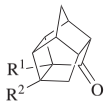
(15) 111

1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Py, reflux, 24 h

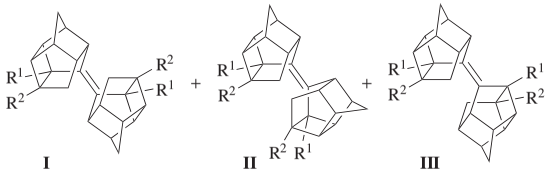


I **II** **III** **IV**

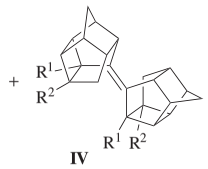
I + **II** + **III** + **IV** (73) 192



1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Py, reflux, 24 h



I **II** **III**

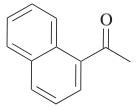
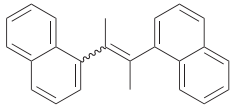
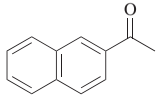
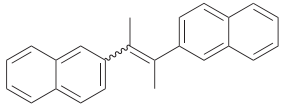
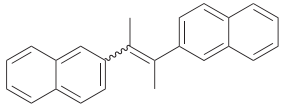
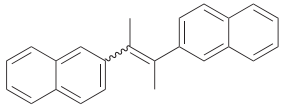
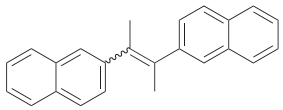


IV

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R^1	R^2	**I** + **II** + **III** + **IV**
H	Me	(50)
Me	H	(62)

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	1. $TiCl_3$, Na/Al_2O_3, THF, reflux, 1 h 2. Reflux, 1 h	 (88), (*E*)/(*Z*) = 82:18	69
	1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. Reflux, 4.5 h	 (68), (*E*)/(*Z*) = 60:40	67
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 6 h	 (68), (*E*)/(*Z*) = 72:28	114
	1. $TiCl_3$, Li, THF, reflux, 3 h; then I_2, 5 min 2. 0–5°, 6 h	 (93), (*E*)/(*Z*) = 64:36	115
	$TiCl_4$, Zn, THF	 (—), (*E*)/(*Z*) = 20:80	140

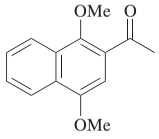
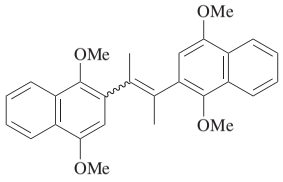
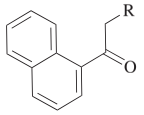
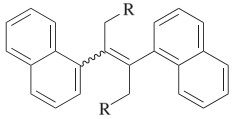
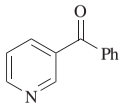
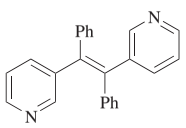
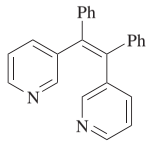
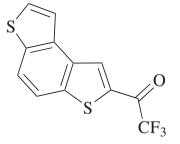
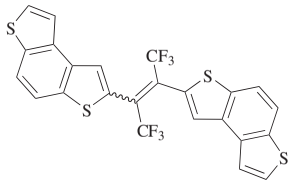
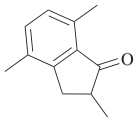
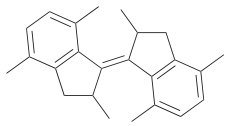
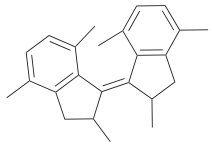
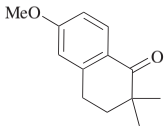
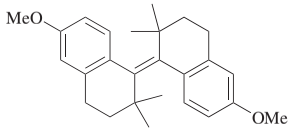
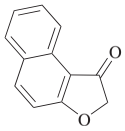
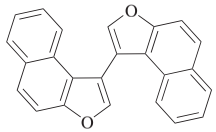
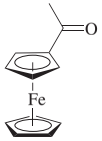
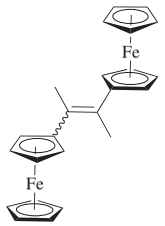
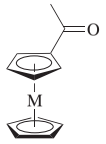
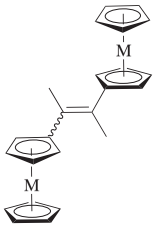
	1. $TiCl_3$, $LiALH_4$, THF, rt 2. Reflux, 3 h		(41.3)	452
C_{12-22}				
	$TiCl_4$, $LiAlH_4$		R: H (—); Me (—); n-C_6H_{13} (—); n-$C_{10}H_{21}$ (—)	453
C_{12}				
	$TiCl_3$, $LiAlH_4$, THF, reflux, 12 h		(13) +  (18)	213
	1. $TiCl_4$, Zn, py, THF, reflux, 2.25 h 2. Reflux, 13.75 h		(16), (*E*)/(*Z*) = 65:35	217

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2 d	 (7) +  (25)	454
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 15 min 2. Reflux, 52 h	 (18)	187
	1. $TiCl_4$, Zn, DME, reflux 2. Reflux, 18 h 3. DDQ, benzene, reflux, 4 h	 (78)	455
	$TiCl_4$, Zn	 (69), (*E*)/(*Z*) = 3:1	47

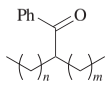


1. $TiCl_4$, $LiAlH_4$, THF, reflux, 3 h
2. Reflux, time

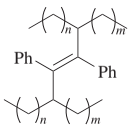


M	Time (h)		(*E*)/(*Z*)	
Fe	3	(54)	—	456
Ru	5	(43)	1.3:1	457

C_{12-20}

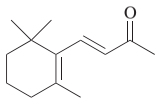


$TiCl_4$, Zn, THF, reflux, 48 h

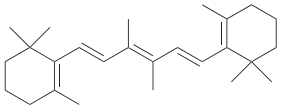


m	*n*		
2	2	(12–80)	
3	3	(12–80)	
3	5	(12–80)	458
5	5	(39)	

C_{13}

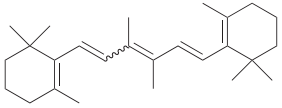


1. $TiCl_4$, $LiAlH_4$, THF, reflux, 20 min
2. Tertiary amine, reflux, 3 h



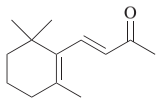
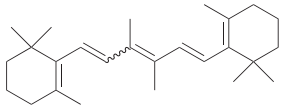
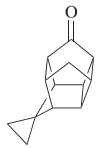
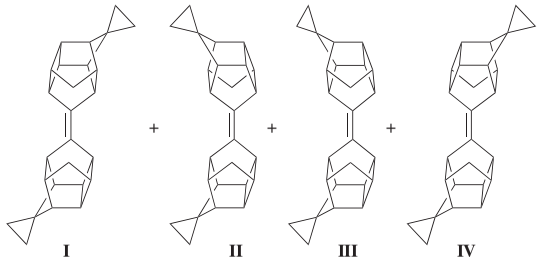
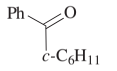
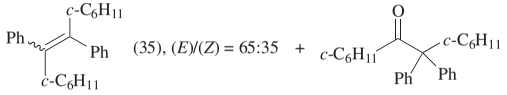
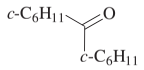
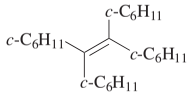
Tertiary amine		
Bu_3N	(91)	110
Proton Sponge[h]	(94)	

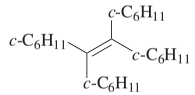
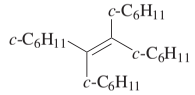
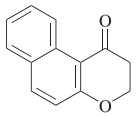
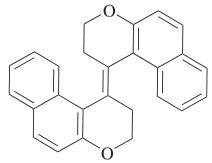
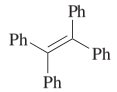
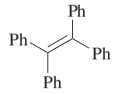
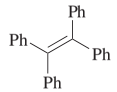
1. $TiCl_3$, $LiAlH_4$, THF
2. Reflux, 4 h



(53), (*E*)/(*Z*) = 5:4 361

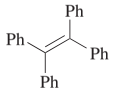
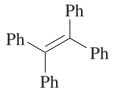
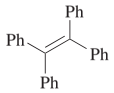
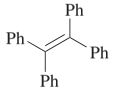
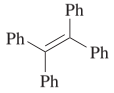
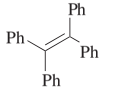
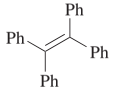
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	1. $TiCl_4$, Zn, CH_2Cl_2/THF, rt, 30 min 2. rt	 (67)	202
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Py, reflux, 40 h	 **I** + **II** + **III** + **IV** (46)	191
	1. $TiCl_3$, Na/Al_2O_3, THF, reflux, 1 h 2. Reflux, 1 h	 (35), (*E*)/(*Z*) = 65:35 + (50)	69
	1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. Reflux, 6.5 h	 (78)	67

	1. $TiCl_3$, K, THF, reflux, 1 h 2. Reflux, 10 h	 (20)	459
	—	 (—)	460
	1. $TiCl_4$, Zn, py, dioxane, –10 to –5° 2. Microwave irradiation, 10 min	 (75)	121
	Ti powder, TMSCl, DME, reflux, 72 h	 (83)	83
	$TiCl_2(THF)_2$, THF, reflux, 24 h	 (58)	34
	1. $TiCl_3$, M, solvent, reflux, time 2. Reflux, 16 h		27

M	Solvent	Time	
Li	DME	1 h	(96)
K	THF	40 min	(80)

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	1. $TiCl_3$, K, naphthalene, THF, reflux, 3 h 2. rt, 7 h	 (78)	67
	1. $TiCl_3$, Li, THF, reflux, 3 h; then KCl, reflux, 1 h 2. rt, 5 h	 (75)	114
	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, time	 Time (h): 2 (87); 12 (91)	73 84
	$TiCl_n$, Zn, THF, reflux	 *n* Time (h): 3 4 (78); 4 5 (97)	7 3
	1. $TiCl_3$, $LiAlH_4$, THF, 0°, 10 min; then reflux, 30 min 2. Reflux, 20 h	 (90)	120
	1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h	 (95)	5
	1. $TiCl_4$, Na/Hg, DME, reflux, 4 h 2. Reflux, 12 h	 (84)	84

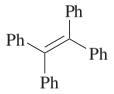
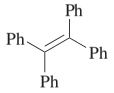
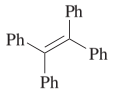
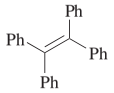
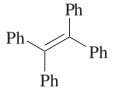
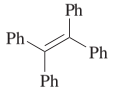
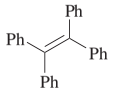
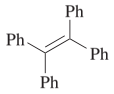
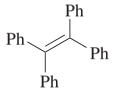
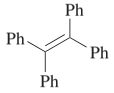
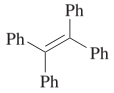
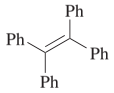
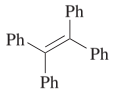
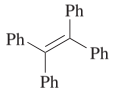
1. $TiCl_4$, $LiAlH_4$, THF, reflux, 20 min 2. Tertiary amine, reflux, 3 h		Tertiary amine Bu_3N (90) Proton Sponge[h] (90)	110
1. $TiCl_4$, M, THF, temp, time 2. rt, 6 h		M Temp Time (h) Li reflux 40 (75) K reflux 8 (>80) Mg reflux 3 (>85)	65
1. $TiCl_4$, $LiAlH_4$, THF, 0°, 30 min; then reflux, 10 min 2. rt, 6 h		(90)	65
1. $TiCl_4$, Zn, py, dioxane, –10 to –5° 2. Microwave irradiation, 5 min		(97)	121
$TiCl_4$, Zn, 120°, 10 h		(87)	311
$TiCl_4$, Hg/Mg, THF, 0°, 2 h; then reflux, 24 h		(87)	331
$AlCl_3$, Zn, MeCN, reflux, 16 h		(77)	88

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	Zn, $AlBr_3$, MeCN, 35°, ultrasonication, 12 h	 (57)	89
	[bmim]Cl($AlCl_3$),[f] Zn, rt, 30 min	 (78)	46
	1. $NbCl_5$, K, DME, 80°, 30 min 2. Reflux, 24 h	 (78)	96
	1. $NbCl_5$, $NaAlH_4$, THF/benzene, 0°, 10 min 2. Reflux, 2 h	 (75)	95
	$InCl_3$, Zn, MeCN, reflux, 6 h	 (80)	104
	WCl_5, $LiAlH_4$, THF, rt, 6 h	 (43)	45
	WCl_6, electroreduction,[e] THF, 4 h	 (50.8)	103

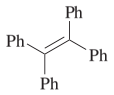
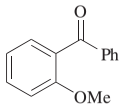
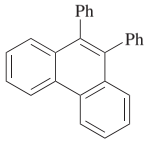
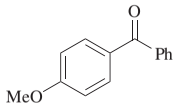
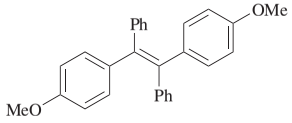
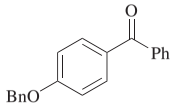
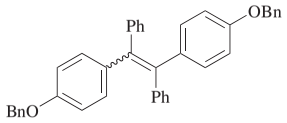
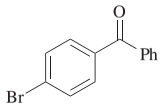
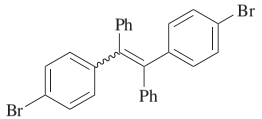
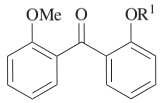
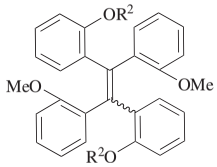
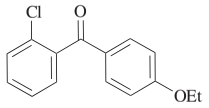
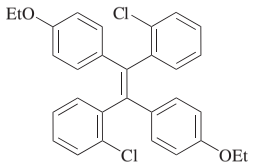
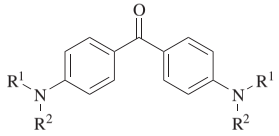
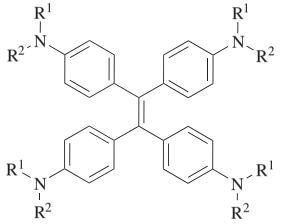
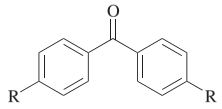
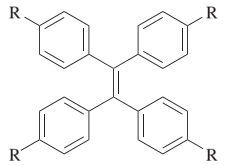
	1. UCl_4, $Li_2Np(TMEDA)_2$, xylene, rt, 1 h 2. rt, 1 h; then 70°, 12 h		(53)	17
	$TiCl_3$, Li, THF		(36)	332
	$TiCl_3/AlCl_3$, Zn, THF, reflux, 20 h		(91)	461
	1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Reflux, 0.5 h		(41), (*E*)/(*Z*) = 1:1	55
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1 h 2. Reflux, 20 h		(78)	418

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	$TiCl_3$, Zn/Cu, DME, 80°, 14 h	 (*E*)/(*Z*) = 1:1 R^1 / R^2: Me / Me (76); *t*-Bu / H (45, 64[i]); CH_2=$CHCH_2$ / CH_2=$CHCH_2$ (48); *t*-$BuPh_2Si(CH_2)_2$ / *t*-$BuPh_2Si(CH_2)_2$ (69); $Ph_3Si(CH_2)_2$ / $Ph_3Si(CH_2)_2$ (57)	462
	1. $TiCl_4$, Zn, py, dioxane, –10 to –5° 2. Microwave irradiation, 10 min	 (81)	121
	$TiCl_4$, Zn, dioxane, reflux, 2–5 h	 R^1 / R^2: –$(CH_2)_2O(CH_2)_2$– (81); H / 4-$MeOC_6H_4$ (72); Me / Ph (77); Me / 4-$MeOC_6H_4$ (83)	463

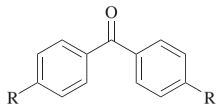
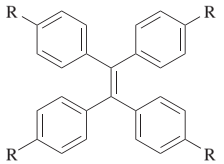
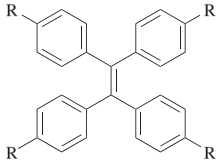
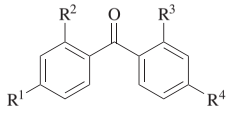
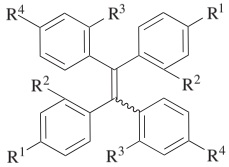


$TiCl_4$, Zn



R	Additive	Solvent	Temp(°)	Time (h)		
Cl	—	—	120	10	(52)	311
$Br(CH_2)_2O$	—	THF	reflux	20	(63)	464
PhO	py	THF	60	18	(34)	465
MeO	py	CH_2Cl_2/THF	50	20	(68)	466
MeO	py	CH_2Cl_2/THF	0–50	24	(70)	467
n-$C_{10}H_{21}O$	py	CH_2Cl_2/THF	50	20	(77)	466
3,4,5-(n-C_8H_{17})$_3C_6H_2O$	py	CH_2Cl_2/THF	60	20	(55)	468
3,4,5-(n-C_9H_{19})$_3C_6H_2O$	py	CH_2Cl_2/THF	60	20	(57)	468
3,4,5-(n-$C_{10}H_{21}$)$_3C_6H_2O$	py	CH_2Cl_2/THF	60	20	(49)	468
3,4,5-(n-$C_{11}H_{23}$)$_3C_6H_2O$	py	CH_2Cl_2/THF	60	20	(51)	468
3,4,5-(n-$C_{12}H_{25}$)$_3C_6H_2O$	py	CH_2Cl_2/THF	60	20	(34)	468
3,4,5-(n-$C_{16}H_{33}$)$_3C_6H_2O$	py	CH_2Cl_2/THF	60	20	(61)	468
CF_3CONH	py	CH_2Cl_2/THF	60	20	(43)	465
n-C_4H_9(Me)CHCONH	py	CH_2Cl_2/THF	60	20	(26)	465
2,4-$Me_2C_6H_3CONH$	py	CH_2Cl_2/THF	60	20	(29)	465

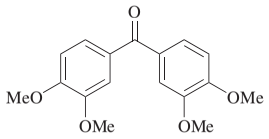
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Py, reflux	 R = H, Time (h) = 6, (92)  Time (h) = 34, (90)	144
	$TiCl_4$, Zn, THF, microwave irradiation, 110°, 10 min	 R = H, (96) R = *t*-BuS, (82)	317
$C_{13–15}$ 	1. $TiCl_3$, Zn/Cu, DME, reflux, 14 h 2. Temp		469

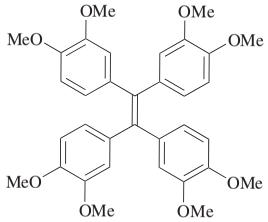
R^1	R^2	R^3	R^4	Temp		(*E*)/(*Z*)
H	MeO	H	H	rt	(36)	1:17
H	MeO	H	H	reflux	(67)	1:13
H	MeO	MeO	H	rt	(76)	—
MeO	H	MeO	H	rt	(76)	1:8
MeO	MeO	H	H	rt	(76)	1:8

H	MeO	Me	H	rt	(26)	—
H	MeO	H	CF_3	rt	(31)	1:9
H	MeO	H	CF_3	reflux	(67)	1:6
H	Me	Me	H	reflux	(70)	—
MeO	Me	Me	MeO	reflux	(85)	—

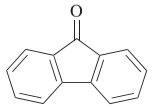
C_{13}



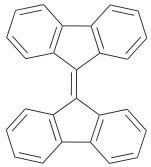
$TiCl_4$, Zn, THF, reflux, 12 h



(92) 470

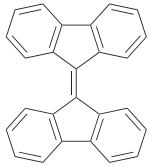


1. Ti powder, TMSCl, DME, reflux, 67 h
2. Reflux, 4 h



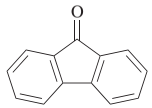
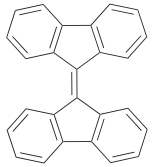
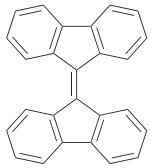
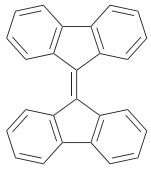
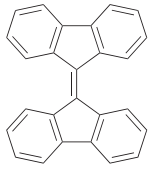
(94) 83

$TiCl_2(THF)_2$, THF, reflux, 24 h



(44) 34

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	1. $TiCl_3$, Li, THF, ultrasonication, 30°, 1 h 2. Ultrasonication, 30°, 1 h	 (65)	312
	1. $TiCl_3$, K, THF, reflux, 40 min 2. Reflux, 16 h	 (85)	27
	1. $TiCl_3$, $LiAlH_4$, THF 2. Reflux, 4 h	 (95)	5
	$TiCl_3$, Zn, DME, reflux, 2 h	 (92)	7, 471

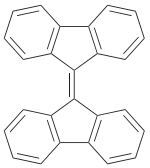
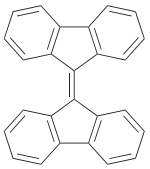
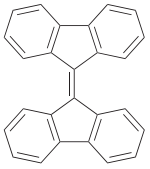
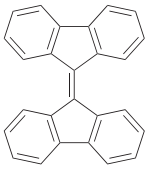
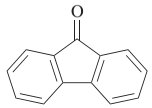
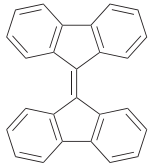
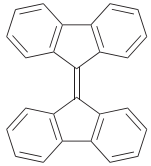
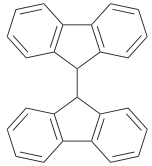
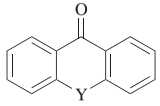
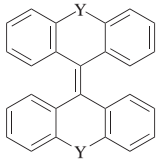
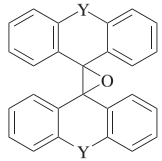
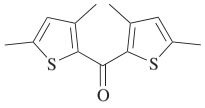
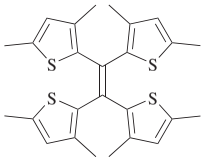
1. $TiCl_4$, Zn, THF 2. Reflux, 16 h		(38)	430
$TiCl_4$, Zn, 120°, 10 h		(54)	311
1. $TiCl_4$, Zn, py, dioxane, –10 to –5° 2. Microwave irradiation, 5 min		(94)	121
$TiCl_4$, Hg/Mg, THF, 0°, 2 h; then reflux, 24 h		(85)	331

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

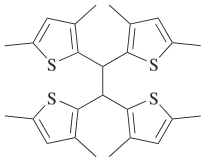
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	VCl, THF, 20–30°, 12 h	 (99)	94
	1. $TiCl_3$, Na/Al_2O_3, THF, reflux, 1 h 2. Temp, time	 +  **I** **II** Temp Time (h) **I** **II** reflux 1 (2) (74) rt 20 (34) (45)	69
	M, $AlCl_3$, MeCN, ultrasonication, 35°, 12 h	 +  **I** **II** Y M **I** **II** O Zn (51) (0) O Al (50) (0) S Zn (36) (40) S Al (48) (0) $(CH_2)_2$ Zn (34) (48) $(CH_2)_2$ Al (17) (54)	89



1. $TiCl_3$, $LiAlH_4$, THF, reflux, 30 min
2. Reflux, 6.5 h

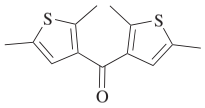


+

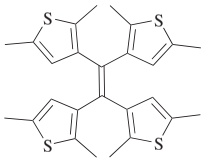


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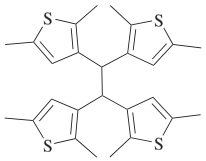
I **I** + **II** (70), **I**/**II** = 4.5:1 **II**



1. $TiCl_3$, $LiAlH_4$, THF, reflux, 30 min
2. Reflux, 7.5 h



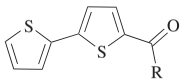
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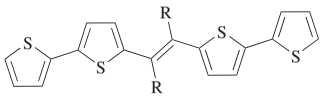
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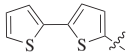
(58) (—)

$C_{13–17}$



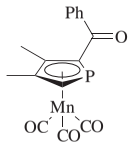
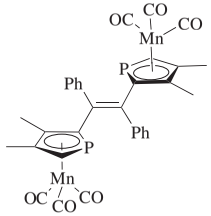
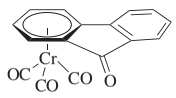
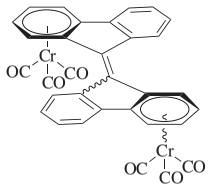
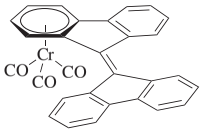
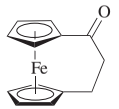
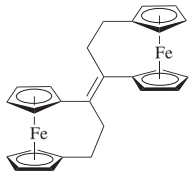
1. $TiCl_4$, Zn, CH_2Cl_2/THF, rt, 6 h
2. Py, reflux, 72 h



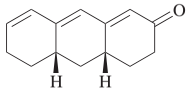
R	
2-thienyl	(95)
Ph	(93)
	(84)

473

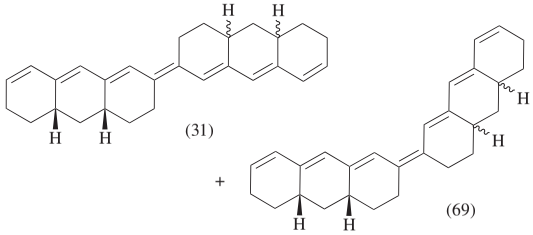
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 48 h	 (41)	208
	$NbCl_3$, THF, rt, 24 h	 (37)[j] +  (43)	97
	$TiCl_3$, Zn, py, DME, reflux, 20 h	 (70)	112

C_{14}

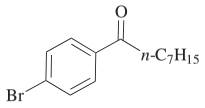


1. $TiCl_4$, Zn, py, THF
2. Reflux, 5 min

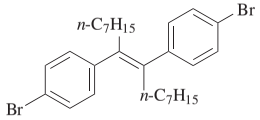


(31) + (69)

403

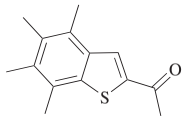


1. $TiCl_4$, Zn, py, THF, reflux
2. Reflux, then addition of ketone over 1 h; then reflux, 5 h

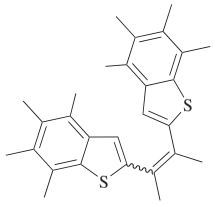


(82)

319



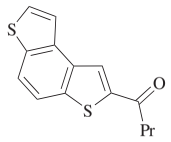
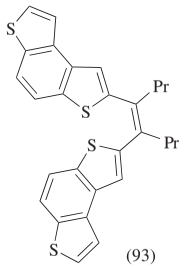
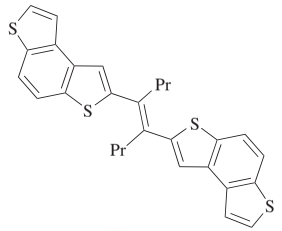
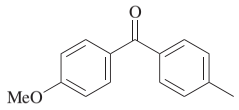
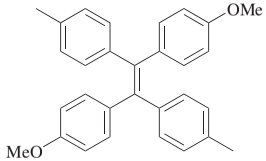
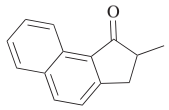
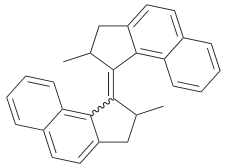
1. $TiCl_4$, Zn, THF, reflux, 2h
2. Py, reflux, overnight



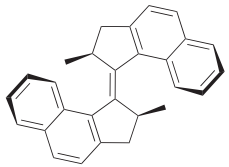
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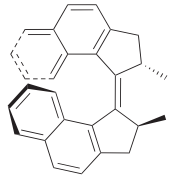
474

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

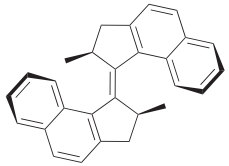
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	$TiCl_4$, Zn, THF, reflux, 3.5 h	 (93) +  (7)	217
	$TiCl_4$, Zn, THF, reflux, 12 h	 (91)	475
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 3 d	 (76), (*E*)/(*Z*) = 2:5	477

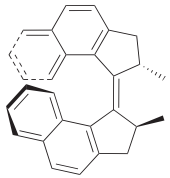
1.$TiCl_3$, $LiAlH_4$, THF,
reflux, 1.5 h
2. Reflux, 96 h

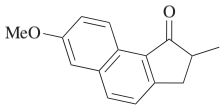


(14) +  (6) 127

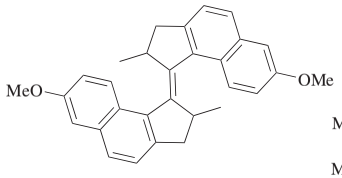
1. $TiCl_3$, $LiAlH_4$, THF,
reflux, 4 h
2. Reflux, 3 h



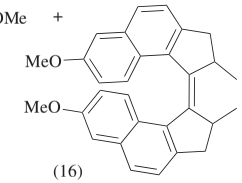
$(21)^k$ +  $(5)^k$ 127



1. $TiCl_4$, Zn,THF, reflux, 1.5 h
2. Reflux, 18 h



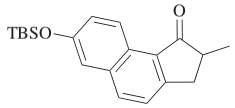
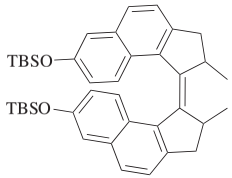
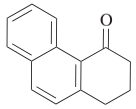
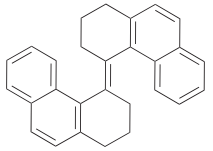
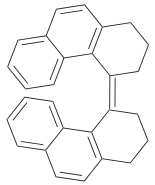
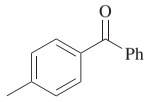
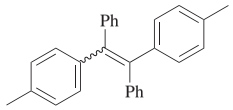
(18)

+ 

(16)

478

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Reflux, 18 h	 (90), (*E*)/(*Z*) = 1:2	478
	1. $TiCl_3$, $LiAlH_4$, THF, 0°, 10 min 2. Reflux, overnight	 (8.3) +  (2.5)	479
	$TiCl_4$, Zn, 120°, 10 h	 (25)	311

C_{15}



1. $TiCl_3$, Na/Al_2O_3, THF, reflux, 1 h
2. Reflux, time

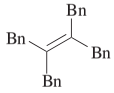


R	Time (h)	
n-C_7H_{15}	1.5	(45)
Bn	1	(72)

69

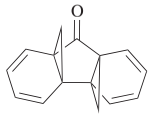


1. $TiCl_4$, Zn, THF, py, 0°
2. Reflux, 20 h

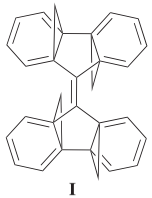


(80)

111

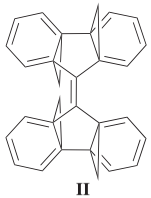


$TiCl_4$, Zn, py, THF, reflux, 20 h



I

\+

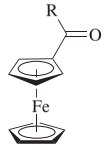


II

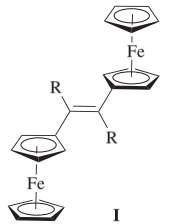
I + **II** (69), **I**/**II** = 9:1

480

C_{15-18}

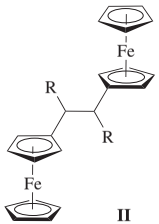


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Py, reflux, time



I

\+

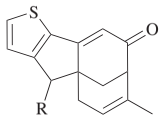
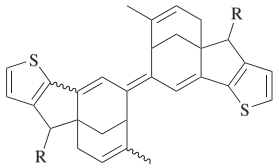
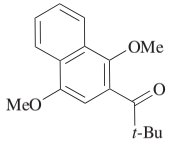
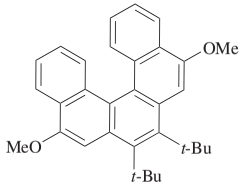
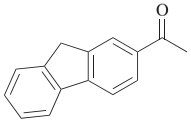
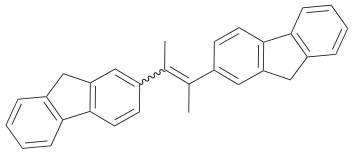


II

R	Time (h)	**I**	**II**
2-furyl	18	(17)	(—)
3,4-$Cl_2C_6H_3$	24	(8)	(—)
3-MeC_6H_4	37	(7)	(16)
4-MeC_6H_4	20	(10)	(18)

481

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15-19}			
	1. $TiCl_4$, Zn, THF, reflux, 30 min 2. Reflux, 30 min	 R: H (89); Bu (48)	450
C_{15}			
	1. $TiCl_3$, $LiAlH_4$, THF, rt 2. Reflux, 3 h	 (1.8)	452
	$TiCl_4$, Zn, py	 (—)	482

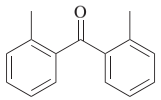
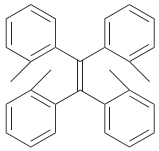
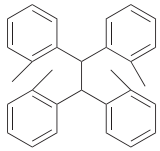
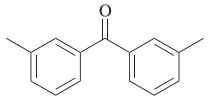
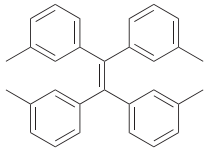
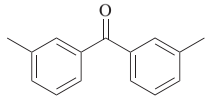
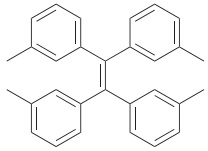
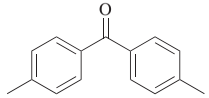
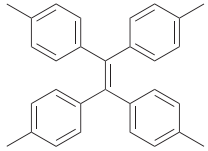
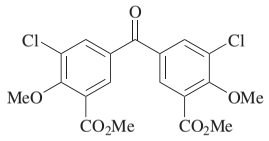
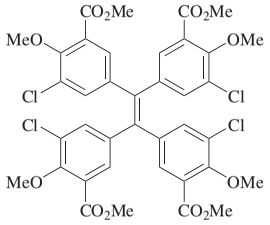
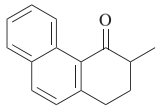
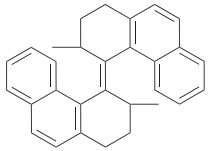
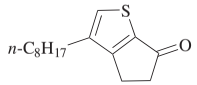
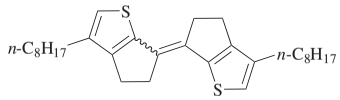
	1. $TiCl_3$, $LiAlH_4$, THF, 0°, 10 min 2. rt, 20 h		(15)	+	 (40)	483
	$TiCl_3$, $LiAlH_4$, THF		(70)			484
	$TiCl_4$, Zn, THF		(98)			484, 485
	$TiCl_4$, Zn, 120°, 10 h		(21)			311

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	$TiCl_4$, Zn, THF, reflux, 2 h	 (53)	486
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1 h 2. Reflux, 20 h	 (8)	487
	1. $TiCl_4$, Zn, THF, reflux, 30 min 2. Reflux, 5 h	 (65), (*E*)/(*Z*) = 5:1	393

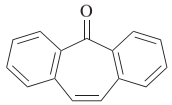
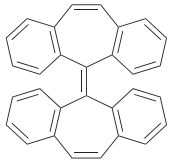
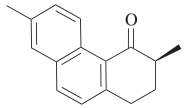
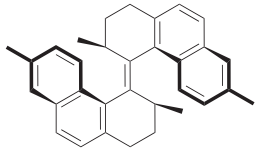
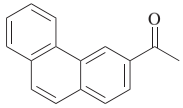
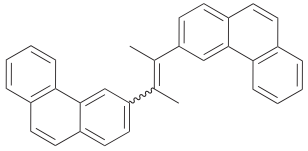
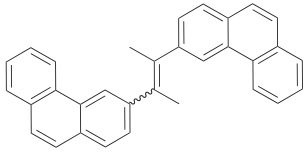
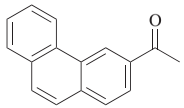
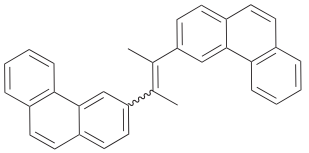
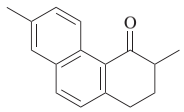
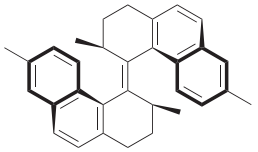
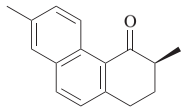
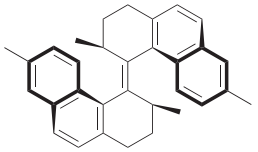
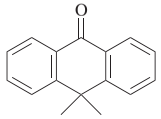
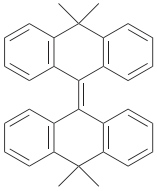
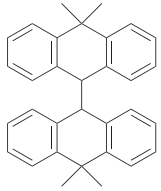
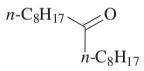
	1. $TiCl_4$, Zn, THF, rt, 1h; then reflux, 5 h 2. Py, 0°, then addition of ketone over 4 h; then reflux, 36 h		(11)	488
C_{16}				
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 40 h		(30)	476
	1. $TiCl_3$, $LiAlH_4$, THF, rt, 1 h 2. Reflux, 24 h		(67), (*E*)/(*Z*) = 1:4	98
	$W(CO)_6$		(12), (*E*)/(*Z*) = 1:4	98

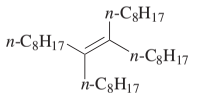
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	Zn, TMSCl	 (38), (*E*)/(*Z*) = 1:4	98
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 7 d	 (9)	489
	$TiCl_4$, Zn, THF	 (30)[k]	490
	1. $TiCl_4$, Zn, THF, rt, 1 h; then reflux, 5 h 2. Py, 0°, 3.5 h; then reflux, 48 h	 +  **I** + **II** (66), **I/II** = 1:3 **I** **II**	491

C_{17}

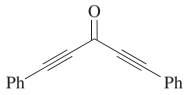


1. $TiCl_4$, Zn, solvent , reflux, 30–40 min
2. Reflux, time

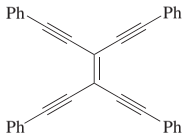


Solvent	Time (h)		
THF/toluene	1.5	(70)	
dioxane	6	(75)[l]	

313

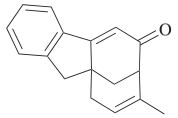


$TiCl_4$, Zn, THF, reflux, 5 d

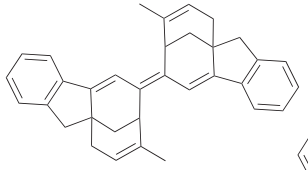


(2.2)

492

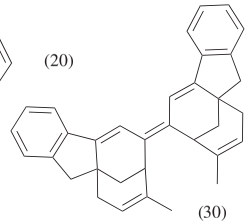


$TiCl_4$, Zn, THF, reflux, 2 h



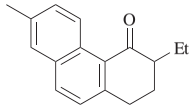
(20)

+

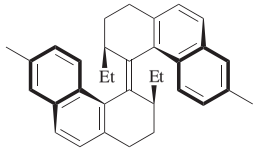


(30)

493



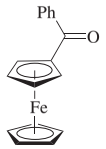
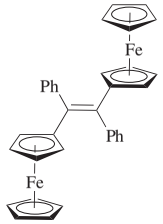
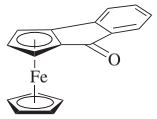
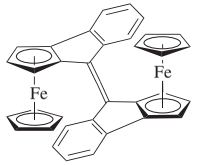
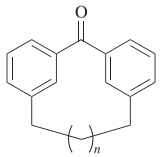
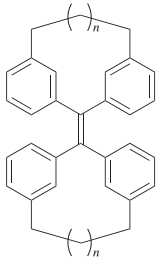
1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Reflux, 7 d



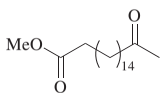
(7.2)

489

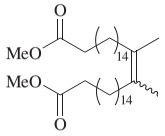
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	1. $TiCl_4$, $LiAlH_4$, THF, reflux, 2 h 2. Bu_3N, reflux, 17 h	 (23)	481
	Zn, TMSCl, THF, 0°, 2 h	 (76)[j]	92
C_{17-19}			
	$TiCl_4$, Zn, THF	 *n*: 2 (90); 3 (94); 4 (98)	485

C_{18}

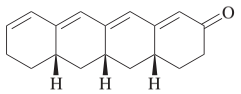


1. $TiCl_3$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 12 h

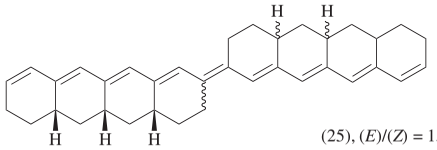


(69)

494



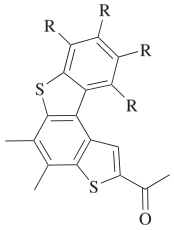
1. $TiCl_4$, Zn, THF, −15° to reflux; then py, reflux, 15 min
2. Reflux, 15 min



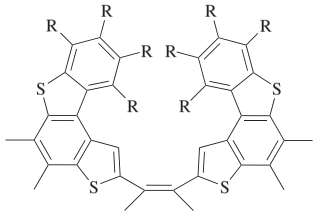
(25), (*E*)/(*Z*) = 15:85

204

$C_{18–22}$



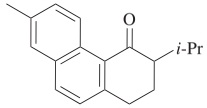
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Py, reflux, overnight



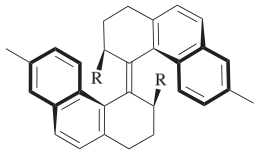
R	
H	(quant)
Me	(quant)

474

C_{18}



1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Reflux, 7 d

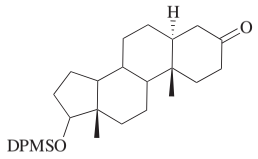
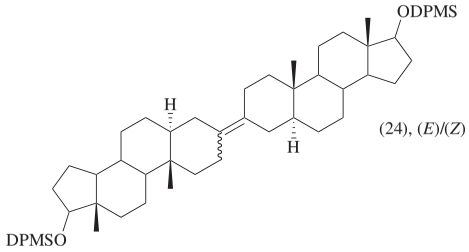
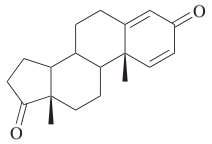
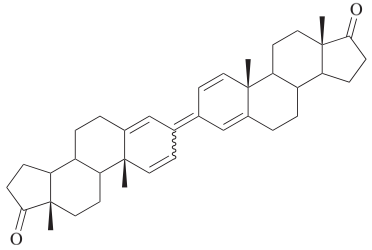


(0.41)

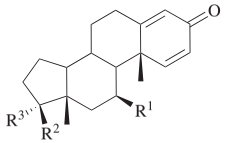
R = *i*-Pr

489

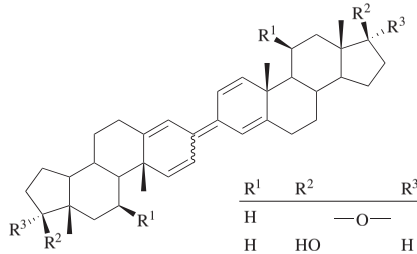
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 15 min 2. Reflux, 20 h	 (24), (*E*)/(*Z*) = 1:1	495
	1. Ti powder, TMSCl, DME, reflux, 67 h 2. Reflux, 1 h	 (84), (*E*)/(*Z*) = 1:1	83

$C_{19–21}$



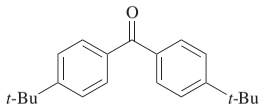
Zn, HCl, THF, reflux, 10 h



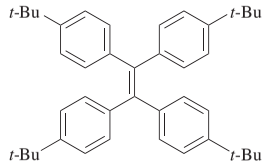
R^1	R^2		R^3		$(E)/(Z)$
H		—O—		(97)	3:2
H	HO		H	(96)	—
H	$AcOCH_2CO$		HO	(85)	—
AcO	$AcOCH_2CO$		HO	(83)	—

90

C_{21}

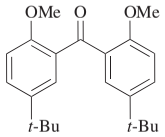


$TiCl_4$, Zn, THF, 60°, 1 h

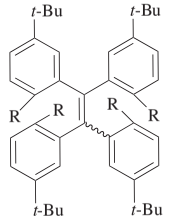


(79)

496



1. $TiCl_3$, Zn/Cu, DME, reflux, 14 h
2. rt

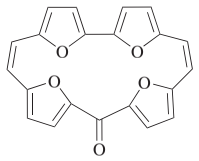
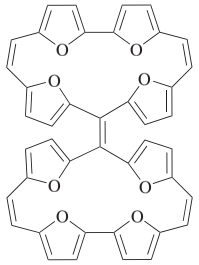
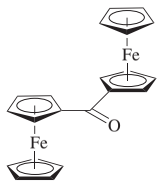
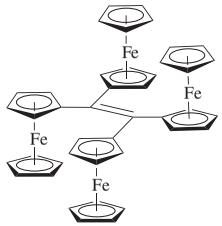
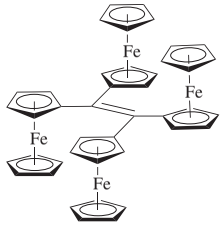


(84)

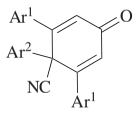
R = MeO

469

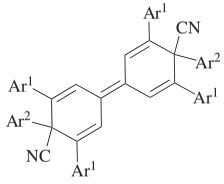
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	1. $TiCl_4$, Zn/Cu, THF, reflux, 30 min 2. Reflux, 2 h	 (43)	497
	Zn, TMSCl, THF, 0°, 2 h	 (73)	92
	1. $TiCl_3(THF)_3$, Li, DME, ultrasonication, 30 min 2. Ultrasonication, 30 min	 (75)	206

$C_{25–27}$

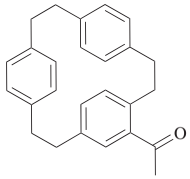


$TiCl_4$, Li, THF, reflux

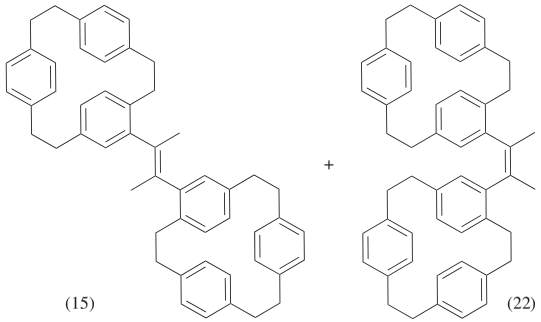


Ar^1	Ar^2	Time (h)		
Ph	Ph	6	(85)	
Ph	4-$O_2NC_6H_4$	8	(45)	130
4-MeC_6H_4	4-$O_2NC_6H_4$	8	(80)	
4-MeC_6H_4	4-ClC_6H_4	10	(82)	

C_{26}

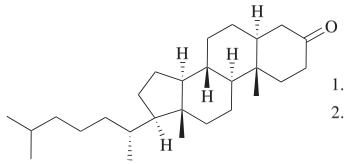
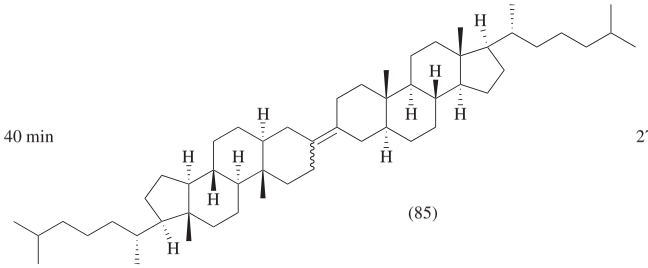
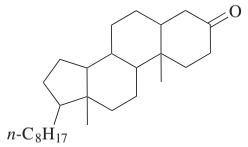
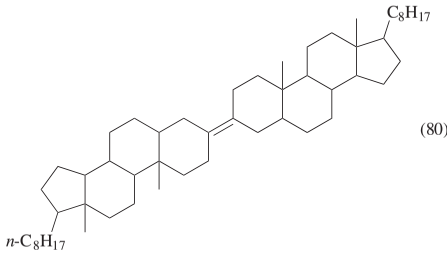


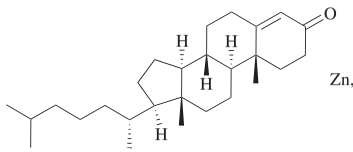
$TiCl_4$, Zn, py, THF, heat



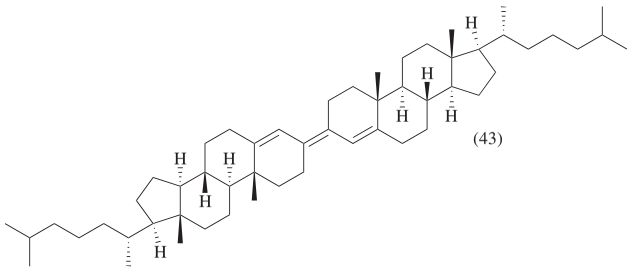
(15) + (22) 498

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

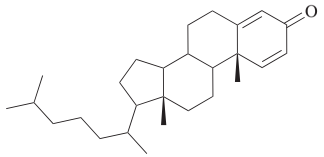
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27}			
	1. $TiCl_3$, K, THF, reflux, 40 min 2. Reflux, 16 h	 (85)	27, 62
	$TiCl_4$, Hg/Mg, THF 0°, 2 h; then reflux, 24 h	 (80)	331



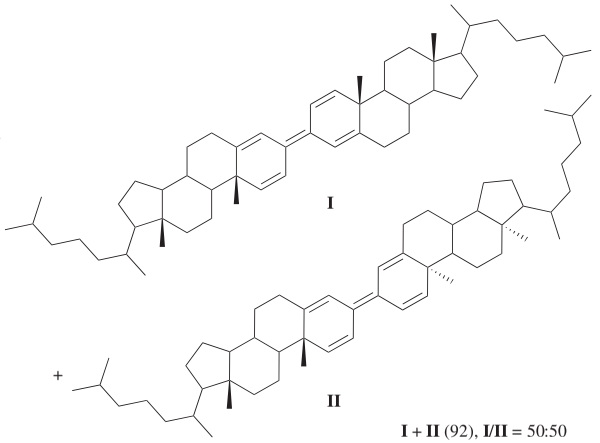
Zn, TMSCl, THF



(43) 91



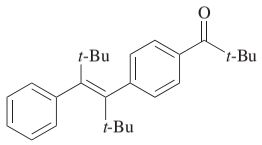
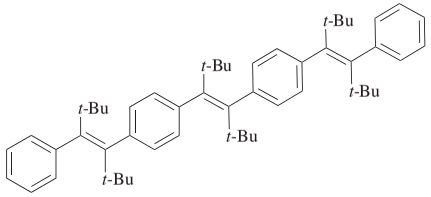
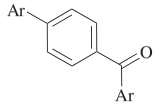
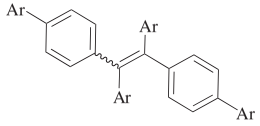
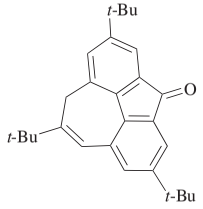
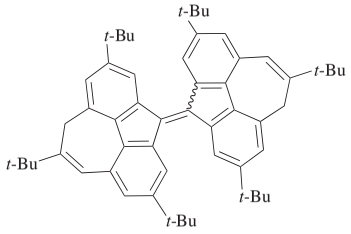
1. $TiCl_4$, Zn, py, THF, 0°
2. 0°, 30 min



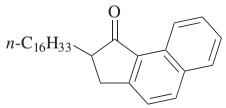
I + **II** (92), **I**/**II** = 50:50

440

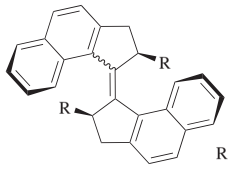
TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{27}				
	$TiCl_4$, Zn, THF		(—)	499
 Ar = 4-*t*-BuC_6H_4	$TiCl_4$, Zn, THF, 60°, 1 h		(63)	500
C_{28}				
	$TiCl_4$, Zn/Cu, THF, reflux, 1 h		(99), (*E*)/(*Z*) = 1:1	501

C_{29}



1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 3 d

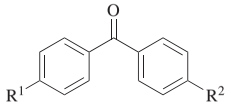


R = *n*-$C_{16}H_{33}$

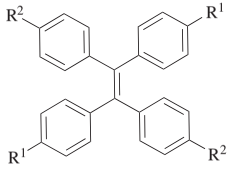
(76), (*E*)/(*Z*) ~3:2

502

$C_{31–41}$

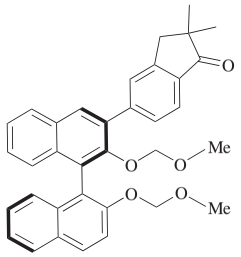
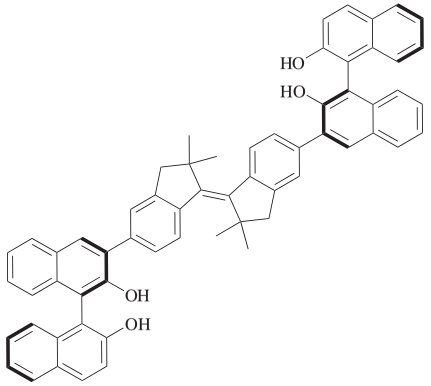
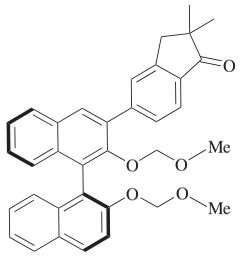
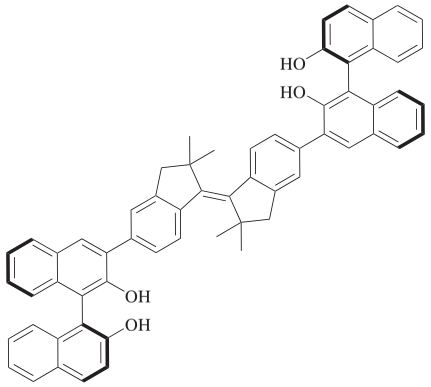


$TiCl_4$, Zn, THF

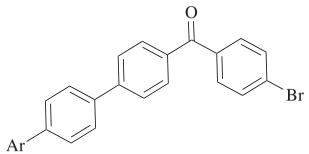


R^1	R^2	Temp(°)	Time (h)		
3,5-$Ph_2C_6H_3$	Br	–40 to reflux	5	(24)	503
4-*t*-BuC_6H_4	4-*t*-BuC_6H_4	60	1	(63)	504, 500
anthracen-9-yl	anthracen-9-yl	60	1	(56.7)	504

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

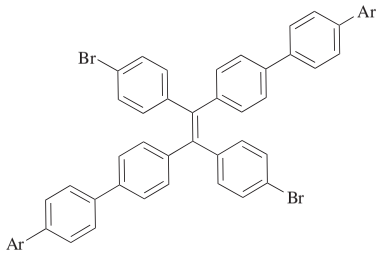
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{31}			
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 12 h 3. 6 N HCl, CH_2Cl_2/MeOH, reflux, 12 h	 (29)	505
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 12 h 3. 6 N HCl, CH_2Cl_2/MeOH, reflux, 12 h	 (21)	505

C_{49}



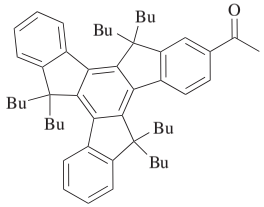
Ar = 3,5-(4-PhC_6H_4)$_2C_6H_3$

$TiCl_4$, Zn, THF, –40° to reflux, 5 h

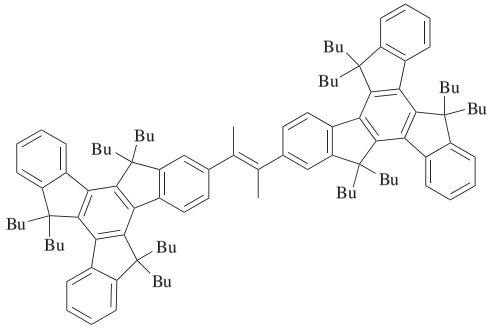


(—) 503

C_{53}

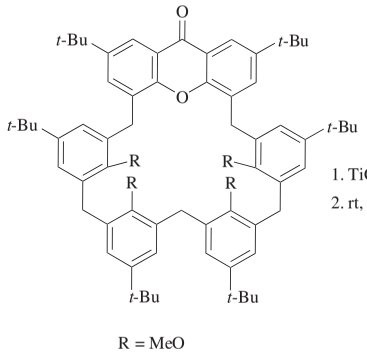
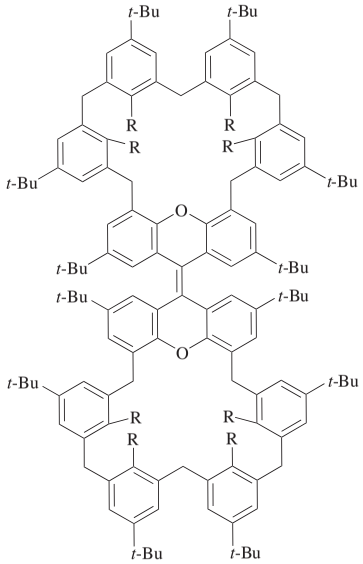


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 3 d



(93) 506

TABLE 1B. HOMOCOUPLING OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{66}  R = MeO	1. $TiCl_4$, $LiAlH_4$, THF, rt, 40 min 2. rt, 2 h; then reflux, 24 h	 (28)	507

[a] The (*E*)-isomer was separated in 5.8% yield by PGC.

[b] A commercial McMurry reagent ($TiCl_3/LiAlH_4$) was used.

[c] The product is a mixture of four diastereomers.

[d] The product was isolated as a THF complex.

[e] The electroreduction was carried out at V ≤ –1900 mV/SCE.

[f] [bmim]Cl($AlCl_3$) is 1-butyl-3-methylimidazolium chloroaluminate.

[g] The ratio of β-*syn*: α-*syn*: β-*anti*: α-*anti* is given.

[h] The Proton Sponge is *N*,*N*,*N*,*N*-tetramethyl-1,8-diaminonaphthalene.

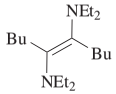
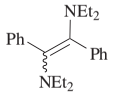
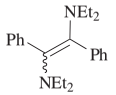
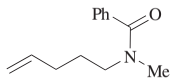
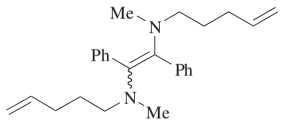
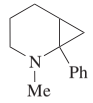
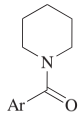
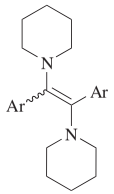
[i] $TiCl_3(DME)_{1.5}$ was used as the titanium source.

[j] The product is a mixture of (*E*)/(*Z*)-*syn*/*anti* isomers.

[k] Optically active starting material was employed.

[l] The yield is based on the amount of ketone consumed.

TABLE 1C. HOMOCOUPLING OF MISCELLANEOUS COMPOUNDS

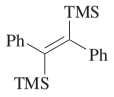
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	Sm, SmI_2, HMPA/toluene, reflux, 26 h	 (23)	105
C_7			
	Sm, SmI_2, THF, 67°, 2–4 h	 (72), (*E*)/(*Z*) = 38:62	105
	1. Yb, ICH_2CH_2I, THF, 67°, 1 h 2. 67°, 4 h	 (45), (*E*)/(*Z*) = 40:60	108
	Sm, SmI_2, THF, 67°, 2–4 h	 (12), (*E*)/(*Z*) = 47:53 +  (41)	105
C_{7-11}			
	Sm, SmI_2, THF, 67°, 2–4 h		105

Ar		(*E*)/(*Z*)
4-ClC_6H_4	(50)	84:16
1-Np	(50)	34:66
2-Np	(67)	87:13

C_7



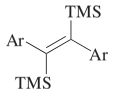
$TiCl_3$, Na/Al_2O_3, DME, 20°, 2.5 h



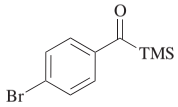
(66) 131



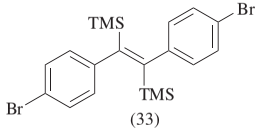
1. $TiCl_3$, Na/Al_2O_3, solvent, reflux, 1 h
2. Reflux, 1 h



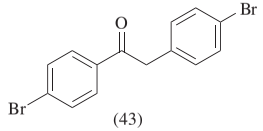
Ar	Solvent		
Ph	DME	(67)	70
4-$MeOC_6H_4$	THF	(56)	



1. $TiCl_3$, Na/NaCl, THF, reflux, 1 h
2. Reflux, 1 h

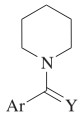


(33) + 70

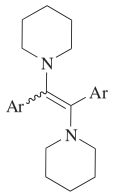


(43)

C_{7-11}



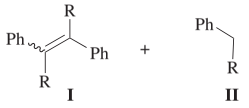
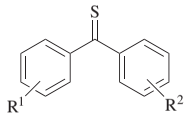
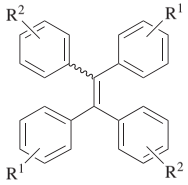
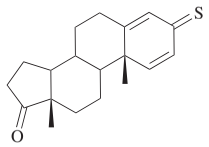
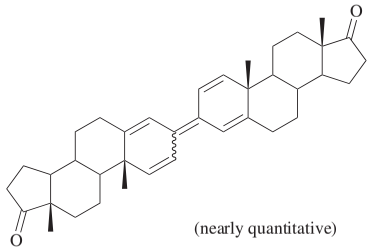
1. M, ICH_2CH_2I, THF, 67°, 1 h
2. 67°, 4 h



Y	Ar	M		(*E*)/(*Z*)
O	4-MeC_6H_4	Yb	(42)	89:11
O	1-Np	Yb	(34)	—
S	Ph	Yb	(67)	—
Se	Ph	Yb	(61)	—
S	Ph	Sm	(82)	83:17
Se	Ph	Sm	(78)	—

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TABLE 1C. HOMOCOUPLING OF MISCELLANEOUS COMPOUNDS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{7–13}$ 	1. $TiCl_3$, Li, THF, reflux, 3 h 2. Py, reflux, 16–18 h	 **I** + **II** R: H (42) (—); Me (45) (—); Bu (32) (38); Ph (26) (43)	138
$C_{13–14}$ 	Cu, DMSO, rt	 R^1 R^2 Time (h) (*E*)/(*Z*): H H 31 (98) —; 4-F 4-F 8 (93) —; 4-Cl 4-Cl 15 (65) —; 4-MeO 4-MeO 20 (73)[a] —; 4-O_2N H 4 (49) 1:1; 4-CF_3 H 12 (98) 1:1; 3-O_2N H 22 (99) 1:1	139
C_{19} 	Zn, HCl, THF, reflux, 10 h	 (nearly quantitative)	90

[a] The reaction was carried out at 80°.

TABLE 2A. MIXED-COUPLING OF ALDEHYDES

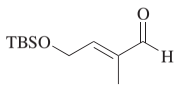
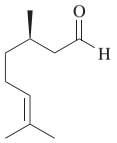
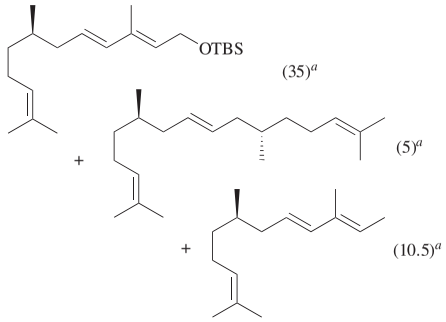
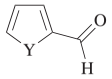
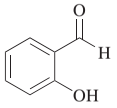
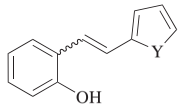
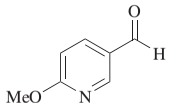
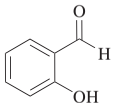
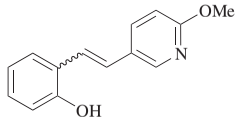
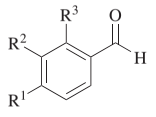
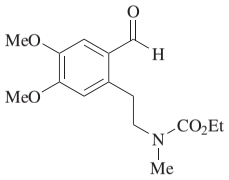
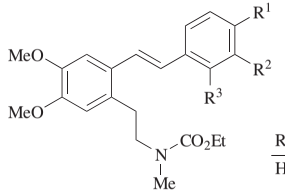
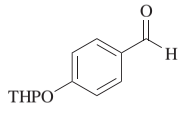
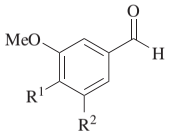
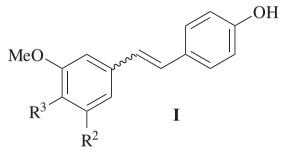
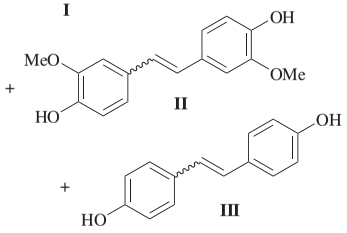
Aldehyde 1	Aldehyde 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. $TiCl_4$, Zn, py, DME, reflux, 2.5 h 2. Reflux, 14 h; then addition of aldehydes; then reflux, 5 h	 (35)[a] + (5)[a] + (10.5)[a]	509, 510
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Reflux	 Y: O (58), S (62)	145
C_6				
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Reflux	 (62)	145

TABLE 2A. MIXED-COUPLING OF ALDEHYDES (*Continued*)

Aldehyde 1	Aldehyde 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$TiCl_3$, Li, DME, reflux		511

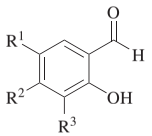
R^1	R^2	R^3	
H	H	H	(55)
$-OCH_2O-$		Br	(67)

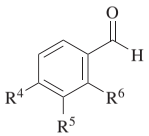
		1. $TiCl_3$, Zn, THF, reflux, 3 h 2. Reflux		346



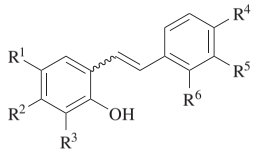
R^1	R^2	R^3	**I**	(*E*)/(*Z*)	**II**	**III**
THPO	H	HO	(25)	45:55	(20)	(15)
H	MeO	H	(22)	48:52	(25)	(19)

C_{7-8}





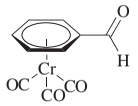
1. $TiCl_4$, Zn, THF, reflux, 2.5 h
2. Reflux

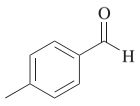


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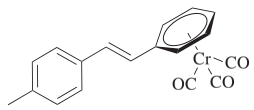
R^1	R^2	R^3	R^4	R^5	R^6	
H	H	H	H	H	H	(60)
H	H	H	MeO	H	H	(75)
H	H	H	H	–CH=CH-CH=CH–		(61)
H	H	H	H	H	MeO	(65)
H	H	H	–OCH_2O–		H	(63)
H	H	H		H	H	(72)
H	H	H	H	CF_3	H	(52)
Cl	H	H	H	H	H	(59)
Me	H	H	H	H	H	(59)
MeO	H	H	H	H	H	(63)
H	H	MeO	H	H	H	(69)
–OCH_2O–		H	H	H	H	(72)

C_7





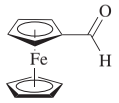
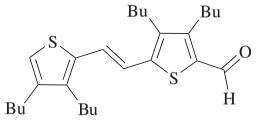
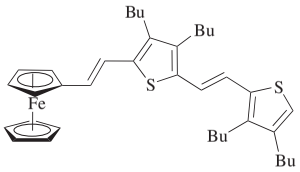
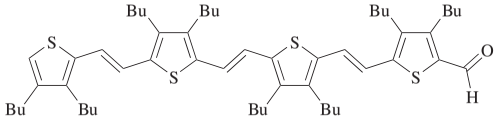
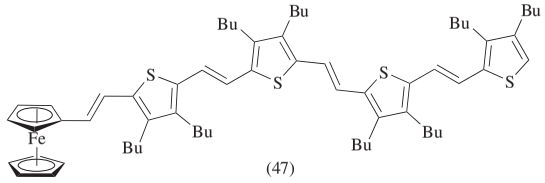
$NbCl_3$, THF, rt, 8 h



(71)

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TABLE 2A. MIXED-COUPLING OF ALDEHYDES (*Continued*)

Aldehyde 1	Aldehyde 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
		1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Py, reflux, overnight	 (quant)	387
		1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Py, reflux, overnight	 (47)	387

[a] Optically active starting material was employed.

TABLE 2B. MIXED-COUPLING OF KETONES

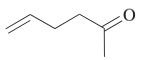
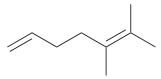
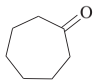
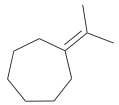
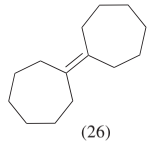
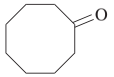
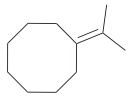
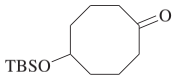
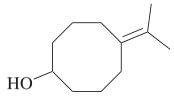
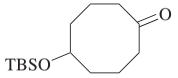
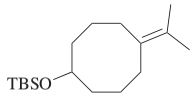
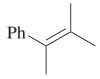
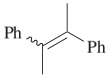
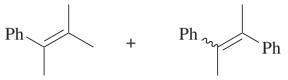
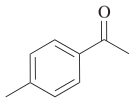
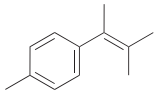
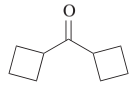
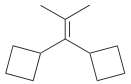
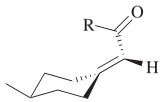
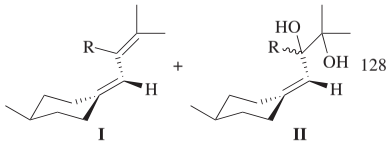
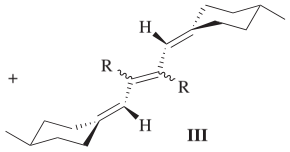
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		$W_2(OCH_2CMe_3)_6(Py)_2$, 22°, 12–22 h	 (36)	99
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (50) +  (26)	27, 141
		$W_2(OCH_2CMe_3)_6(Py)_2$, 22°, 12–22 h	 (44)	99
		1. $TiCl_3(AlCl_3)$, Li, THF, rt, 12 h 2. rt, 5 h; then addition of ketones; then rt, 14 h	 (38)	512
		$TiCl_3(AlCl_3)$, Li, heat	 (52)	513
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (65) +  (16)	27, 514

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		$InCl_3$, Zn, MeCN, reflux, 13 h	 (65) + (15)	104
		$W_2(OCH_2CMe_3)_6(Py)_2$, 22°, 12–22 h	 (66)	99
		$TiCl_3$, Li	 (30)	185
		1. $TiCl_4$, $LiAlH_4$, THF, reflux, 1 h 2. Temp, time	 **I** + **II**	128

R	Temp	Time (h)	**I**	**II**	**III**
Me[a]	0°	1	(—)	(52)	(4)
Ph[a]	rt	3.5	(40)	(24)	(—)

+  **III**

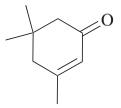
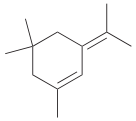
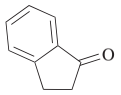
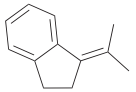
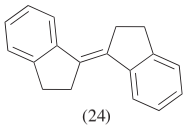
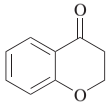
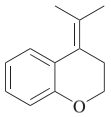
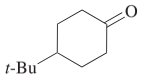
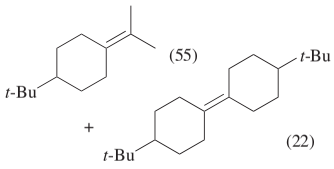
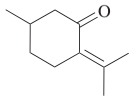
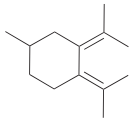
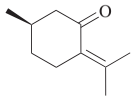
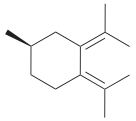
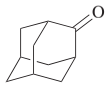
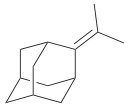
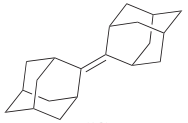
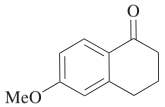
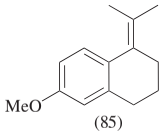
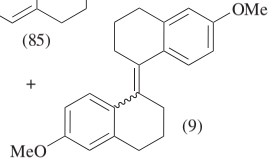
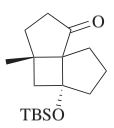
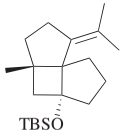
	1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h		(63)	27, 141
	1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (71) +  (24)		27, 141
	1. $TiCl_4$, Zn, py, dioxane, −10 to −5° 2. Microwave irradiation, 10 min		(10)	121
	1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (55) + (22)		27, 141

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (55)	27, 141
		—	 (50)	196
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (63) +  (12)	27, 141
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (85) +  (9)	27, 141

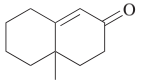


1. $TiCl_3$, Li, DME, reflux, 1 h
2. rt, 4 h; then addition of ketones; then reflux, 12 h

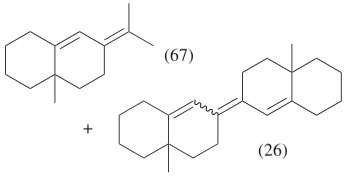


(75.6)

321

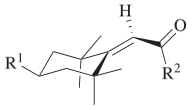


1. $TiCl_3$, Li, DME, reflux, 1 h
2. rt, 2 h; then reflux, 16 h

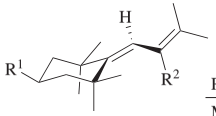


(67) + (26)

27, 141



1. $TiCl_4$, $LiAlH_4$, THF, reflux, 1 h
2. 60°, 20 h

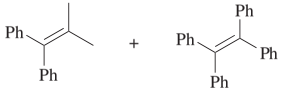


R^1	R^2	
Me	Me	(53)[a]
TBSO	Me	(73)[a]
TBSO	Ph	(85)[a]

128



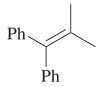
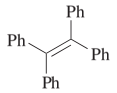
1. $TiCl_3$, Li, DME, reflux, 1 h
2. rt, 2 h; then reflux, 16 h



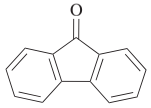
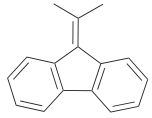
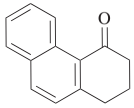
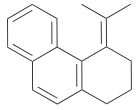
(94) + (trace)

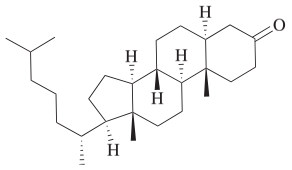
27, 141

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

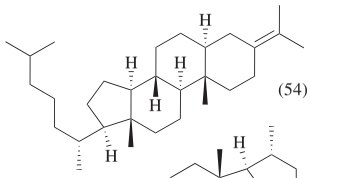
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		$TiCl_3$, Li, DME	 (—)	515
		1. $TiCl_4$, Zn, py, dioxane, −10 to −5° 2. Microwave irradiation, 10 min	 (52)	121
		MCl_3, Zn, MeCN, reflux	 **I** +  **II**	

M	Time (h)	**I**	**II**	
Al	22	(71)	(24)	88
In	18	(55)	(20)	104

		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (84)	27, 141
		$TiCl_3$, $LiAlH_4$, THF, reflux, 2 h	 (31)	516

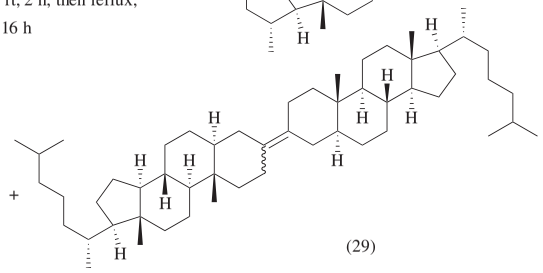


1. $TiCl_3$, Li, DME, reflux, 1 h
2. rt, 2 h; then reflux, 16 h



(54)

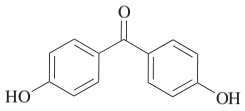
27, 141



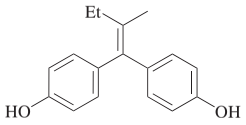
(29)

C_4





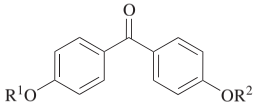
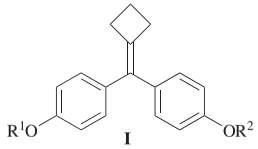
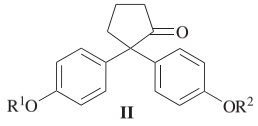
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux in the dark, 2 h



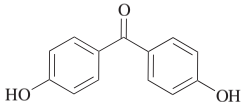
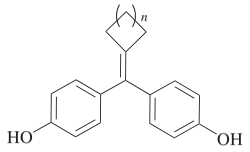
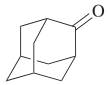
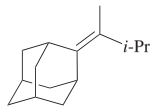
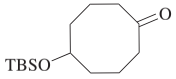
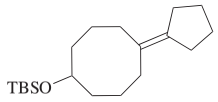
(91)

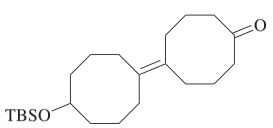
517

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

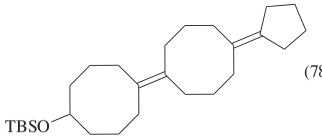
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		1. $TiCl_4$, M, THF, reflux, 2 h 2. Reflux, time	 **I**	189
			+  **II**	

R^1	R^2	M	Time (h)	**I**	**II**
H	H	Mg/HgCl	4	(18)	(74)
Me	Me	Mg/HgCl	20	(87)	(trace)
Me	H	Zn	2	(18)	(57)

C_{4-7}					
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2 h		*n* 1 (8) 2 (83) 3 (72) 4 (62)	518
C_5					
		$TiCl_3$, Li		(7)	519
		1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 4 h 2. Reflux, 3 h		(95)	412



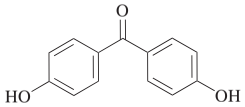
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 4 h
2. Reflux, 3 h



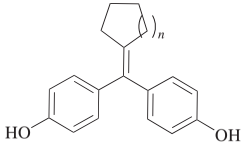
(78) 412

C_{5-6}

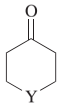




1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 4 h

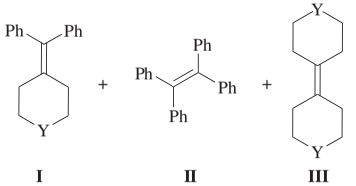


n		
1	(83)	189
2	(72)	





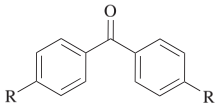
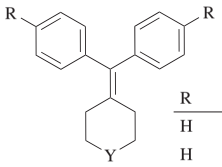
1. $TiCl_4$, Zn,THF, reflux, 2.5 h
2. Py, reflux



I **II** **III** 144

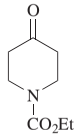
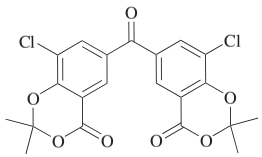
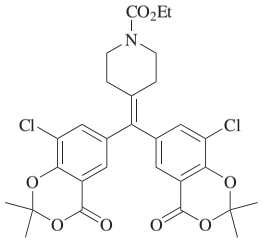
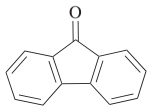
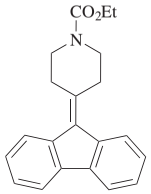
Y	**I**	**II**	**III**
CH_2	(78)	(2)	(10)
PhN	(92.5)	(5)	(0.5)
$AcHNCH_2$	(90.5)	(4)	(2)

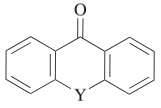
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $TiCl_3$, Li, DME, reflux, 2 h 2. rt, 4 h; then reflux, 13 h		

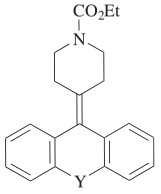
R	Y		
H	CH_2	(86)	520
H	O	(93)	520
H	S	(76)	520
H	EtO_2CN	(93)	521, 520
HO	EtO_2CN	(53)	521
AcO	EtO_2CN	(82)	521
HO	CH_2	(87)	521

C_5

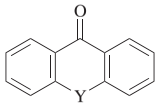
		1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 14 h		(32.1)	522
		1. $TiCl_3$, Li, DME, reflux, 2 h 2. rt, 4 h; then reflux, 13 h		(70)	521



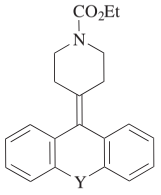
1. $TiCl_3$, Li, DME, reflux, 2 h
2. rt, 4 h; then addition of ketones; then reflux, 13 h



Y		
—	(52)	
H, H	(93)	
O	(27)	523
S	(51)	
$(CH_2)_2$	(44)	

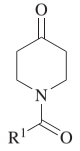
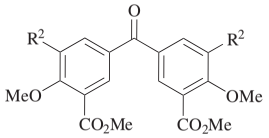
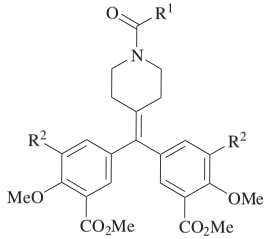


1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Reflux, 14 h

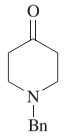
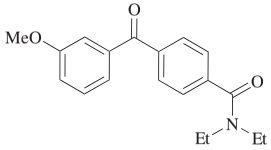
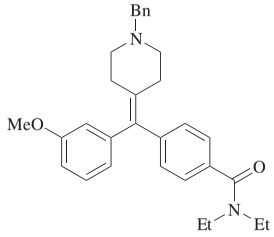


Y		
CH=CH	(77.9)	522
$(CH_2)_2$	(80.2)	

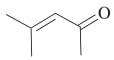
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

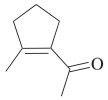
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. $TiCl_4$, Zn, THF, reflux, 1–2 h 2. Reflux, 12–15 h		522

R^1	R^2	
MeO	Cl	(48.8)
MeO	Me	(56.4)
EtO	Cl	(58.3)
EtO	Me	(61.7)
$MeO_2C(CH_2)_3$	Cl	(13.0)
$MeO_2C(CH_2)_3$	Me	(14.4)

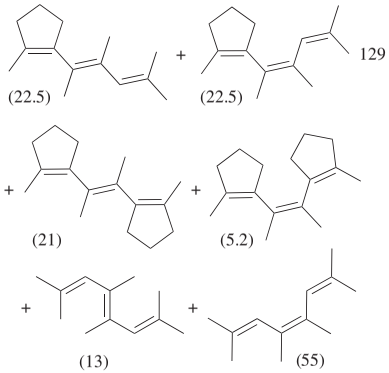
		1. $TiCl_4$, Zn, DME, reflux, 2 h 2. Reflux, 4 h		(65)	524

C_6



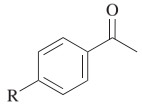


1. $TiCl_4$, Mg, –60° to rt, 3–4 h; then rt, 20 h
2. Reflux, 15 h

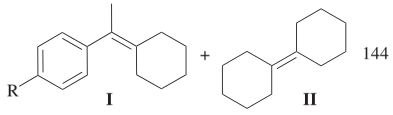


129





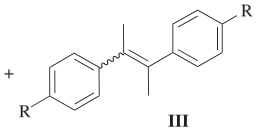
1. $TiCl_4$ (*x* eq), Zn, THF, reflux, 2.5 h
2. Py, reflux



I **II**

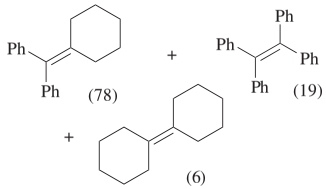
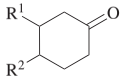
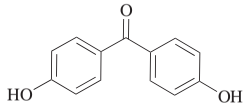
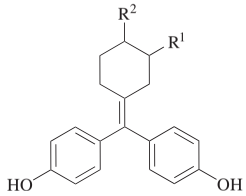
144

R	*x*	**I**	**II**	**III**
H	5.0	(32)	(29)	(27)
HO	5.0	(30)	(31)	(26)
HO	2.0	(70)	(13)	(8)
MeO	2.0	(69)	(14)	(9)
	2.0	(60)	(17)	(14)



III

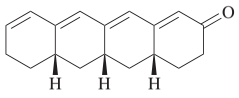
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (78) + (19) + (6)	27
C_{6-9}				
		1. $TiCl_4$, Zn, THF, reflux, time 1 2. Reflux, time 2		

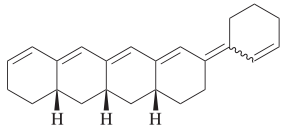
R^1	R^2	Time 1 (h)	Time 2 (h)		
MeO_2C	H	2	2	(81)	518, 525
MeO_2CCH_2	H	2	2	(~80)	525
$(MeO_2C)_2CH$	H	2	2	(74)	518
$AcO(CH_2)_3$	H	2	2	(70)	518
HO	H	1	3	(50.4)	526
H	AcO	2	2	(83)	518
H	MeO_2C	2	2	(~80)	525
H	EtO_2C	2	2	(77)	518, 525
H	MeO_2CCH_2	2	2	(71)	518, 525
H	HO	1	3	(58.0)	526

C_6





1. $TiCl_4$, Zn, THF, −15° to reflux; then py, reflux, 15 min
2. Reflux, 15 min



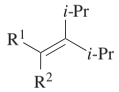
(38) 204

C_7

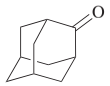




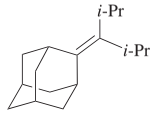
—



R^1	R^2		
Me	*i*-Pr	(27)	527
Me	Ph	(—)	527
Et	Ph	(25)	527
i-Pr	Ph	(15)	527
$(CH_3)_2CD$	Ph	(17)	527
i-Bu	Ph	(23)	527
t-Bu	Ph	(4)	527
Me	2-MeC_6H_4	(61)	528

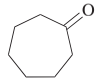
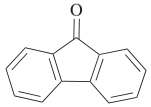
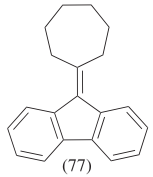
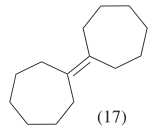
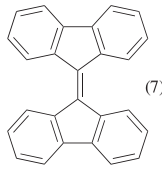
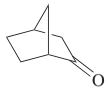
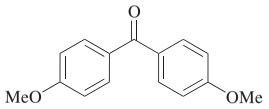
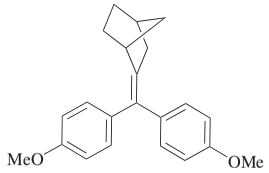


$TiCl_3$, Li



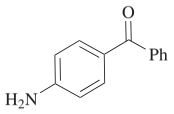
(7) 519

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

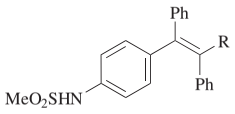
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (77) +  (17)	27
			+  (7)	
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Reflux, 1.5 h	 (65)	529

C_{8-15}





1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2.5 h
3. $MeSO_2Cl$, Et_3N, CH_2Cl_2, rt, 15 h

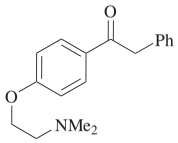


530

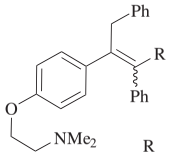
R	
Me	(60)
Et	(63)
Bu	(64)
n-C_6H_{13}	(62)
c-C_6H_{11}	(60)
n-C_8H_{17}	(65)

C_{8-11}





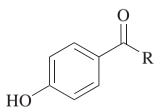
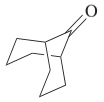
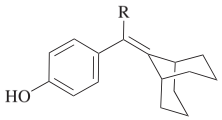
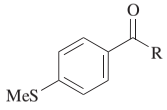
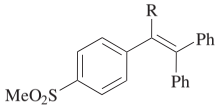
$TiCl_4$, Zn, dioxane, reflux, 4 h



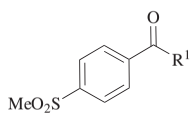
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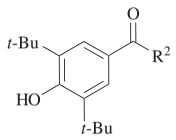
R		(*E*)/(*Z*)
Et	(69)	1:4
Bu	(48)	1:2
$ClCH_2CH_2$	(41)	1:1
$BrCH_2$	(39)	9:1
Me_3CH_2BrCH	(34)	6:1
O_2NCH_2	(42)	1:11
Pr	(46)	1:2
$ClCH_2$	(44)	1:2

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

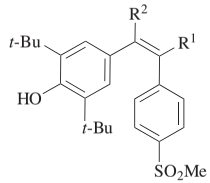
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-13} 		$TiCl_4$, Zn	 R: Me (—); 4-HOC_6H_4 (—)	532
C_{8-22} 		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2.5 h 3. Oxone, MeOH/THF/H_2O, rt, 15 h	 R: Me (62); Et (70); Bu (72); *n*-C_5H_{11} (—); *n*-C_6H_{13} (66); *n*-C_7H_{15} (68); *n*-C_9H_{19} (68); *n*-$C_{15}H_{31}$ (76)	533, 534

C_{8-14}





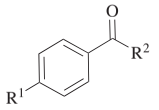
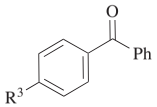
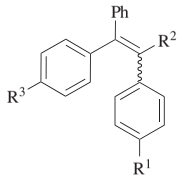
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2.5 h



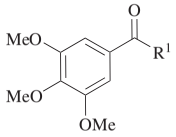
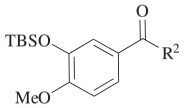
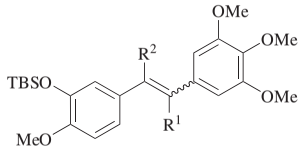
57

R^1	R^2		(*E*)/(*Z*)
Me	Ph	(38)	27:73
Et	Ph	(22)	0:100
Bu	Ph	(25)	0:100
n-C_7H_{15}	Ph	(27)	0:100
Ph	Me	(30)	0:100
Ph	Et	(35)	0:100
Ph	Bu	(32)	0:100
Ph	*n*-C_7H_{15}	(34)	0:100
Ph	*n*-$C_{15}H_{31}$	(37)	0:100

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

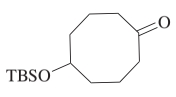
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2.5 h		58

R^1	R^2	R^3		$(E)/(Z)$
MeS	Me	Me	(65)	>35:65
MeO_2S	Me	Me	(64)	>34:66
MeS	Et	Me	(60)	>40:60
MeO_2S	Et	HO	(75)	<1:99

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-13} 		1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux, 5 h		535

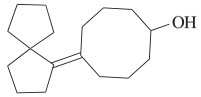
R^1	R^2	
Me	Ph	(72)
Et	Ph	(68)
Ph	Me	(41)
Ph	Et	(66)
Ph	Ph	(31)

C_8





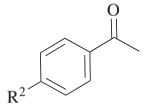
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 4 h
2. Reflux, 3 h
3. HF



(45) 412

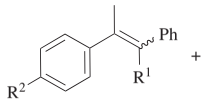
C_{8-13}



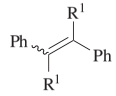


1. $TiCl_4$, Zn, THF, reflux, 2.5 h
2. Py, reflux

R^1	R^2	**I**	**II**	**III**
Me	Me	(41)	(28)	(29)
Me	HO	(58)	(18)	(15)
Me	MeO	(62.2)	(12)	(12.5)
Me	H_2N	(60.2)	(16)	(13)
Me		(76.7)	(9)	(6)
Ph	H	(65)	(12)	(13)
Ph	HO	(71)	(13)	(7)
Ph	MeO	(92)	(4)	(2)
Ph	H_2N	(80)	(12)	(5)
Ph		(94)	(3)	(1.4)

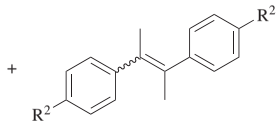


I



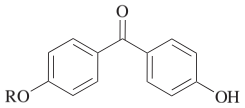
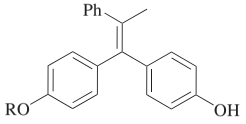
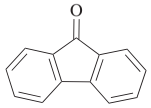
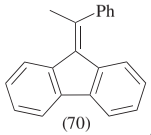
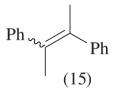
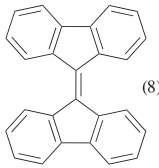
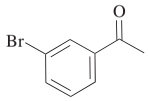
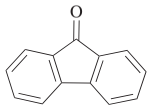
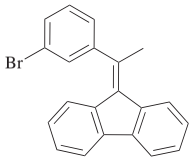
II

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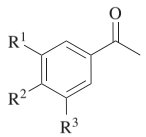


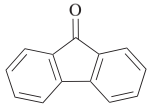
III

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

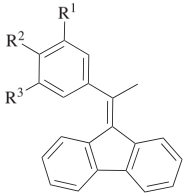
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 3 h	 R: H (78); $Me_2N(CH_2)_2$ (46)	536
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (70) +  (15) +  (8)	27
		1. $TiCl_3$, Mg, THF, reflux, 3.3 h 2. Reflux, 2.5 h	 (6)	537

C_{8-11}



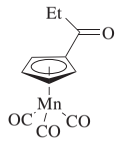


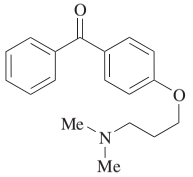
1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1 h
2. rt, 3.5 h



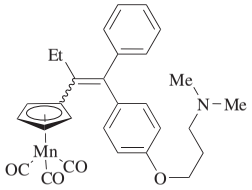
R^1	R^2	R^3		
H	H	H	(25)	
H	Br	H	(6)	
MeO	H	H	(26)	537
Me	H	H	(22)	
Me	Me	H	(17)	
Me	Me	Me	(17)	
CF_3	H	H	(23)	

C_8

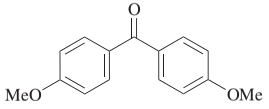




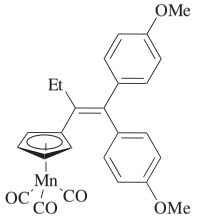
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 1 h



(54) 538

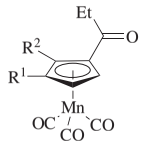
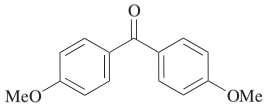
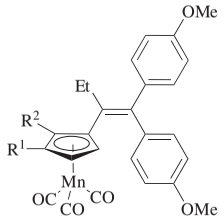
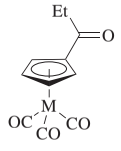
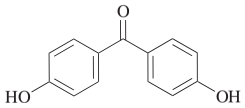
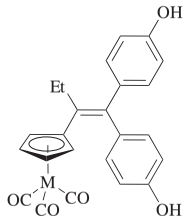
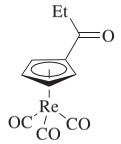
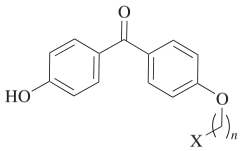
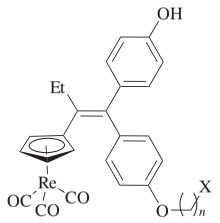


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2 h



(83) 539

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

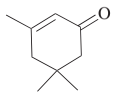
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2 h		540
C_8 		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2 h		541
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2 h		542, 543

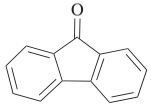
R^1	R^2		
H	H	(83)	
H	Me	(64)	
Me	H	(48)	

M		
Mn	(96)	
Re	(86)	

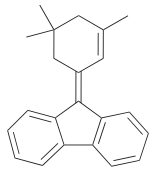
n	X		
2	Br	(64)	
3	Br	(>60)	
4	Br	(>60)	
5	Br	(>60)	
8	Cl	(>60)	

C_9



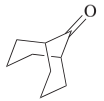


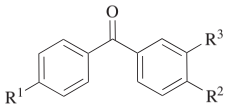
1. $TiCl_4$, Mg, THF, rt, 20 h
2. 0° to rt, 36 h



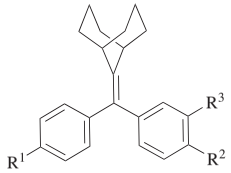
(40)

544





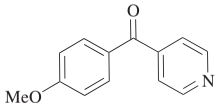
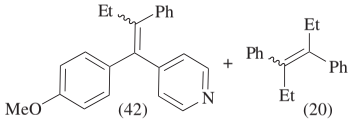
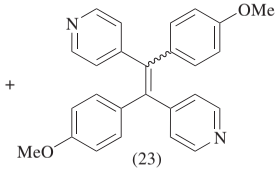
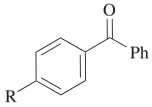
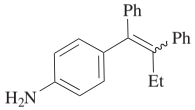
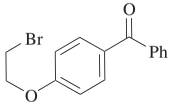
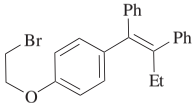
1. $TiCl_4$, Zn, THF, reflux, 2.5 h
2. Reflux, 1.5 h



R^1	R^2	R^3	
HO	H	H	(82)
HO	F	H	(67)
HO	HO	H	(78)
MeO	H	MeO	(61)
MeO	MeO	MeO	(67)

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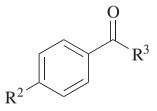
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. $TiCl_4$, Zn, dioxane 2. Reflux, 4 h	 (42) + (20) +  (23)	545
		1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Reflux, time		546
		$TiCl_4$, Zn, THF, reflux, 8 h	 (—)	547

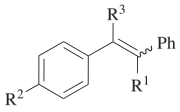
R	Time		dr
H_2N	3 d	(38)	85:15
O_2N	4 h	(55)	85:15

C_{9-17}





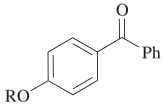
1. $TiCl_4$, Zn, THF, reflux, time 1
2. Reflux, time 2



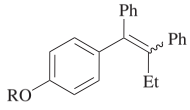
R^1	R^2	R^3	Time 1 (h)	Time 2 (h)		(*E*)/(*Z*)	
Et	BnO	Ph	1.5	0.5	(86.9)	1:5	55
Np	MeO_2S	*n*-C_5H_{11}	2	2.5	(68)	>39:61	58

C_9



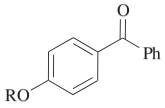


1. $TiCl_3$, Li, DME, reflux, 1 h
2. 18°, 2 h; then reflux, 12–20 h

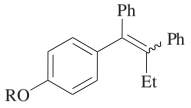


142

R		(*E*)/(*Z*)
H	(93)	1:9
Me	(76)	3:8
$Cl(CH_2)_2$	(68)	1:4
$Br(CH_2)_2$	(—)	1:4
$Me_2N(CH_2)_2$	(88)	1:3



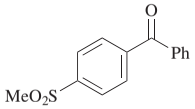
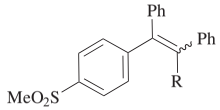
1. $TiCl_4$, Zn, THF, reflux, 1–2 h
2. Reflux, 2–4 h



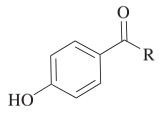
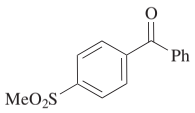
142

R		(*E*)/(*Z*)
H	(98)	1:7
$Cl(CH_2)_2$	(55)	0:100

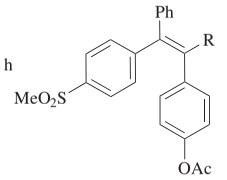
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-15} 		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2.5 h		59

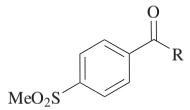
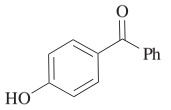
R		
Et	(62)	
Pr	(—)	
Bu	(—)	
n-C_6H_{13}	(—)	
n-C_8H_{17}	(—)	

C_{9-11}  

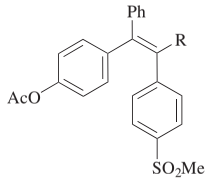
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2.5 h
3. AcCl, Et_3N, ether, rt, 1.5 h



R		
Et	(62)	59
Bu	(67)	

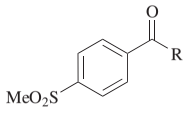
C_{9-22}  

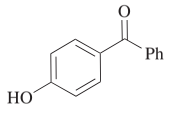
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2.5 h
3. AcCl, Et_3N, ether, rt, 15 h



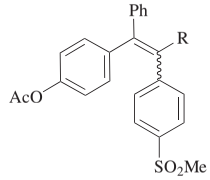
R		
Et	(72)	
Bu	(68)	534
n-C_7H_{15}	(67)	
n-$C_{15}H_{31}$	(70)	

C_{9-16}





1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2.5 h
3. AcCl, Et_3N, ether, rt, 15 h

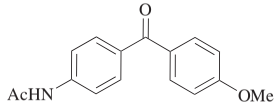


58

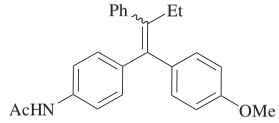
R		(*E*)/(*Z*)
Et	(72)	<1:99
Pr	(68)	<1:99
n-C_5H_{11}	(70)	<1:99
n-C_6H_{13}	(70)	<1:99
n-C_9H_{19}	(63)	<1:99

C_9



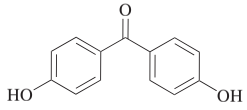


$TiCl_3$, $LiAlH_4$, THF, rt, 20 h

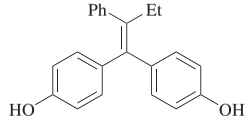


(40), (*E*)/(*Z*) = 2:1

54



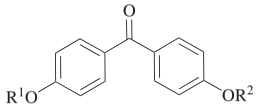
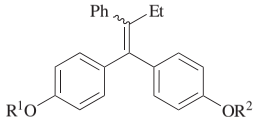
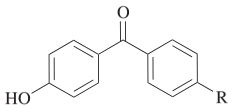
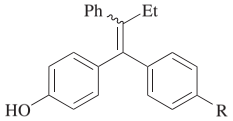
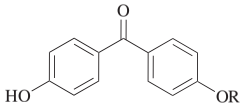
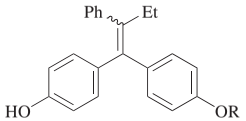
$TiCl_4$, Zn, THF, reflux

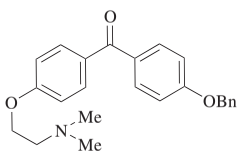


(73)

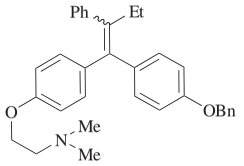
548

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

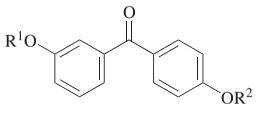
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux in the dark, 2.5 h		53
			R^1 / R^2 / (%) / (*E*)/(*Z*) / dr Bn / H / (72) / 4:1 / — 2,3,5,6-F_4-4-CF_3C_6 / Bn / (60) / — / 2:1	
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 4 h		549
			R / (%) / (*E*)/(*Z*) H / (95) / — PivO / (69) / —	
		$TiCl_4$, Zn, THF		52
			R / (%) / (*E*)/(*Z*) *t*-BuCO / (—) / 14:1 BnO_2C / (—) / (—) Bn / (—) / (—) Ph_3C / (—) / (—)	



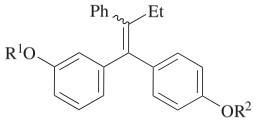
1. $TiCl_4$, Zn, THF, 60°, 2 h
2. 65°, 4 d



(52) 550

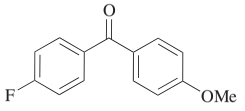


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 5 h

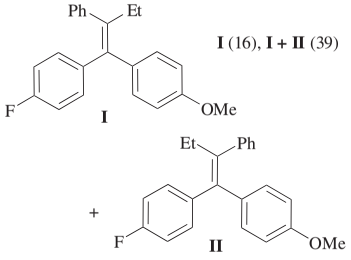


56

R^1	R^2		(*E*)/(*Z*)
Piv	H	(65)	100:1
H	$Et_2N(CH_2)_2$	(60)	2:1

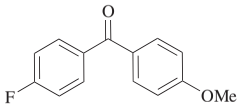
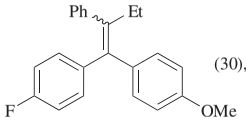
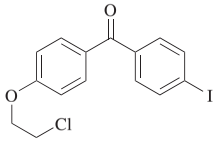
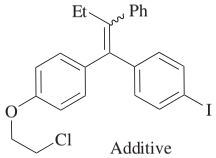
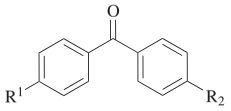
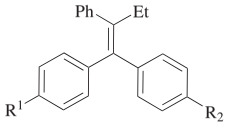


$TiCl_3$, $LiAlH_4$, THF, reflux, 4 h

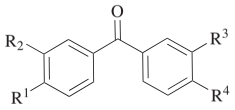


I (16), **I** + **II** (39) 54

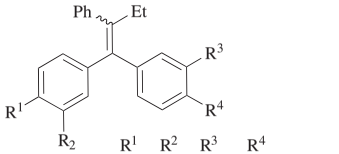
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. $TiCl_4$, Zn, ether 2. rt, 16 h; then reflux, 4 h	 (30), (*E*)/(*Z*) = 3:1	54
		1. $TiCl_4$, Zn, dioxane, additive, reflux, 2 h 2. Reflux, 2.5 h		51
			Additive (56.5) (*E*)/(*Z*) 3.9:1 none dppe (63) 4.1:1	
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 4 h		551

R^1	R^2	
HO	BnO	(—)
HO	$Br(CH_2)_2O$	(40)
Br	HO	(70)
MeO	Me	(55)



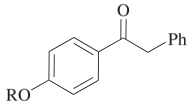
$TiCl_4$, Zn, THF



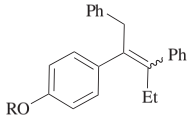
R^1	R^2	R^3	R^4	
HO	H	BnO	H	(71)
H	HO	H	BnO	(<61)

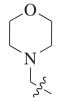
552





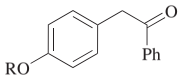
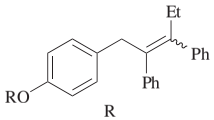
$TiCl_4$, Zn, reflux, 4 h

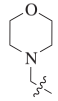


R		(*E*)/(Z)
Me_2NCH_2	(49.0)	1:4
Et_2NCH_2	(41.9)	5:6
	(74.8)	1:2
	(80.3)	1:2
	(40.5)	1:2

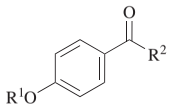
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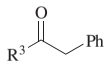
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$TiCl_4$, Zn, reflux, 4 h		554

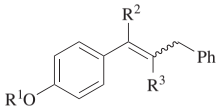
R		(*E*)/(*Z*)
Me_2NCH_2	(71.2)	6:5
Et_2NCH_2	(40.2)	9:1
	(18.9)	6:5
	(38.4)	6:1
	(29.2)	3:1

C_9





$TiCl_4$, Zn, reflux, 4 h



554

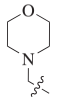
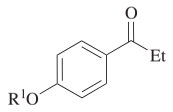
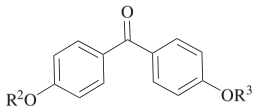
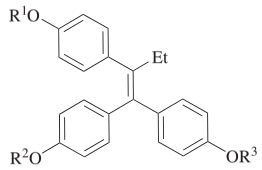
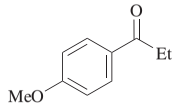
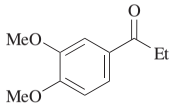
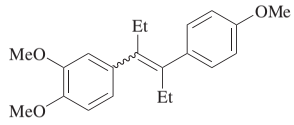
R^1	R^2	R^3		$(E)/(Z)$
Me_2NCH_2	Et	Ph	(44.3)	0:>100
Et_2NCH_2	Et	Ph	(34.7)	0:>100
	Et	Ph	(24.7)	1:5
	Et	Ph	(39.2)	1:5
	Et	Ph	(29.2)	1:5
Me_2NCH_2	Ph	Et	(69.0)	1:2
Et_2NCH_2	Ph	Et	(71.5)	1:2
	Ph	Et	(68.4)	1:2
	Ph	Et	(65.1)	1:2
	Ph	Et	(67.9)	1:2

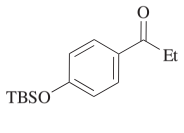
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

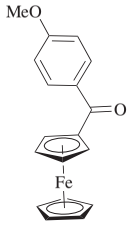
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. $TiCl_4$, Zn, THF, reflux, time 1 2. Reflux, time 2		

R^1	R^2	R^3	Time 1 (h)	Time 2 (h)		
H	H	H	2	3	(51)	536
Me		Me	1.5	4	(60)	555

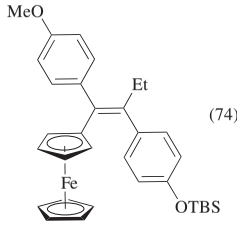
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h		(55)	556

C_9

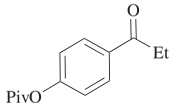


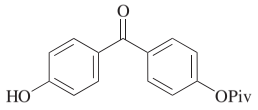


$TiCl_4$, Zn, THF, reflux

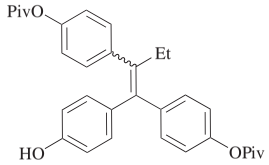


(74), (*E*)/(*Z*) = 7:93 548

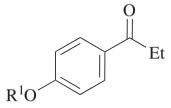


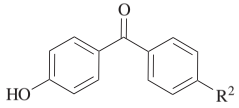


$TiCl_4$, Zn, THF,
reflux, 4 h

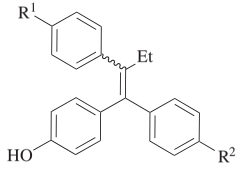


(67) 557





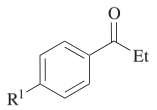
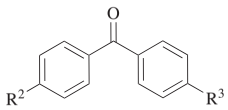
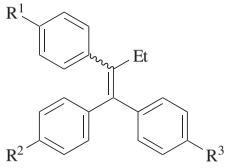
1. TiCl4, Zn, THF,
reflux, 2 h
2. Reflux, 2 h



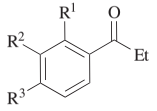
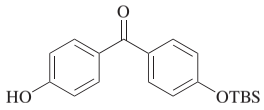
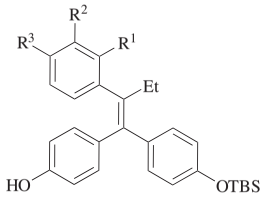
558

R^1	R^2		dr
Piv	H	(70)	1:1
Piv	PivO	(67)	1:5
TBS	TBSO	(75)	1:1

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

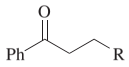
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 12 h		559

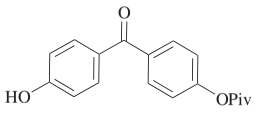
R^1	R^2	R^3		$(E)/(Z)$
H	HO	H	(84)	1:1
H	HO	HO	(39)	1:1
HO	H	H	(83)	1:1

		1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Reflux, 4 h		555

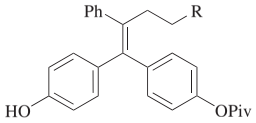
R^1	R^2	R^3	
H	H	TBSO	(87)
PivO	H	H	(41)
H	PivO	H	(49)
H	H	PivO	(67)
MeO	H	H	(21)
H	MeO	H	(29)
H	H	MeO	(54)

C_9



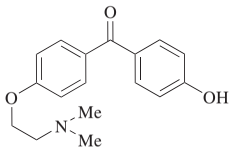


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 5 h

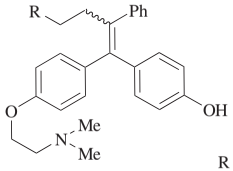


R		(*E*)/(*Z*)
H	(82)	>100:1
Cl	(47)	>100:1

560

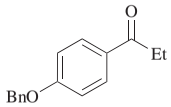


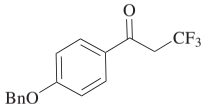
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 5 h



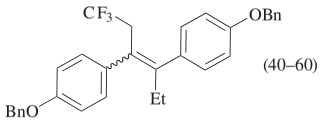
R		(*E*)/(*Z*)
H	(57)	32:1
Cl	(63)	16:1

560



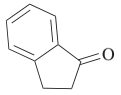


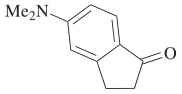
$TiCl_3$, Zn/Cu, THF



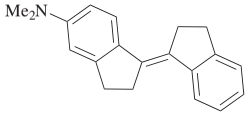
(40–60)

425





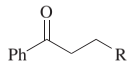
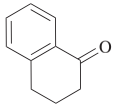
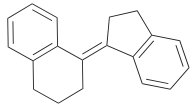
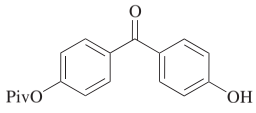
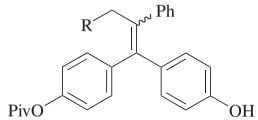
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2 h



(—)

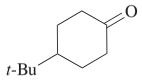
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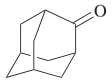
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		1. $TiCl_4$, Zn, THF 2. Reflux, 18 h	 (8)	187
C_{10-12} 		$TiCl_4$, Zn, THF, heat		553

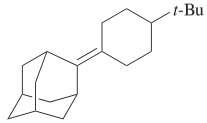
R	
$Cl(CH_2)_2$	(—)
$Cl(CH_2)_3$	(—)
$Cl(CH_2)_4$	(—)
$MeO_2C(CH_2)_2$	(—)
$MeO_2C(CH_2)_3$	(—)
$MeO_2C(CH_2)_4$	(—)

C_{10}

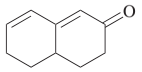


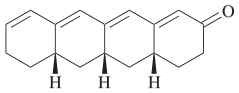


1. $TiCl_3$, $LiAlH_4$, THF, reflux, 15 min
2. Reflux, 4 h

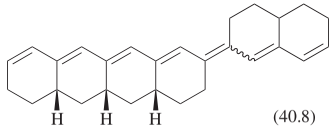


(27.5) 562

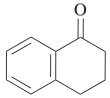


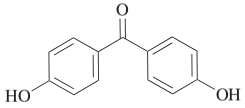


1. $TiCl_4$, Zn, THF, –15° to reflux; then py, reflux, 15 min
2. Reflux, 15 min

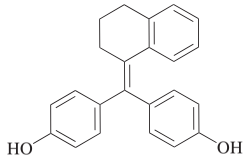


(40.8) 204



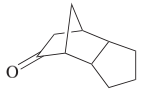
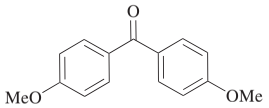
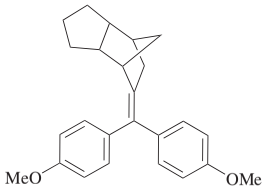
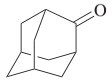
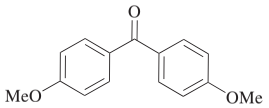
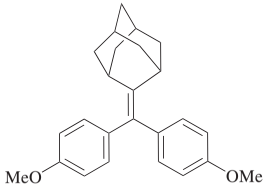
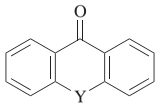
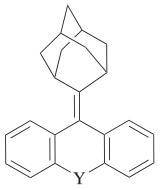


Ti(0), THF, reflux

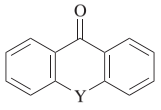


(46) 563

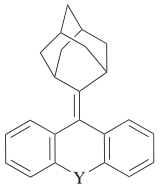
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Reflux, 1.5 h	 (64)	529
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Reflux, 1.5 h	 (54)	529
		$TiCl_3$, $LiAlH_4$, Et_3N, THF, reflux, 40 h		

Y		
PhN, BnN, CH_2, nil	(30–79)	564
EtO_2CCH_2N	(63)	565

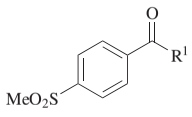


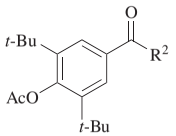
1. $TiCl_3$, $LiAlH_4$, Et_3N, THF, reflux, 1 h
2. Reflux, 30 min; then addition of ketones; then reflux, 5 h



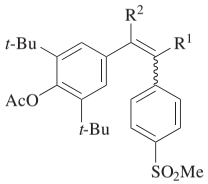
Y		
—	(29)	
MeN	(74)	
EtO_2CCH_2N	(63)	566
PhN	(51)	
BnN	(76)	
CH_2	(64)	

C_{11-14}



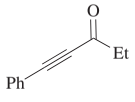


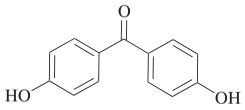
1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2.5 h



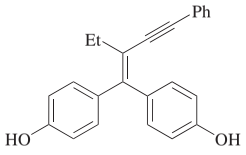
R^1	R^2		$(E)/(Z)$	
Ph	Bu	(57)	6:94	57
Bu	Ph	(55)	0:100	
Ph	n-C_7H_{15}	(57)	17:83	
n-C_7H_{15}	Ph	(45)	22:78	

C_{11}



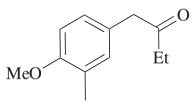
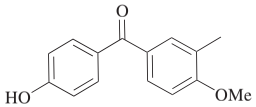
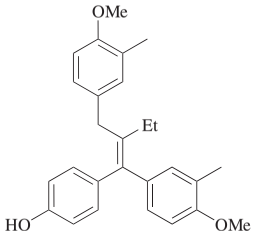
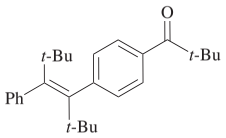
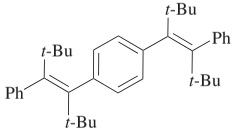
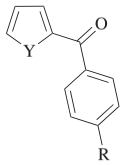
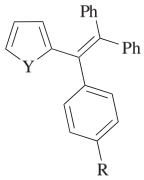
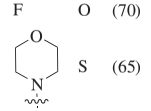


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2 h

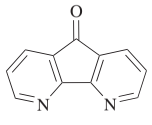


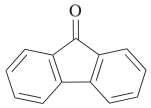
(71.7) 567

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

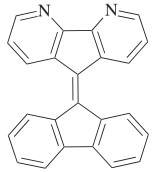
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
		1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Reflux, 4 h	 (70)	555
		$TiCl_4$, Zn, THF	 (—)	499
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Py, reflux	 	568

R	Y	
F	O	(70)
	S	(65)



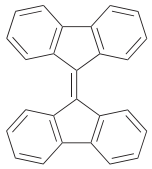


$TiCl_3$, $LiAlH_4$, THF, reflux, 12 h



(4)

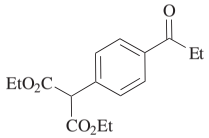
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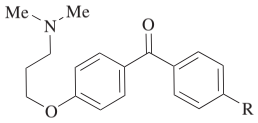


(14)

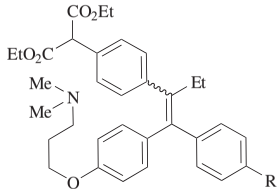
213

C_{12}





$TiCl_4$, Zn, THF, heat, 3 h

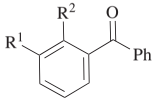


R		(*E*)/(*Z*)
H	(85)	0:100
HO	(55)	20:80

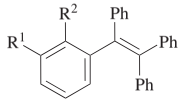
569

C_{13}



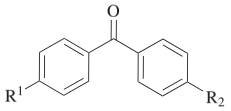
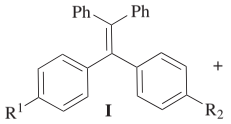
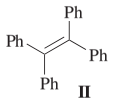
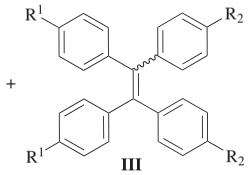


1. $TiCl_4$, Zn, THF, reflux, 2.5 h
2. Py, reflux



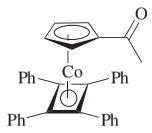
R^1	R^2		
H	HO	(64)	
H	H_2N	(72)	568
H		(61)	
HO	H	(62)	

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

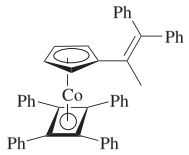
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Py, reflux, time	 +  **I** **II**  **III**	144

R^1	R^2	Time (h)	**I**	**II**	**III**
H	Me	6	(44)	(28)	(28)
Me	Br	5	(39)	(30)	(30)
Me	Me	34	(73)	(13)	(8)
H		16	(62)	(16)	(13)
H		36	(53)	(20)	(16)
H		38	(52)	(21)	(15)

		36	(65)	(15)	(11)
H	HO	32	(66)	(14)	(10)
HO	HO	36	(69)	(14)	(10)
H	MeO	—	(62)	(16)	(12)
MeO	MeO	34	(59)	(17)	(13)
H	$HO(CH_2)_2O$	30	(60)	(17)	(14)
$HO(CH_2)_2O(CH_2)_2O$	$HO(CH_2)_2O(CH_2)_2O$	38	(89)	(4)	(3)
H	H_2N	13	(80)	(10)	(7)
H	$PhHNCH_2$	15	(68)	(12)	(9)

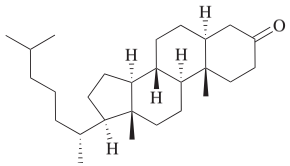
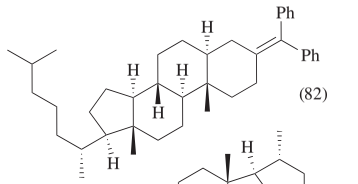
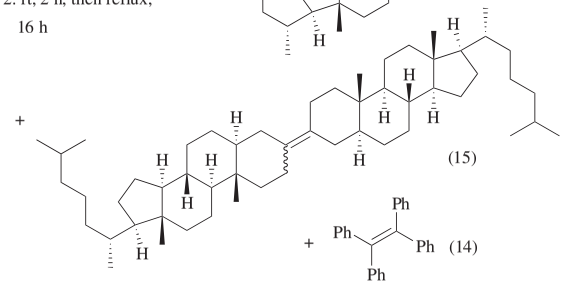
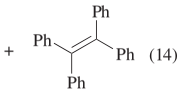
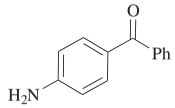
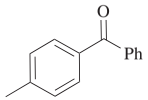
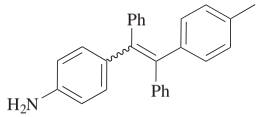
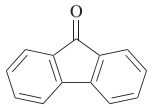
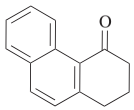
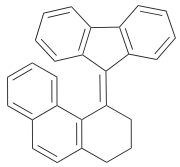
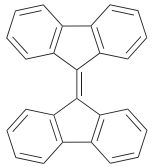


1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 2 h
2. Reflux, 12 h



(71) 570

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h, then reflux, 16 h	 (82) +  (15) +  (14)	27
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Py, reflux	 (76)	144
		$TiCl_3$, $LiAlH_4$, THF	 (25) +  (35)	516

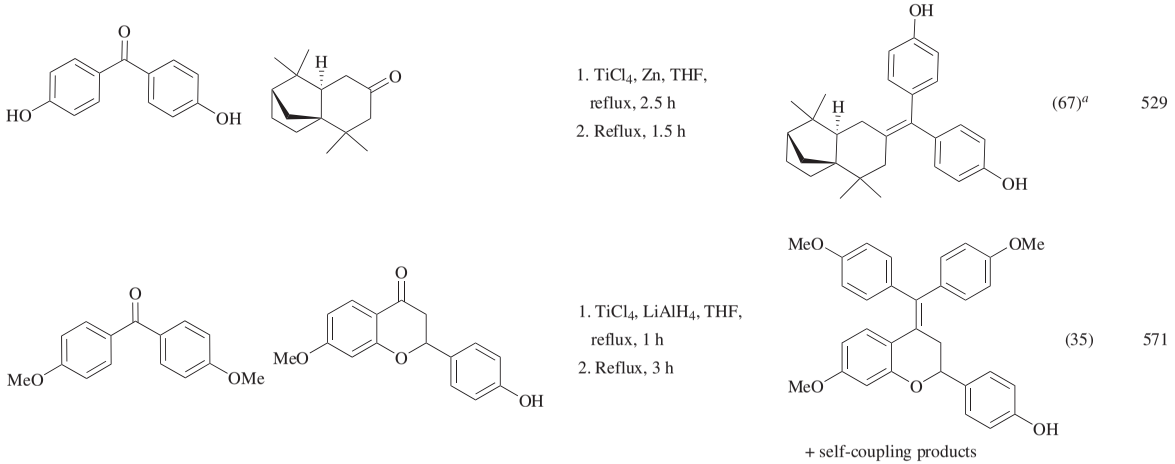
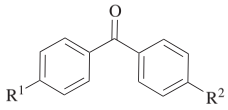
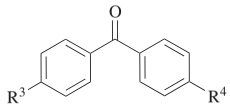
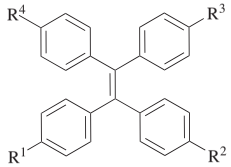
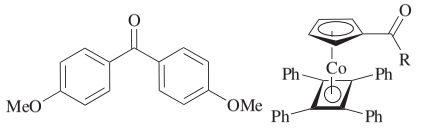

HO
OH
O
H
O
1. TiCl4, Zn, THF, reflux, 2.5 h
2. Reflux, 1.5 h
OH
H
OH
(67)a
529
MeO
OMe
O
MeO
O
OH
1. TiCl4, LiAlH4, THF, reflux, 1 h
2. Reflux, 3 h
MeO
OMe
MeO
O
OH
(35)
571
+ self-coupling products

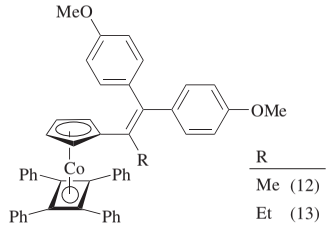
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		1. $TiCl_4$, Zn, THF, reflux, 2.5 h 2. Py, reflux		568

R^1	R^2	R^3	R^4	
H	H	H	HO	(66)
H	H	HO	HO	(69)
H	H	MeO	MeO	(59)
H	H	H	H_2N	(80)
HO	HO	H	Br	(69)
H	H	H	Me	(44)
H	H	H		(62)
H	H	H		(61)
H	H			(73)
H	Br			(77)

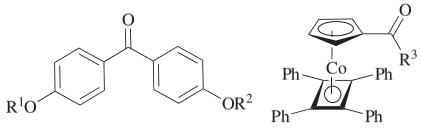


1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 2.5 h
2. Reflux, overnight

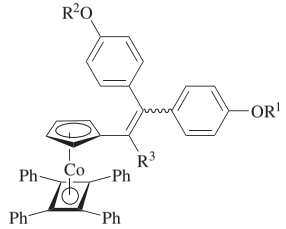


R	
Me	(12)
Et	(13)

550



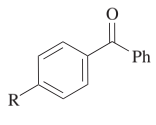
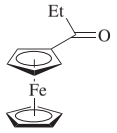
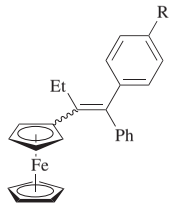
1. $TiCl_4$, Zn, THF, 60°, 2 h
2. Temp, time



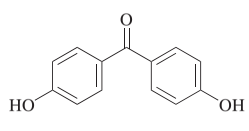
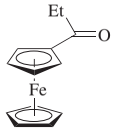
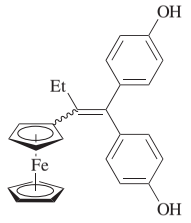
550

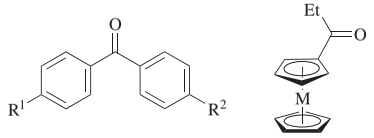
R^1	R^2	R^3	Temp (°)	Time (d)	
H	H	Me	50	4	(90)
H	H	Et	50	4	(26)
Bn	Bn	Me	65	2	(40)
Bn	Bn	Et	50	4	(20)
H	$Me_2N(CH_2)_2$	Me	50	4	(9)

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

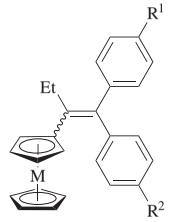
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13-14} 		1. $TiCl_4$, Zn, THF, reflux, time 1 2. Reflux, time 2		

R	Time 1 (h)	Time 2 (h)		(*E*)/(*Z*)	dr	
Cl	1.5	4	(58)	50:50	—	572
Br	1.5	4	(13)	36:64	—	572
CF_3	1.5	4	(22)	55:45	—	572
H_2N	1.5	4	(54)	—	55:45	546
MeO	2.5	15	(66)	—	—	573

C_{13} 		1. $TiCl_4$, Zn, THF, 60°, 2 h 2. 65°, 2 d		(56)	550

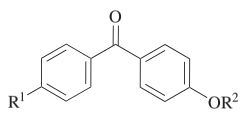
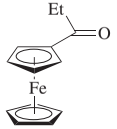
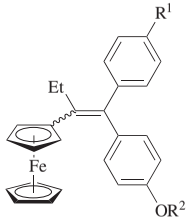


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, time

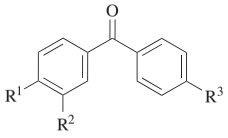


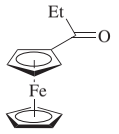
M	R^1	R^2	Time (h)		
Fe	HO	HO	1.5	(52.5)	574
Fe	MeO	MeO	5	(86)	575
Fe	MeS	MeS	5	(30)	575
Fe	*t*-BuS	*t*-BuS	5	(25)	575
Ru	HO	HO	2	(96)	541
Ru	HO	$Br(CH_2)_2O$	2	(76)	576
Ru	HO	$Br(CH_2)_3O$	2	(91)	576
Ru	HO	$Br(CH_2)_4O$	2	(83)	576
Ru	HO	$Br(CH_2)_5O$	2	(94)	576

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

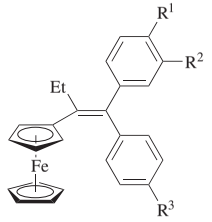
Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		$TiCl_4$, Zn, THF, reflux		

R^1	R^2		
H	H	(—)	577
HO	H	(53)	548, 574
HO	$Br(CH_2)_5$	(50.7)	577
HO	$Cl(CH_2)_8$	(46.5)	577
H	$Br(CH_2)_5$	(50)	577
H	$Cl(CH_2)_8$	(39)	577

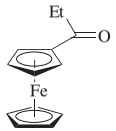


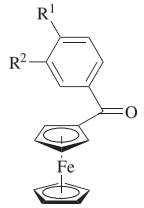


1. $TiCl_4$, Zn, THF, reflux, time
2. Reflux, 2 h

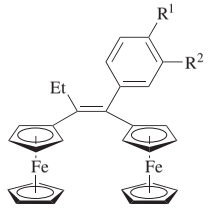


R^1	R^2	R^3	Time (h)		
H	H	HO	1.5	(36)	578
HO	H	$Br(CH_2)_2O$	1.5	(46)	578
H	H	H	2	(25)	579
H	HO	H	2	(19)	579
H	HO	HO	2	(58)	579



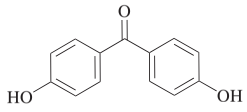
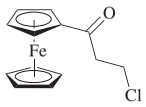
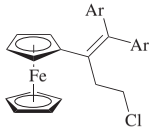
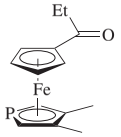
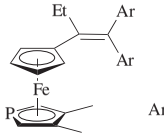
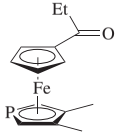
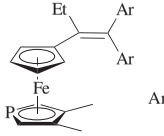
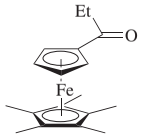
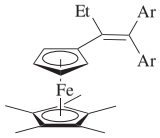
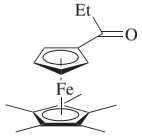
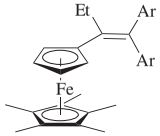


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2 h

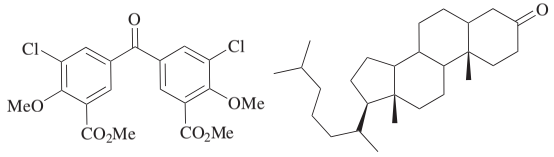


R^1	R^2		
HO	H	(39)	579
H	HO	(39)	

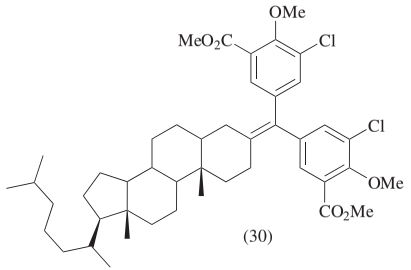
TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 		1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Heat, 2 h	 (47) Ar = 4-HOC_6H_4	541
		$TiCl_4$, Zn	 (16) Ar = 4-HOC_6H_4	580
		1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Reflux, 2 h	 (16) Ar = 4-HOC_6H_4	541
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Heat, 2 h	 (19) Ar = 4-HOC_6H_4	541
		$TiCl_4$, Zn	 (14) Ar = 4-HOC_6H_4	580

C_{15}



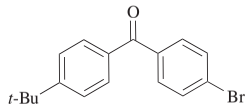
1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h
2. Reflux, 5.5 h

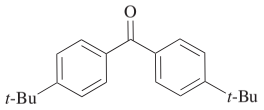


581

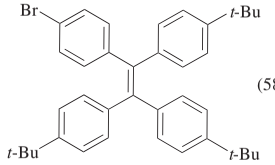
(30)

C_{17}





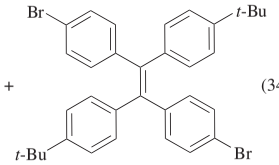
$TiCl_4$, Zn, THF, 60°, 1 h



(58)

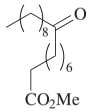
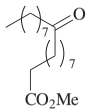
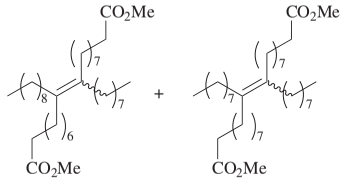
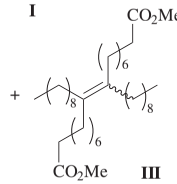
582

+



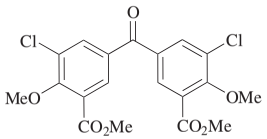
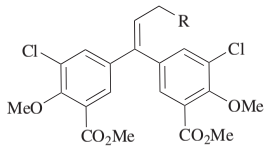
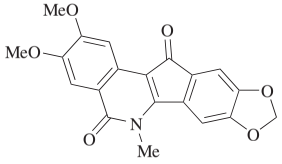
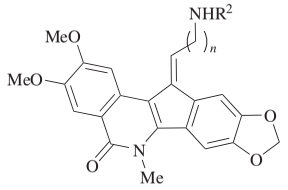
(34)

TABLE 2B. MIXED-COUPLING OF KETONES (*Continued*)

Ketone 1	Ketone 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 		1. $TiCl_4$, Zn, THF, rt, 10 min 2. Reflux, overnight	 **I** + **II** +  **III** **I** + **II** + **III** (83)	494

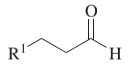
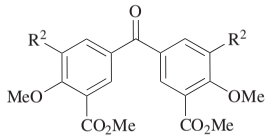
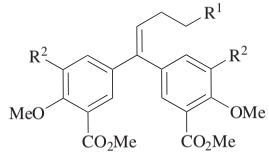
[a] Optically active starting material was employed.

TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES

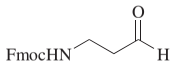
Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-3} 		1. $TiCl_4(THF)_2$, Zn, THF, reflux, 2 h 2. Reflux, time	 R = BocHN, Time (h) = 3, (23) R = $FmocHNCH_2$, Time (h) = 2.5, (72)	583
C_{2-6} 		1. $TiCl_4(THF)_2$, Zn, THF, reflux, 4 h 2. Reflux, 4 h 3. 4 N HCl, rt, overnight		584

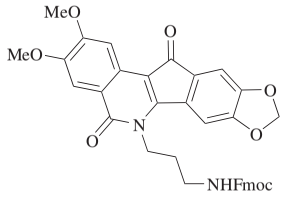
n	R^1	R^2	
1	H	H	(30)
1	$BocHN(CH_2)_3$	$H_2N(CH_2)_3$	(24)
2	Me	Me	(48)
2	$BocHN(CH_2)_3$	$H_2N(CH_2)_3$	(36)
3	Me	Me	(48)
3	Boc	H	(35)
4	Boc	H	(20)
5	H	H	(45)

TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES (*Continued*)

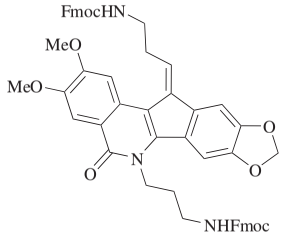
Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		1. $TiCl_4(THF)_2$, Zn, THF, reflux, 1 h 2. Reflux, 14 h		585

R^1	R^2	
MeO_2CHN	Cl	(32)
MeO_2CHN	Me	(38.8)
MeO_2CHN	Br	(38.1)
EtO_2CHN	Cl	(33.3)
EtO_2CHN	Me	(41.5)
i-BuO_2CHN	Cl	(39.8)
i-BuO_2CHN	Me	(32)
	Cl	(32)
	Br	(51)

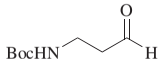


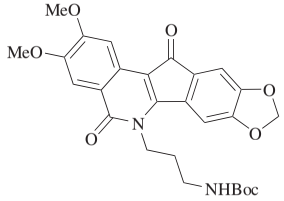


1. $TiCl_4(THF)_2$, Zn, THF, reflux, 4 h
2. Reflux, 4 h

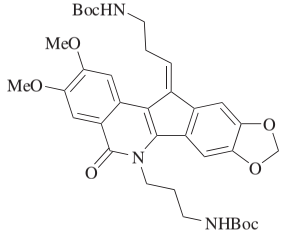


(63) 586

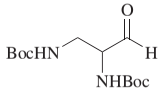


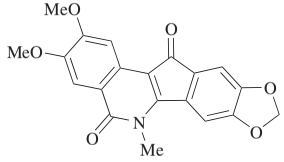


1. $TiCl_4(THF)_2$, Zn, THF, reflux, 4 h
2. Reflux, 4 h
3. K_2CO_3, Boc_2O, rt, 12 h

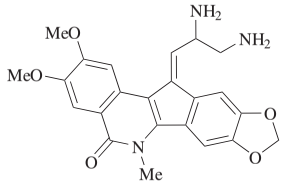


(39) 586



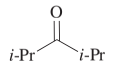
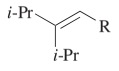
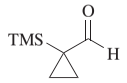
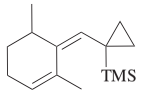
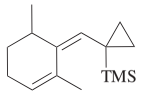
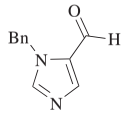
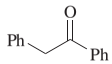
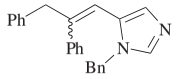


1. $TiCl_4(THF)_2$, Zn, THF, reflux, 4 h
2. Reflux, 4 h
3. 4 N HCl, rt, overnight

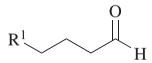


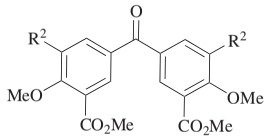
(45) 584

TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES (*Continued*)

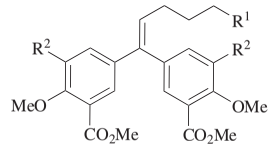
Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{4\text{-}7}$				
		—	 R: *i*-Pr (7); Ph (10)	527
		$TiCl_3$, Li (or Zn/Cu), DME, heat		(30–60)	587
		1. $TiCl_3$, Zn/Cu, DME, reflux, 4 h 2. rt, 3 h; then reflux, 30 h		(60)	143
		1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 3 h		(—)	588

C_{4-10}





1. $TiCl_4(THF)_2$, Zn, THF, reflux, 1–3 h
2. Reflux, time

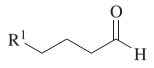
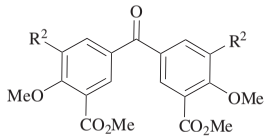
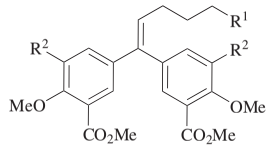


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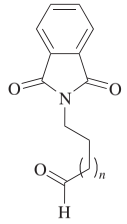
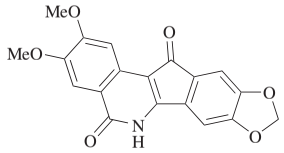
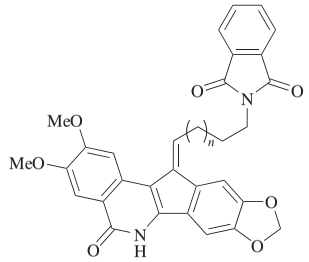
Continued on next page.

R^1	R^2	Time (h)	
Et	F	0.5	(66)
Et	Me	0.5	(87)
Et	CF_3	1	(52)
ethynyl	Cl	1.5	(25)
ethynyl	Br	2	(27)
CH_2=CH	Cl	1.5	(16)
CH_2=CH	Br	1.5	(52.5)
Ph	Cl	2	(58.22)
Ph	Br	2	(64)
MeO_2C	F	0.75	(46)
MeO_2C	Me	0.75	(49)
MeO_2C	CF_3	1	(48)
EtO_2C	Cl	3	(40.8)
EtO_2C	Me	14	(20.8)
EtO_2C	Br	20	(22)
PrO_2C	Cl	14	(40.5)
PrO_2C	Me	14	(48.8)
PrO_2C	Br	16	(20.4)
i-PrO_2C	Cl	14	(38.5)
i-PrO_2C	Me	14	(26.9)

TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES (*Continued*)

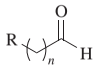
Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{4–10}$ 		1. $TiCl_4(THF)_2$, Zn, THF, reflux, 1–3 h 2. Reflux, time		585

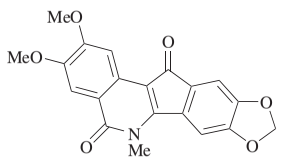
R^1	R^2	Time (h)	
i-PrO_2C	Br	20	(33.6)
Me_2NCO	Cl	14	(40)
Me_2NCO	Me	5	(17.4)
(1-piperidyl)CO	Cl	14	(40.5)
(1-piperidyl)CO	Me	14	(31)
$TMS(CH_2)_2OCO$	Me	14	(28)
TMS	Cl	1.5	(73)
MeSCO	Cl	14	(30)
EtSCO	Cl	14	(20)

Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{4–5}$ 		1. $TiCl_4(THF)_2$, Zn, THF, reflux, 4 h 2. Reflux, 4 h 3. 4 N HCl, rt, overnight		584

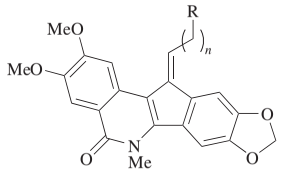
n	
1	(44)
2	(45)

C_{4-6}





1. $TiCl_4(THF)_2$, Zn, THF, reflux, 3-6 h
2. Reflux, 1-2.5 h



589

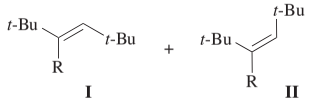
n	R	
3	Cl	(43)
3	Br	(30)
4	Br	(33)
5	Br	(21)

C_5





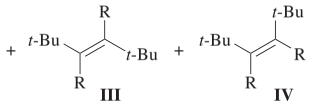
1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1 h
2. Reflux, 66 h



404

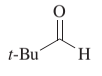
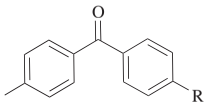
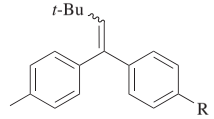
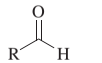
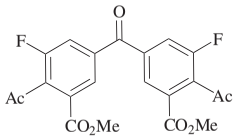
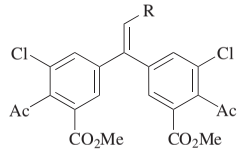
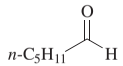
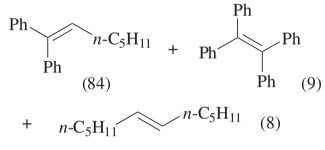
I **II**

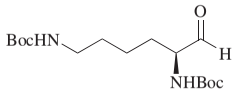
R	**I**	**II**	**III**	**IV**
Me	(33.8)	(17.5)	(17.8)	(17.3)
Et	(60.4)	(23.7)	(3.3)	(0.2)

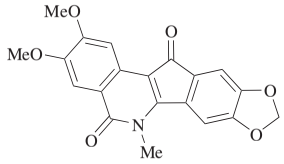


III **IV**

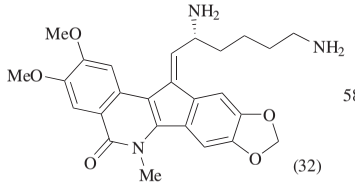
TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES (*Continued*)

Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. $TiCl_4$, Zn, THF 2. Reflux, 2 h	 R = H_2N (9) 63:37; Me_2N (75) 77:23; HO (94) 70:30; MeO (95) 66:34; Br (89) 49:51	590
C_{5-6}				
		1. $TiCl_4(THF)_2$, Zn, THF, reflux, 1 h 2. Reflux, time	 R = $MeO_2C(CH_2)_3$ 45 min (46); n-C_5H_{11} 30 min (66)	591
C_6				
		1. $TiCl_3$, Li, DME, reflux, 1 h 2. rt, 2 h; then reflux, 16 h	 (84) + (9) + (8)	27





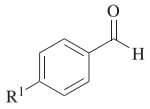
1. $TiCl_4(THF)_2$, Zn, THF, reflux, 4 h
2. Reflux, 4 h
3. 4 N HCl, rt, overnight



584

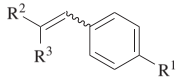
(32)

C_7



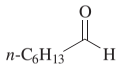


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Reflux, 2.5 h



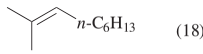
58

R^1	R^2	R^3		$(E)/(Z)$
MeS	4-HOC_6H_4	Ph	(63)	>49:51
MeO_2S	4-BrC_6H_4	Ph	(64)	>44:56
H	4-$MeSC_6H_4$	n-C_7H_{15}	(61)	>35:65
MeO_2S	Np	Ph	(68)	>47:53
MeO_2S	4-HOC_6H_4	Ph	(67)[a]	<10:90





$W_2(OCH_2CMe_3)_6(py)_2$, 22°, 12–22 h



(18)

99





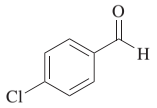
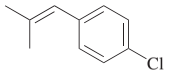
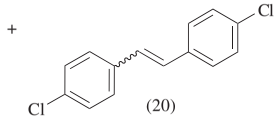
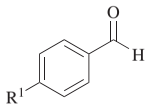
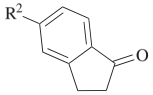
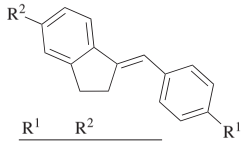
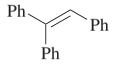
MCl_3, Zn, MeCN, reflux



I + **II**

M	Time (h)	**I**	**II**	
Al	20	(78)	(16)	88
In	12	(60)	(40)	104

TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES (*Continued*)

Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$AlCl_3$, Zn, MeCN, reflux, 19 h	 (75) +  (20)	88
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2 h		561
		1. Aldehyde, {4-*t*-Bu-calix[4]-$(O)_4$}$_2Nb_2Na_2(THF)_6$, THF, rt, overnight 2. Ketone, rt, 3 h	 (92)	592

R^1	R^2	
Me_2N	H	(—)
H	Me_2N	(—)

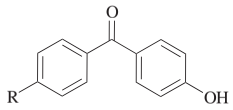
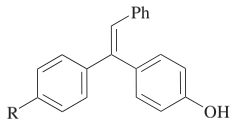
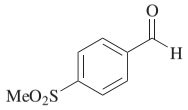
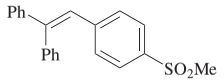
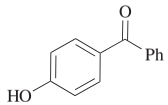
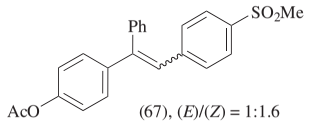
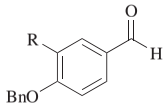
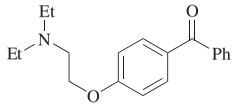
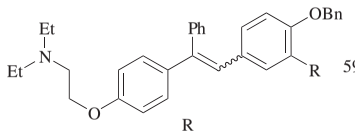
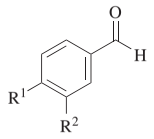
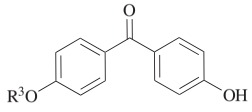
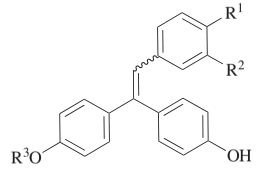
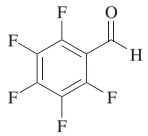
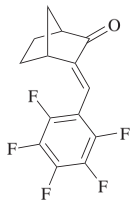
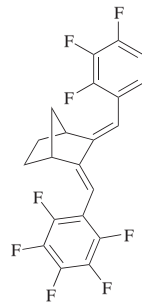
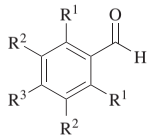
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 4 h		R H (30) BnO (34)	549
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2.5 h		(70)	534
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2.5 h 3. AcCl, Et_3N, ether, rt, 1.5 h		(67), (*E*)/(*Z*) = 1:1.6	534
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 2 h		R H (49) MeO (36)	593

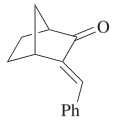
TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES (*Continued*)

Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 3 h		536

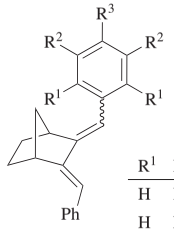
R^1	R^2	R^3		$(E)/(Z)$
MeO	MeO	$Me_2N(CH_2)_2$	(39)	1:1
MeO	H	$Me_2N(CH_2)_2$	(45)	1:1
HO	H	H	(40)	—
HO	MeO	H	(46)	—

		$TiCl_4$, Zn, THF, reflux	 (—)	594



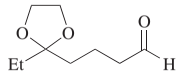


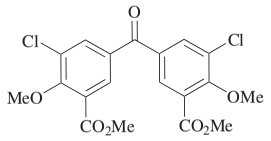
$TiCl_4$, Zn, THF, reflux



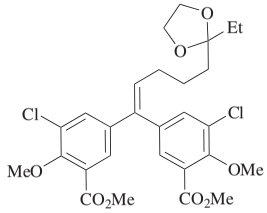
R^1	R^2	R^3		dr
H	H	F	(—)	95:5
H	F	H	(—)	—
F	F	H	(—)	—
F	F	F	(30)	—

595

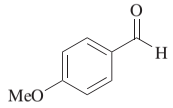


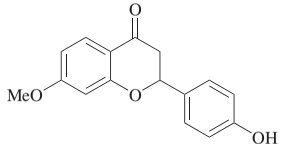


1. $TiCl_4(THF)_2$, Zn, THF, reflux, 2 h
2. Reflux, 1.5 h

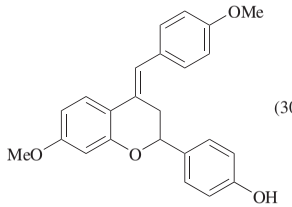


(77.5) 591





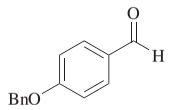
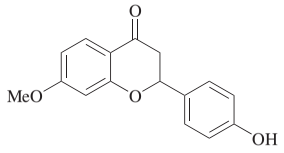
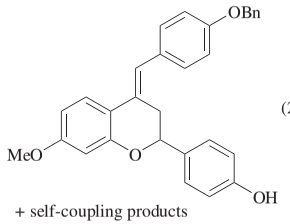
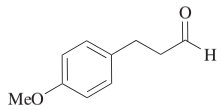
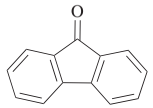
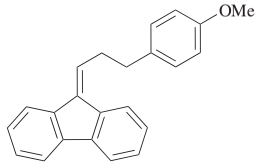
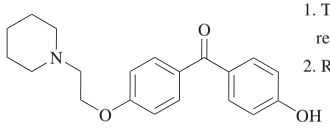
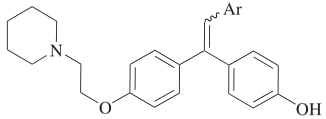
1. $TiCl_4$, $LiAlH_4$, THF, reflux, 1 h
2. Reflux, 3 h



(30) 571

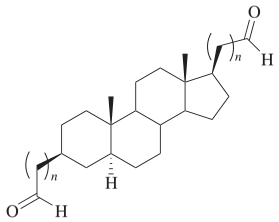
+ self-coupling products

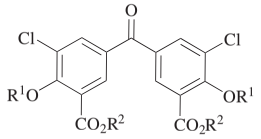
TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES (*Continued*)

Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$TiCl_4$, Zn, THF, reflux	 (20) + self-coupling products	571
C_9				
		1. $TiCl_4(THF)_2$, Zn, THF, reflux, 4 h 2. Reflux, 3 h	 (94)	586
C_{11}				
		1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 3.2 h		596

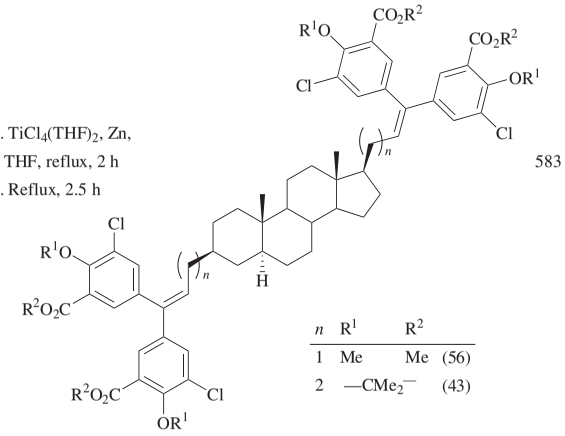
Ar		(*E*)/(*Z*)
5-HO-1-Np	(60)	1:1.8
6-HO-1-Np	(66)	1:1
6-HO-2-Np	(35)	19:1

$C_{23–25}$





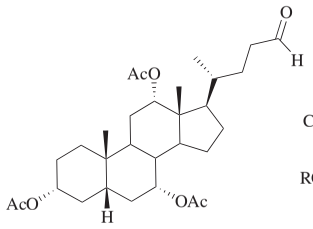
1. $TiCl_4(THF)_2$, Zn,
   THF, reflux, 2 h
2. Reflux, 2.5 h

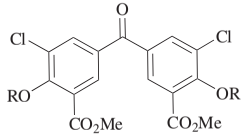


583

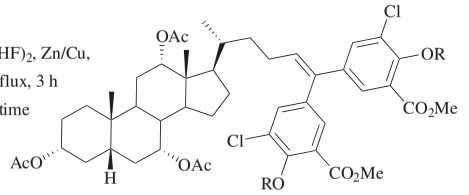
n	R^1	R^2	
1	Me	Me	(56)
2	—CMe_2—		(43)

C_{24}





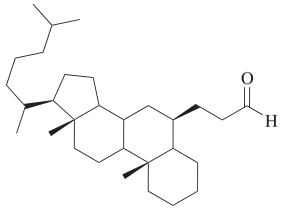
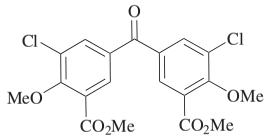
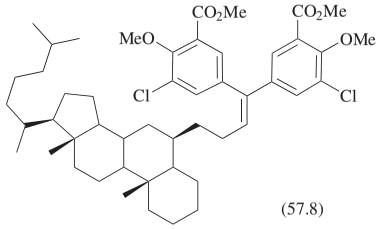
1. $TiCl_4(THF)_2$, Zn/Cu,
   DME, reflux, 3 h
2. Reflux, time



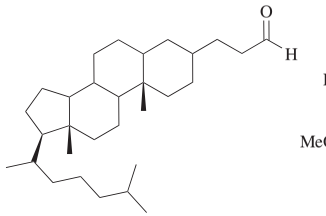
597

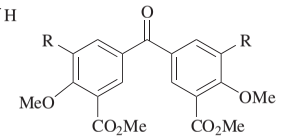
R	Time (h)	
Me	12	(25)
Ac	24	(25)

TABLE 2C. MIXED-COUPLING OF ALDEHYDES AND KETONES (*Continued*)

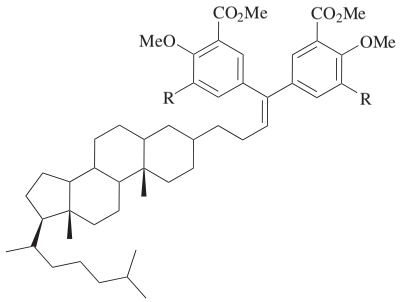
Aldehyde	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30} 		1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 1.5 h 2. Reflux, 1 h	 (57.8)	598

C_{30}

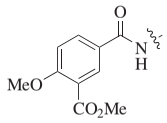
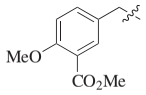




1. $TiCl_4(THF)_2$, Zn, THF, reflux, time
2. Reflux, 1 h

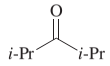
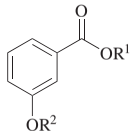
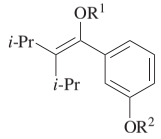
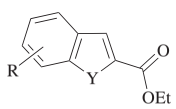
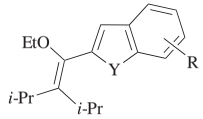
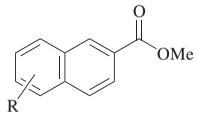
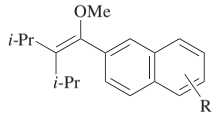
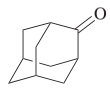
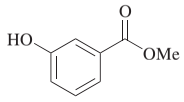
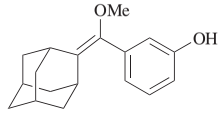


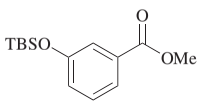
599

R	Time (h)	
	0.5	(25)
	1	(33)

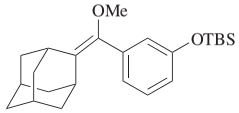
[a] The yield was obtained after acetylation of the hydroxyl group.

TABLE 2D. MIXED-COUPLING BETWEEN KETONES AND CARBOXYLIC ACID DERIVATIVES

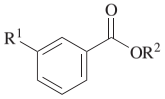
Ketone	Carboxylic Acid Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. $TiCl_3$, $LiAlH_4$, Et_3N, THF, reflux, 15 min 2. Reflux, 20 min 3. Reflux, 30 min	 R^1 R^2 Me Me (42.2) Et Me (60) *i*-Pr Me (67) *t*-Bu Me (47) Me TBS (52)	135
		—	 R Y 5-MeO, 6-MeO, 7-MeO O, S (30–50)	600
		1. $TiCl_3$, $LiAlH_4$, Et_3N, THF, reflux, 30 min 2. Reflux, 30 min 3. Reflux, 1.5 h	 R 3-MeO (52.1) 4-MeO (44.2) 5-MeO (47.7) 6-MeO (47.7) 7-MeO (28.2) 8-MeO (34.9)	601
C_{10}				
		1. $TiCl_4$, $LiAlH_4$, Et_3N, THF, reflux, 1 h 2. Reflux, 45 min 3. Reflux, 1.5 h	 (27)	602



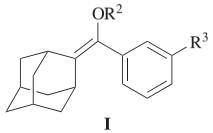
1. $TiCl_3$, $LiAlH_4$, Et_3N, THF, reflux, 30 min
2. Reflux, ~25 min
3. Reflux, 5 h



(48) 603

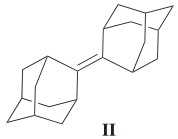


$TiCl_3$, $LiAlH_4$, Et_3N, THF, 70°, 20 h



I

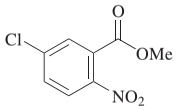
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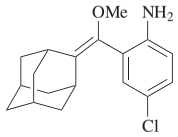
II

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R^1	R^2	R^3	**I**	**II**
TBSO	Me	TBSO	(41–59)	(—)
Cl	Me	Cl	(40)	(22)
F	Et	F	(38)	(19)
Br	Et	H	(38)	(11)
HS	Et	H	(52)	(—)
t-BuS	Et	*t*-BuS	(60)	(—)

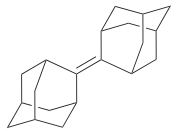


$TiCl_3$, $LiAlH_4$, Et_3N, THF, 70°, 20 h



(17)

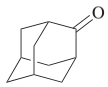
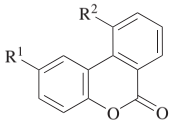
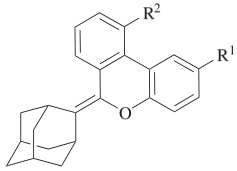
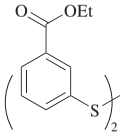
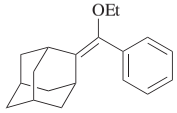
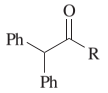
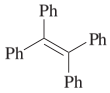
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(35)

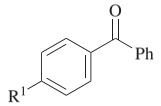
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TABLE 2D. MIXED-COUPLING BETWEEN KETONES AND CARBOXYLIC ACID DERIVATIVES (*Continued*)

Ketone	Carboxylic Acid Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		—	 R^1 = H, R^2 = TBSO (~25); R^1 = TBSO, R^2 = H (~25)	604
		$TiCl_3$, $LiAlH_4$, Et_3N, THF, 70°, 20 h	 (57)	136
C_{13}				
		$TiCl_4$, Zn; then 3% HCl	 **I** +  **II**	134

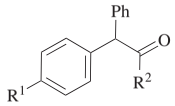
R	**I**	**II**
Me	(69.8)	(15.1)
Ph	(68.6)	(24.1)
4-$MeOC_6H_4$	(66.7)	(30.1)
4-ClC_6H_4	(52.2)	(27.1)
3-ClC_6H_4	(47.8)	(21.1)
3-MeC_6H_4	(60.6)	(18.1)

C_{13-14}

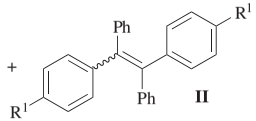




$TiCl_4$, Zn; then 3% HCl



I

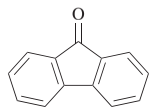


II

R^1	R^2	**I**	**II**
H	Ph	(46.6)	(30.1)
H	Bn	(49.0)	(18.1)
Cl	1-$NpCH_2$	(70.3)	(20.7)
H	1-$NpCH_2$	(66.7)	(24.0)
Me	1-$NpCH_2$	(48.6)	(29.6)
MeO	1-$NpCH_2$	(44.4)	(25.5)

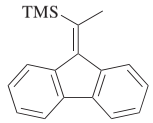
134

C_{13}





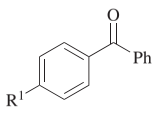
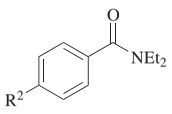
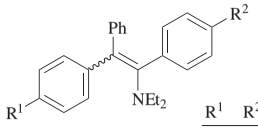
Ketone, Yb, THF, rt, 3 d; then acylsilane, rt, 1 d



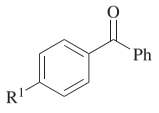
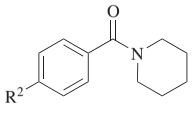
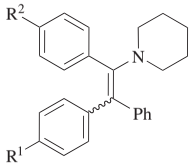
(36)

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TABLE 2D. MIXED-COUPLING BETWEEN KETONES AND CARBOXYLIC ACID DERIVATIVES (*Continued*)

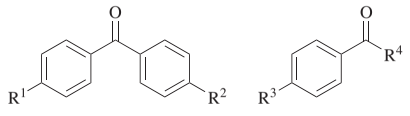
Ketone	Carboxylic Acid Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{13–19}$ 		SmI_2, Mg, THF, 67°		107

R^1	R^2	Time (h)	
H	H	6	(65)
Cl	H	6	(57)
Me	H	6	(60)
Ph	H	6	(63)
H	Cl	7	(63)
H	MeO	6	(65)

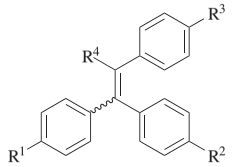
Ketone	Carboxylic Acid Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{13–14}$ 		SmI_2, Mg, THF, 67°		107

R^1	R^2	Time (h)	
H	Cl	6	(67)
Me	H	5	(68)

C_{13-19}



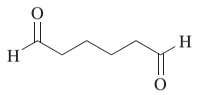
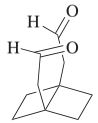
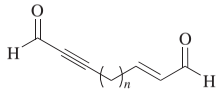
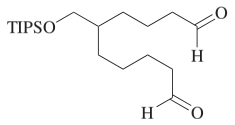
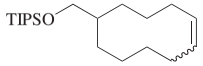
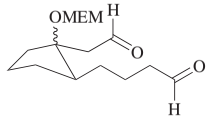
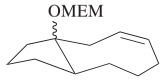
SmI_2, Mg, THF, 67°



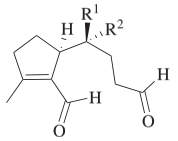
106

R^1	R^2	R^3	R^4	Time (h)	
H	H	H	Et_2N	3	(80)
H	Me	H	Et_2N	3	(78)
Me	Me	H	Et_2N	3	(76)
H	Cl	H	Et_2N	4	(68)
H	Ph	H	Et_2N	3	(81)
H	Me	H		3	(83)
H	H	MeO	Et_2N	3	(75)
H	Me	MeO	Et_2N	3	(73)
Me	Me	MeO	Et_2N	3	(67)
H	Ph	MeO	Et_2N	3	(75)
H	H	Cl	Et_2N	4	(67)
H	Me	Cl	Et_2N	4	(65)
H	H	Cl		4	(63)

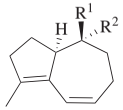
TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 8 h 3. Reflux, 14 h	 (96)[a]	73, 74
C_{10} 	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 1.5 h 2. Reflux, 4 h 3. Reflux, overnight	 (9.3)	605
$C_{10–14}$ 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 5 h 2. rt, 30 h 3. rt	 *n*: 4 (5); 5 (38); 6 (16); 7 (37); 8 (44)	227
C_{11} 	$TiCl_3$, Zn/Cu, DME, reflux	 (86), (*E*)/(*Z*) = 1.7:1	606
	1. $TiCl_3$, C_8K, DME, reflux, 2 h 2. rt, 40 h 3. rt, 6 h; then reflux, 5 h	 (10)	607

C_{12}



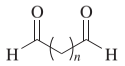
$TiCl_4$, Zn



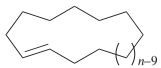
R^1	R^2	
Me	H	(70)
H	Me	(60)

259

C_{12-16}



1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h
2. Reflux, 9 h
3. Reflux, 12 h



n	
10	(76)
11	(52)
14	(85)

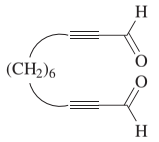
27

1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h
2. Reflux, 9–30 h
3. Reflux, 12–14 h

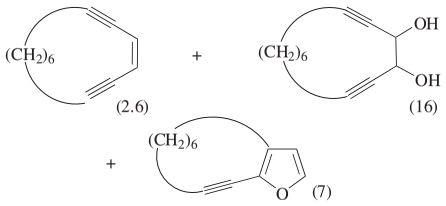


n		
10	(76)	61
11	(52)	61
12	(71)	61, 27
14	(85)	61

C_{12}



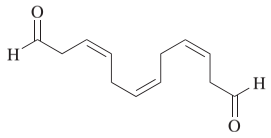
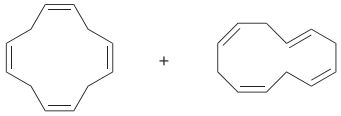
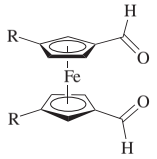
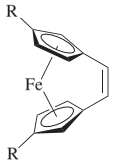
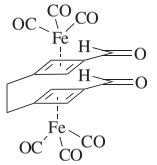
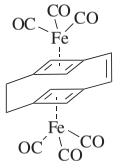
1. $TiCl_4$, Zn, py, THF, 0°
2. 0°, 4 h
3. rt, overnight



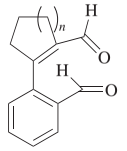
(2.6) + (16) + (7)

227

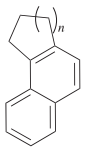
TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	1. $TiCl_3$, Zn/Cu, DME, reflux, time 1 2. Reflux, time 2 3. Reflux, time 3	 + **I** **II** Time 1 (h) / Time 2 (h) / Time 3 (h) / **I** / **II** 1 / 16 / 27 / (2) / (4) 3 / 40 / 5 / (2.3) / (9)	608 609
C_{12-20} 	1. $TiCl_3$, Zn/Cu, DME, reflux, time 1 2. Reflux, 20 h 3. Reflux, time 2	 R / Time 1 (h) / Time 2 (h) H / 1.5 / 10 / (44) *t*-Bu / 12 / 12 / (45)	238 610
C_{12} 	1. $TiCl_3$, Zn, DME, reflux, 1 h 2. Reflux, 16 h 3. Reflux, 2 h	 (58)	207

$C_{13–15}$



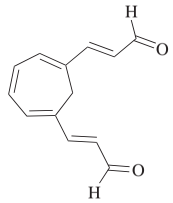
1. $TiCl_4$, Zn, THF, reflux, 2 h,
2. 0°, 30 min
3. Reflux, 2 h



n	
1	(65)
2	(65)
3	(65)

243

C_{13}

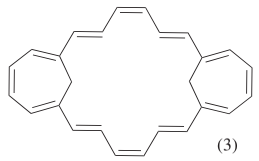


1. $TiCl_3$, $LiAlH_4$, DME, reflux, 30 min
2. Reflux, 15 h
3. Reflux, 4 h



(12)

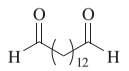
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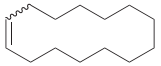
(3)

226

C_{14}

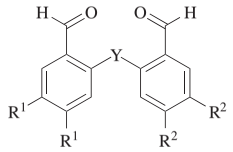


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, 80°, 4 h
2. 80°, 35 h
3. 80°, 6 h

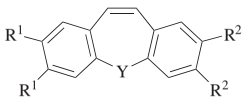


(80) dr 9:1

6

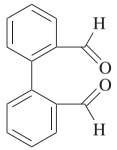
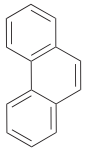
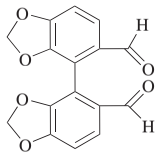
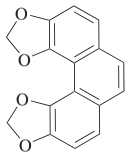
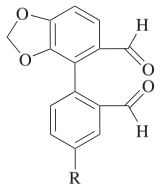
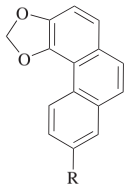
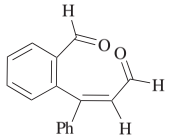
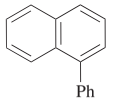


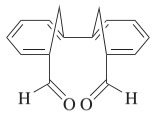
1. $TiCl_4$, Zn, py, THF, reflux, 2.5 h
2. rt, 4 h
3. rt, 16 h; then reflux, 4 h



Y	R^1	R^2		
S	H	H	(95)	611
S	MeO	H	(70)	612
S	MeO	MeO	(80)	611
Se	MeO	H	(73)	612
Se	MeO	MeO	(80)	613
Me_2Ge	H	H	(36)	613

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	1. $TiCl_4$, Zn, THF, reflux, 2 h, 2. 0°, 30 min 3. Reflux, 2 h	 (67)	243
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 5 h 2. Reflux, 3 h 3. Reflux, 20 h	 (45)	614
	$TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 40 h	 R: H (57), MeO (45)	614
C_{16}			
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. 0°, 30 min 3. Reflux, 2 h	 (60)	243



$TiCl_4$, Zn, py, THF



(35–40)

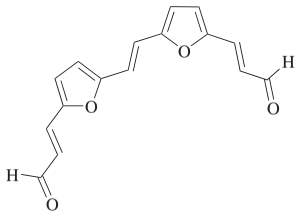
225

WCl_6, BuLi

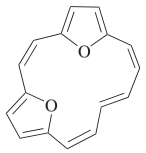


(10)

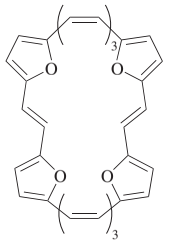
225



1. $TiCl_4$, Zn/Cu, py, reflux, 1 h
2. Reflux, 24 h
3. Reflux, 2 h

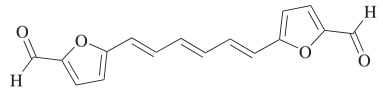


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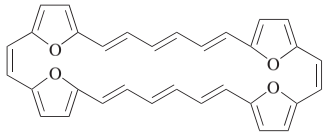


(6)

615



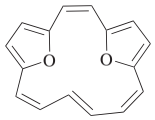
1. $TiCl_4$, Zn/Cu, THF, reflux, 1 h
2. Reflux, 6.5 d
3. Reflux, 3 h



(8)

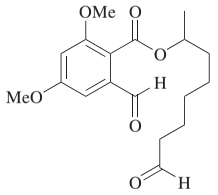
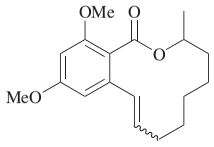
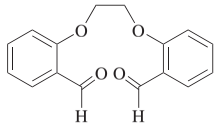
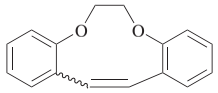
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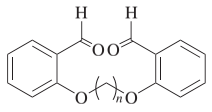
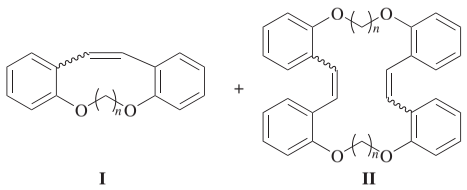
(7)

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	1. $TiCl_3$, C_8K, DME, reflux, 1.5 h 2. rt, 10 h 3. Reflux, 5.5 h	 (60–82), (*E*)/(*Z*) = 3.5:1	617
	1. $TiCl_4$, Zn, solvent, reflux, 2.5 h 2. rt 3. Reflux, time		618, 619

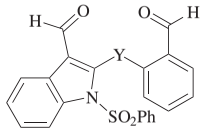
Solvent	Time (h)		(*E*)/(*Z*)
DME	16	(64)	40:60
THF	24	(58)	8:3

C_{16-18}

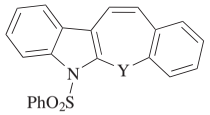
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux	 **I** + **II**	620

n	(*E*)-**I**	(*Z*)-**I**	**II**
2	(57)	(23)	(12)
4	(54)	(22)	(8)

C_{16}



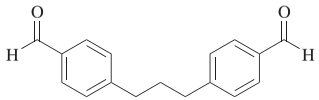
1. $TiCl_4$, Zn, py, THF, reflux, 2.5 h
2. 4 h
3. rt, 16 h; then reflux, 4 h



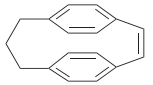
Y	
S	(77)
Se	(73)

612

C_{17}

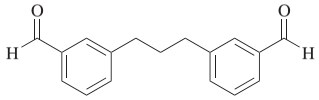


1. $TiCl_4$, Zn/Cu, py, DME, reflux, 2 h
2. Reflux, 60 h
3. Reflux, 12 h

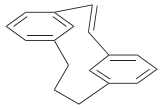


(14)

234

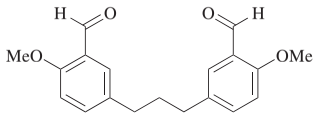


1. $TiCl_4$, Zn/Cu, py, DME, reflux, 1 h
2. Reflux, 60 h
3. Reflux, 12 h

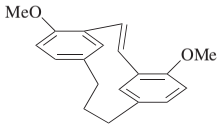


(58)

234



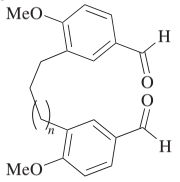
1. $TiCl_4$, Zn, THF
2. Py, reflux, 60 h
3. Reflux, 8 h



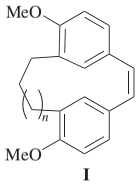
(28)

621

C_{17-18}

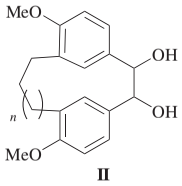


1. $TiCl_4$, Zn, THF
2. Py, reflux, 60 h
3. Reflux, 8 h



I

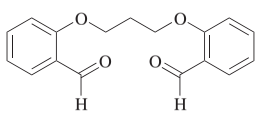
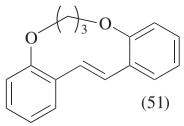
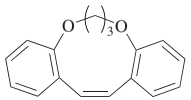
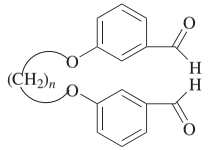
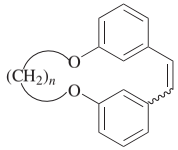
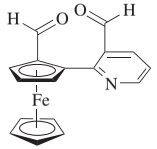
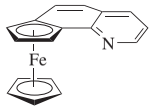
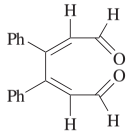
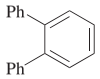
+



II

n	**I**	**II**	
1	(23)	(65)	622, 623
2	(36)	(53)	623

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	$TiCl_4$, Zn, THF/toluene	 (51) +  (36)	624
C_{17-26} 	1. $TiCl_4$, Zn, THF, –10° 2. Dropwise addition, reflux 3. Reflux, 5 h		233
C_{17} 	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Py, rt 3. Reflux, 3 h	 (64)	625
C_{18} 	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. 0°, 30 min 3. Reflux, 2 h	 (60)	243

n		(*E*)/(*Z*)
3	(65)	0:100
6	(95)	90:10
12	(64)	95:5

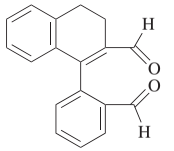
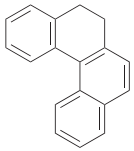
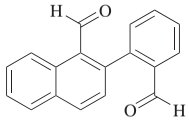
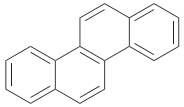
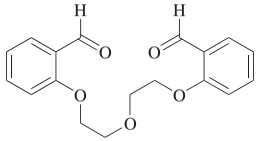
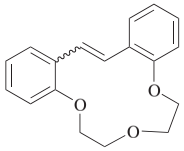
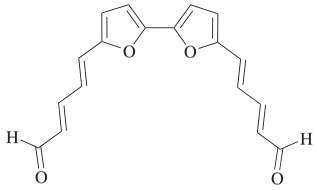
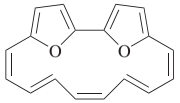
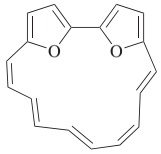
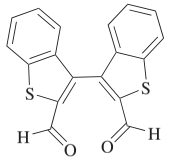
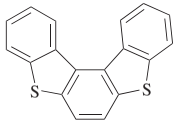
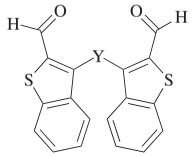
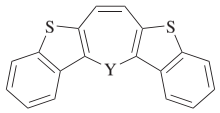
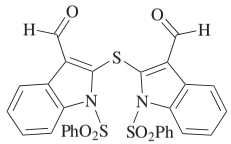
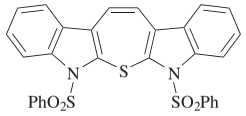
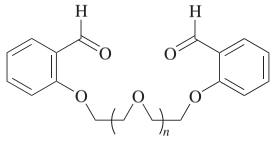
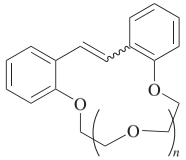
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. 0°, 30 min 3. Reflux, 2 h		(62)	243
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. 0°, 30 min 3. Reflux, 2 h		(58)	243
	1. $TiCl_4$, Zn, dioxane, reflux, 1 h 2. Dropwise addition, reflux 3. Reflux, 6.3 h		(82.5), (*E*)/(*Z*) = 60:40	626
	1. $TiCl_4$, Zn, py, THF, reflux, 30 min 2. 100–110°, 18 h 3. 100–110°, 6 h		(3) +  (9)	787a, 787b

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}			
	1. $TiCl_4$, Zn, py, THF, reflux, 3 h 2. rt 3. Reflux, overnight	 (66)	627
	1. $TiCl_4$, Zn, py, THF, reflux, 2.5 h 2. rt, 4 h 3. rt, 16 h; then reflux, 4 h		611 613 613 613
		Y S (86) Se (97) Me_2Si (75) Me_2Ge (81)	
	1. $TiCl_4$, Zn, py, THF, reflux, 2.5 h 2. rt, 4 h 3. rt, 16 h; then reflux, 4 h	 (79)	611
C_{18-20}			
	$TiCl_4$, Zn, dioxane		628
		n (*E*)/(*Z*) 1 (83) 60:40 2 (43) 48:52	

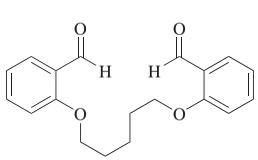
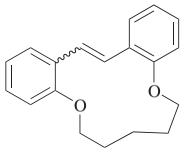
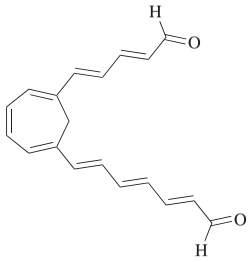
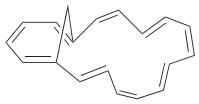
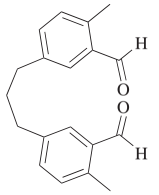
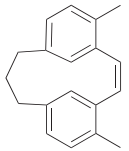
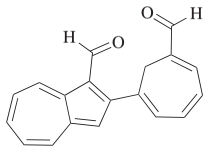
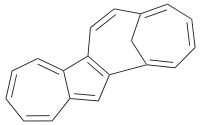
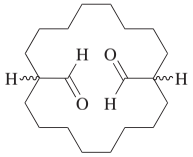
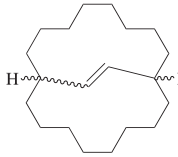
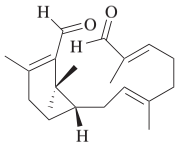
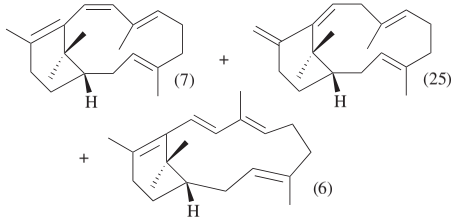
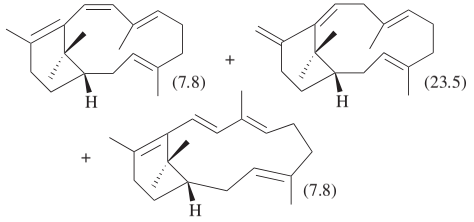
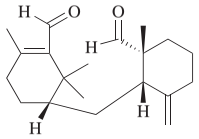
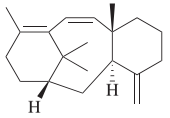
C_{19} 	1. $TiCl_4$, Zn, dioxane, reflux, 1 h 2. Dropwise addition, reflux 3. Reflux, 20 h		(63.5), (*E*)/(*Z*) = 38:62	626
	1. $TiCl_3$, $LiAlH_4$, DME, reflux, 30 min 2. Reflux, 12 h 3. Reflux, 3 h		(12)	226
	1. $TiCl_4$, Zn, THF 2. Reflux, 60 h 3. Reflux, 8 h		(18)	629
	$TiCl_3$, $LiAlH_4$		(5–10)	630

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME 2. Reflux, 24 h 3. Reflux, 3.5 h	 (19.5)	631
	1. $TiCl_3$, Zn/Cu, DME 2. 22 h	 (7) + (25) + (6)	272
	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 22 h 3. Reflux, 3 h	 (7.8) + (23.5) + (7.8)	271

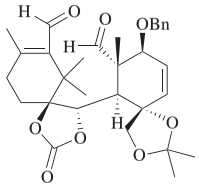


1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h
2. Reflux, 24 h
3. Reflux, 18 h

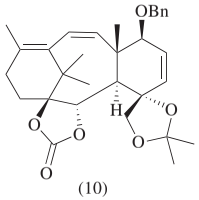


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262

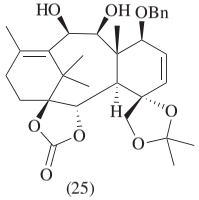


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 3.5 h
2. 70°, 1 h
3. 70°, 30 min



(10)

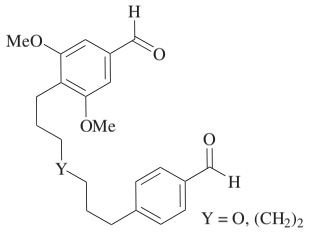
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(25)

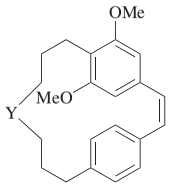
261

C_{20-22}



Y = O, $(CH_2)_2$

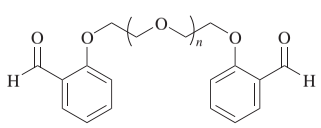
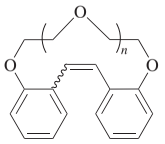
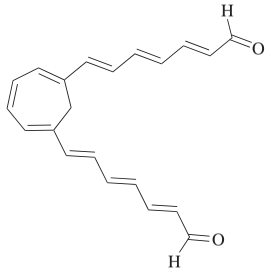
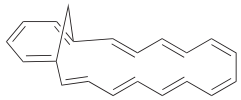
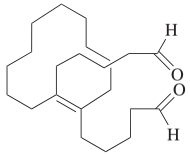
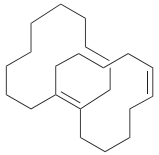
1. $TiCl_4(THF)_2$, Zn, THF, reflux, 30 min
2. Reflux
3. Reflux, 3 h



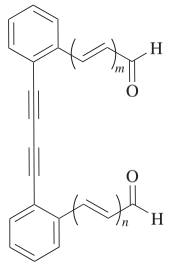
(5–15)

632

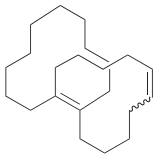
TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{20–26}$ 	1. $TiCl_4$, Zn/Cu, THF, reflux, 30 min 2. Reflux, 50 h 3. Reflux, 1 h	 *n* (*E*)/(*Z*) 2 (95) 48:52 3 (93) 65:35 4 (91) 35:65 5 (94) 60:40	633
C_{21} 	1. $TiCl_3$, $LiAlH_4$, DME, reflux, 30 min 2. Reflux, 14 h 3. Reflux, 4 h	 (4.5)	226
C_{22} 	1. $TiCl_3$, Zn/Cu, DME 2. Reflux, 34 h 3. Reflux, 14 h	 (40)	634

C_{22-30}

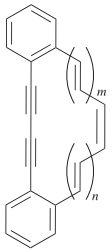


1. $TiCl_3$, Li, DME, reflux, 2 h
2. Reflux, 16 h
3. Reflux, 3 h



(44) 219

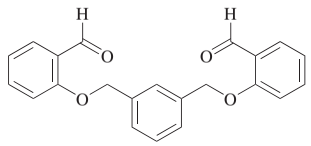
1. $TiCl_3$, $LiAlH_4$, solvent, reflux, time 1
2. Reflux, time 2
3. Reflux, 5 h



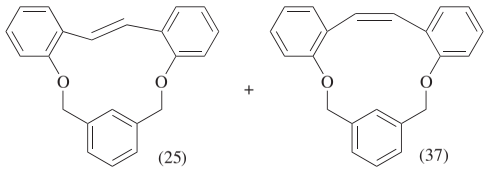
m	*n*	Solvent	Time 1 (min)	Time 2 (h)	
1	1	THF	15	10	(27)
1	2	DME	30	8	(20)
2	2	DME	30	6	(14)
2	3	DME	30	8	(8.7)
3	3	DME	30	10	(4)

229

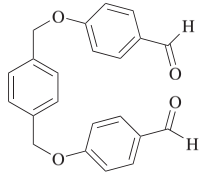
C_{22}



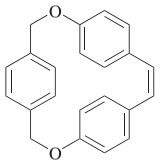
1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Dropwise addition, reflux
3. Reflux, 6 h



(25) + (37) 635

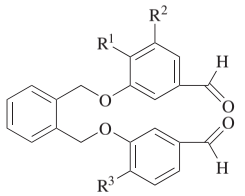
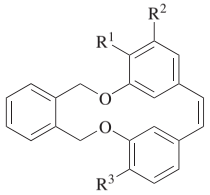
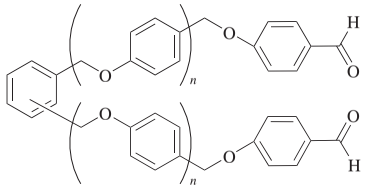
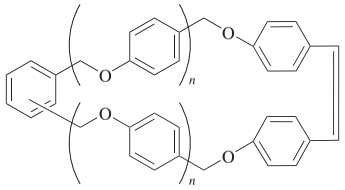
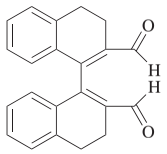
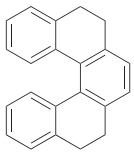
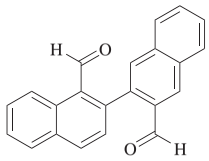
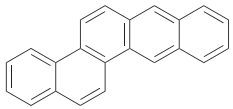


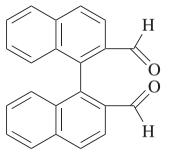
$TiCl_4$, Zn, THF, 24 h



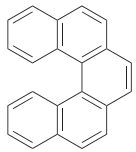
(53) 636

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	1. $TiCl_3$, Zn/Cu, THF, reflux, 1 h 2. Reflux, 8 h 3. Reflux, 13 h	 R^1 R^2 R^3 H H H (62) MeO H H (57) H MeO MeO (65) MeO H MeO (65) H H MeO (10)	637
C_{22-36} 	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 16 h 3. Reflux, 24 h	 *n* Isomer 0 2- (55) 0 3- (60) 0 4- (53) 1 2- (25) 1 3- (30) 1 4- (35)	638
C_{22} 	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. 0°, 30 min 3. Reflux, 2 h	 (62)	243
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. 0°, 30 min 3. Reflux, 2 h	 (57)	243



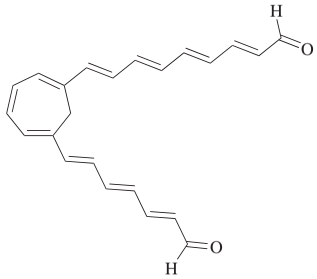
$TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux



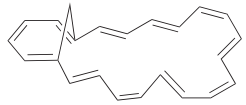
(21)

639

C_{23}



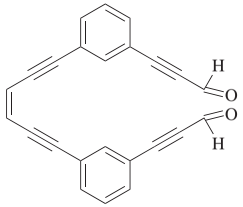
1. $TiCl_3$, $LiAlH_4$, DME, reflux, 30 min
2. Reflux, 12 h
3. Reflux, 3 h



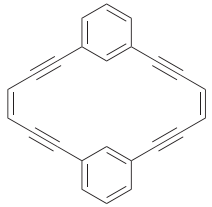
(7.5)

226

C_{24}



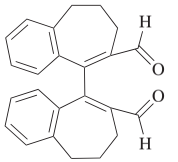
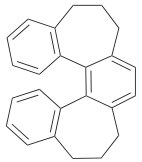
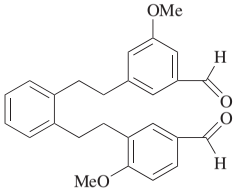
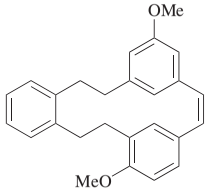
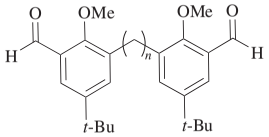
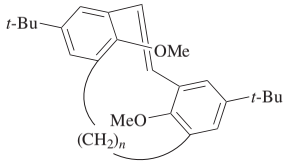
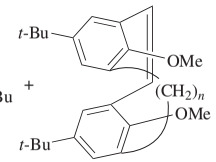
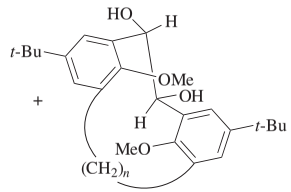
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 5 h
2. –78°, 5 h



(69)

640

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24} 	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. 0°, 30 min 3. Reflux, 2 h	 (58)	243
	$TiCl_3$, Zn/Cu, THF, reflux	 (65)	641
C_{24-27} 	1. $TiCl_4$, Zn, THF 2. Reflux, 60 h 3. Reflux, 8 h	 **I** +  **II**  **III**	642

n	I	II	III
2	(0)	(0)	(18.3)
3	(0)	(1.0)	(29.1)
4	(2.1)	(2.0)	(56.5)
5	(0)	(27.4)	(15.3)

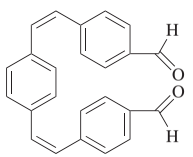
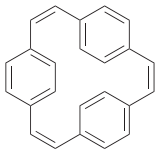
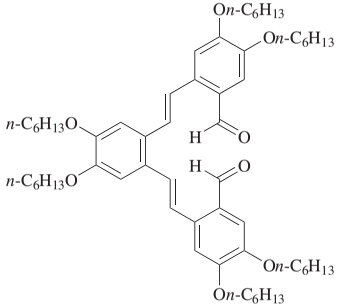
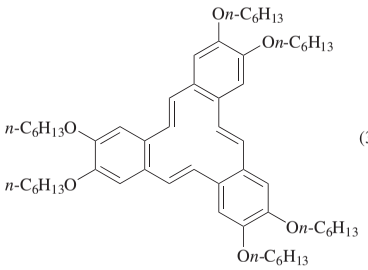
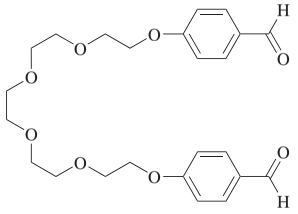
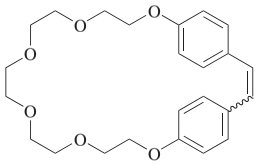
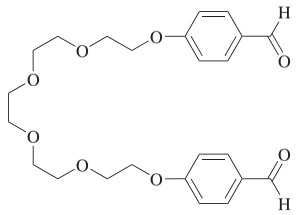
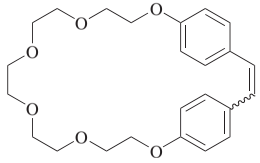
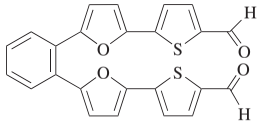
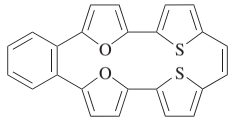
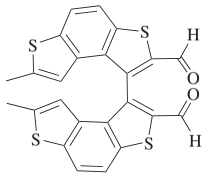
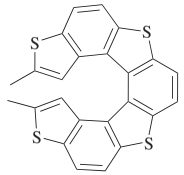
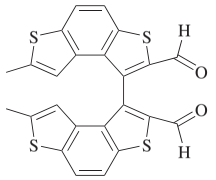
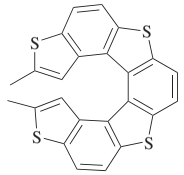
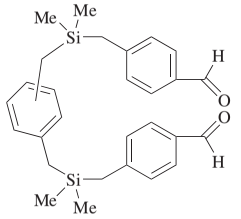
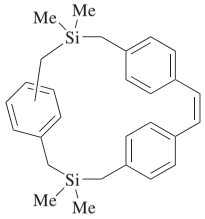
C_{24} 	1. $TiCl_4$, Zn, py, THF, reflux, 1 h 2. "Several h" 3. Reflux		(50)	643
	$TiCl_3$, Zn/Cu		(37)	644
	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 30 min 3. Reflux, 30 min		(61), (*E*)/(*Z*) = 46:54	85

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24} 	1. Ti, TMSCl, DME, reflux, 24 h 2. Reflux, 45 min 3. Reflux, 6 h	 (52) dr 72:28	85
	$TiCl_4$, Zn, py, THF, reflux, 5 h	 (18)	151
	$TiCl_3(DME)_{1.5}$, Zn/Cu, DME	 (78)	645
 **I**	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 2 h 3. Reflux, 36 h	 **II** (*P*)–**II**; (52) er >99.5:0.5 from (*S*)–**I** (*M*)–**II**; (53) er >99.5:0.5 from (*R*)–**I**	245

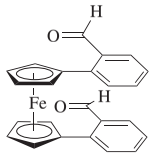


1. $TiCl_4$, Zn, DME,
   reflux, 1 h
2. Dropwise addition, rt
3. Reflux, 24 h

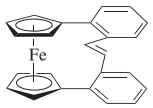


Isomer		
2-	(13)	
3-	(10)	

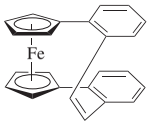
356



1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Py, reflux, 21 h
3. Reflux, 10 h

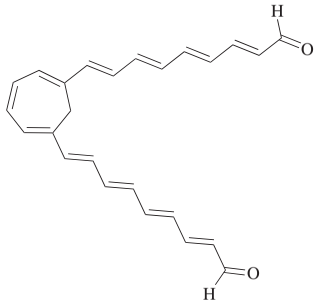


(5.3) + (14.3)

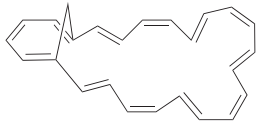


646

C_{25}



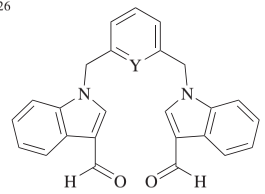
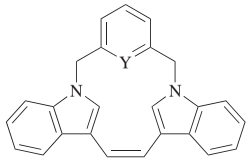
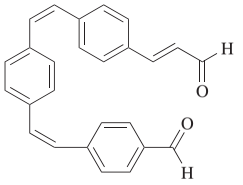
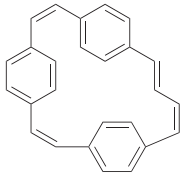
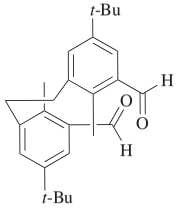
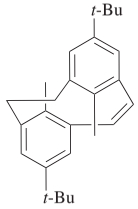
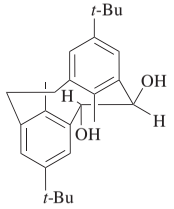
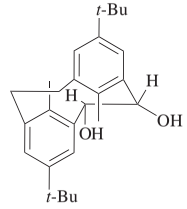
1. $TiCl_3$, $LiAlH_4$, DME,
   reflux, 30 min
2. Reflux, 12 h
3. Reflux, 4 h

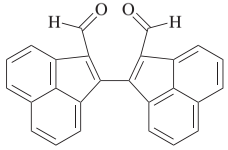


(7.3)

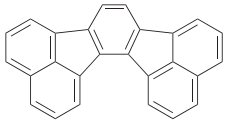
226

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{25–26}$ 	1. $TiCl_4$, Zn, py, THF, reflux, 1 h 2. Addition in one lot, reflux 3. Reflux, overnight	 Y: N (36); CH_2 (24)	647 648, 647
C_{26} 	1. $TiCl_4$, Zn, py, THF, reflux, 1 h 2. Dropwise addition, reflux 3. Reflux	 (48)	649
	$TiCl_4$, Zn, py, THF, reflux, 60 h	 (4.3) +  (7.3) +  (1.5)	650



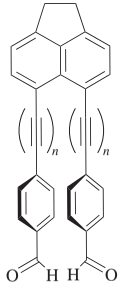
1. $TiCl_4$, Zn, THF, reflux, 2 h,
2. 0°, 30 min
3. Reflux, 2 h



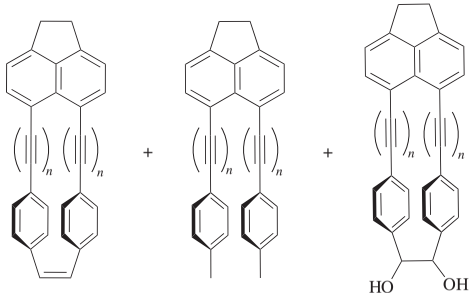
(56)

243

C_{26-30}



1. $TiCl_4$, Zn, THF, reflux, 1.5 h
2. Py, reflux, 9.5 h
3. Reflux, 10 h

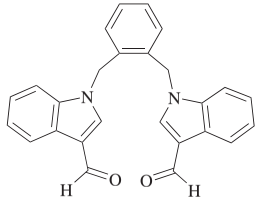


I + **II** + **III**

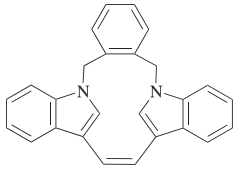
651

n	**I**	**II**	**III**
0	(24)	(12.5)	(2.5)
1	(32)	(8.5)	(15)

C_{26}



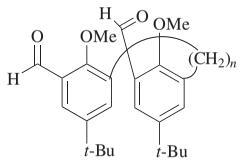
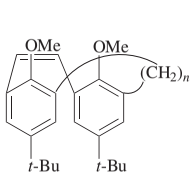
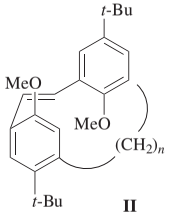
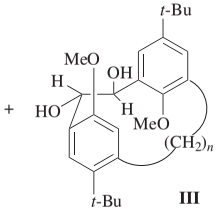
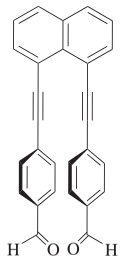
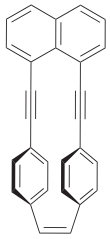
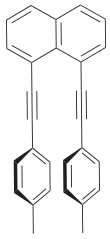
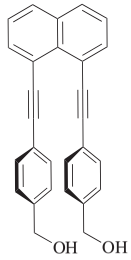
1. $TiCl_4$, Zn, py, THF, reflux, 1 h
2. Addition in one lot, reflux
3. Reflux, overnight



(19)

648, 647

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{27–28}$ 	1. $TiCl_4$, Zn, THF 2. Reflux, 60 h 3. Reflux, 8 h	 **I** +  **II** +  **III** *n* **I** **II** **III** 5 (27) (0) (32) 6 (10) (5) (16)[b]	652
C_{28} 	1. $TiCl_4$, $LiAlH_4$, THF, reflux, 2 h 2. Bu_3N, reflux, 8 h 3. Reflux, 10 h	 (7.5) +  (35) +  (11)	651

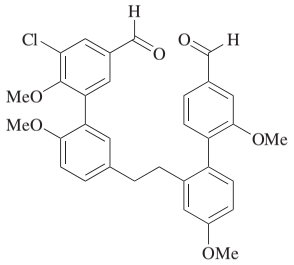
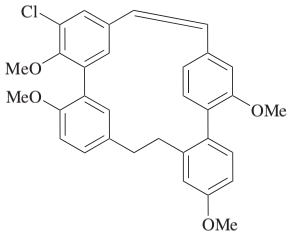
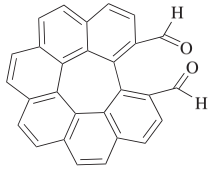
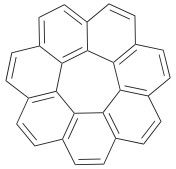
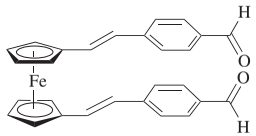
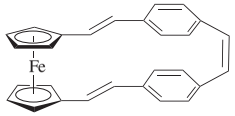
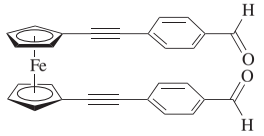
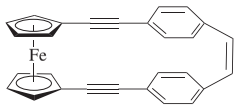
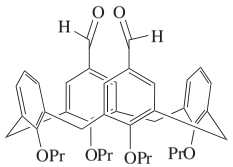
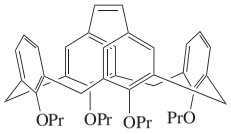
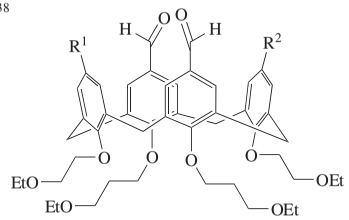
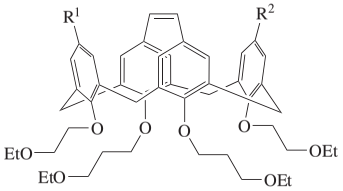
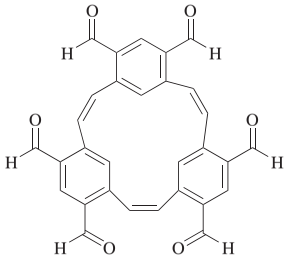
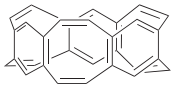
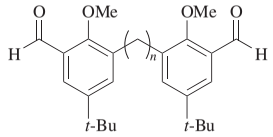
	1. $TiCl_3(DME)_2$, Zn/Cu, DME, 80°, 5 h 2. 80°, 6 h 3. 80°, 8 h		(70)	653
	1. $TiCl_3$, $LiAlH_4$, DME, reflux, 30 min 2. Dropwise addition, reflux 3. Reflux, 4 h		(35)	244, 654
	1. $TiCl_4$, $LiAlH_4$, THF, 0°, 20 min 2. Reflux, 6 h 3. Reflux, 7 h		(2.2)	655, 656
	1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Py, reflux, 11 h 3. Reflux, 10 h		(15)	655, 656

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

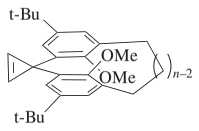
Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30} 	1. $TiCl_3$, Zn, THF 2. Reflux, 2 h 3. Reflux, 15 h	 (30)	241
C_{30-38} 	1. $TiCl_4$, Mg, $HgCl_2$, THF, –10° 2. –10° 3. –10°, 20 min; then rt, time		240
C_{30} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, 100°, 2 h 2. Dropwise addition, 95° 3. 95°, 5 h; then rt, overnight	 (8)	657, 232

R^1	R^2	Time	
H	H	16 h	(30)
Me	H	10 h	(27)
Me	Me	10 h	(15)
t-Bu	*t*-Bu	40 min	(25)

$C_{30–32}$

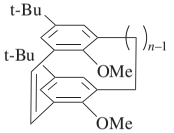


1. $TiCl_4$, Zn, THF
2. Reflux, 60 h
3. Reflux, 8 h



I

+

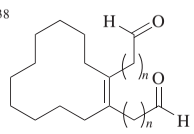


II

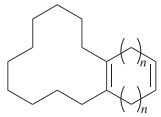
658

n	**I**	**II**
8	(13)	(48)
10	(52)	(42)

$C_{32–38}$



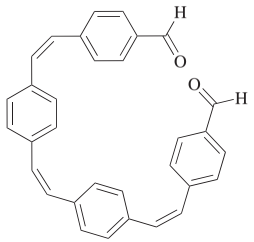
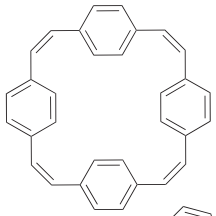
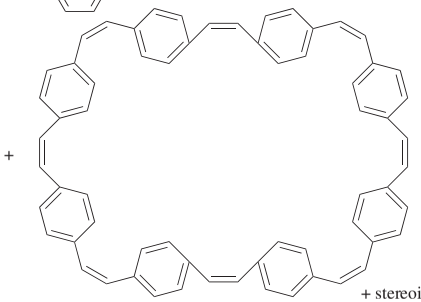
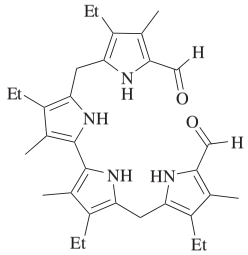
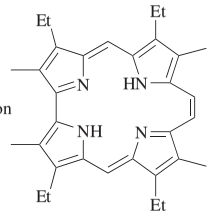
$TiCl_3$, Li, DME, heat, 20 h

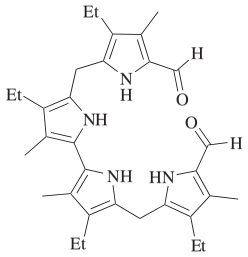


n	
9	(77)
10	(70)
12	(75)

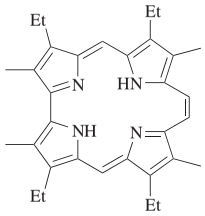
659

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{32} 	1. $TiCl_4$, Zn, THF/toluene, reflux, 2 h 2. rt, 30 min 3. rt, 12 h; then reflux, 5 h	 (21) + stereoisomers +  (37) + stereoisomers	314
	$TiCl_4$, Zn, THF, then air oxidation	 (2)	660



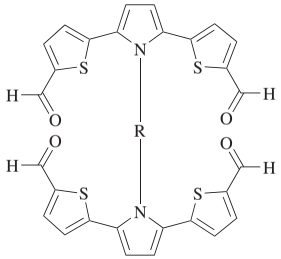
1. $TiCl_4$, Zn, CuCl, THF, reflux, 1 h
2. 0°, 30 min
3. 0°, 5 min
4. $FeCl_3$, 2 h



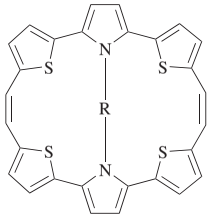
(3)

661

$C_{32–38}$



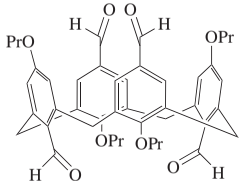
1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 1.5 h
2. Reflux
3. Reflux, 18 h



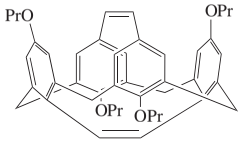
R	
$(CH_2)_4$	(58)
$(CH_2)_6$	(24)
$[(CH_2)_3O(CH_2)_2]_2O$	(51)

662

C_{32}



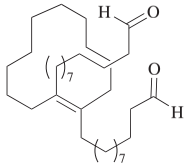
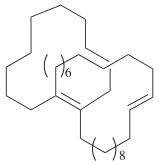
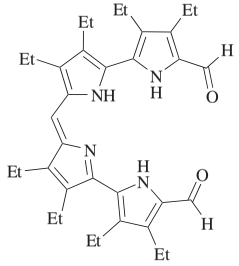
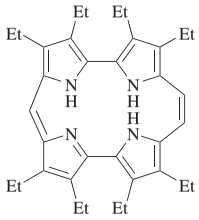
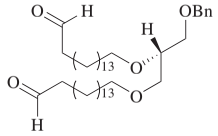
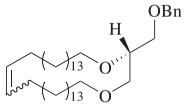
1. $TiCl_3$, Zn, THF
2. Reflux, 2 h
3. Reflux, 15 h



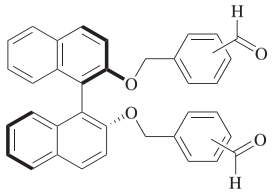
(25)

241

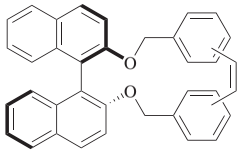
TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{34} 	1. $TiCl_3$, Li, DME, reflux, 2 h 2. Reflux, 16 h 3. Reflux, 3 h	 (56)	219
C_{35} 	1. $TiCl_4$, Zn, CuCl, THF, reflux, 2 h 2. Reflux, 20 min 3. Reflux, 5 min 4. $FeCl_3$	 (23)	663
	1. $TiCl_3$, Zn/Cu, DME 2. Reflux, 100 h 3. Reflux 14 h	 (53) dr 4:1	664

C_{36}



1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Addition in one lot, reflux
3. Reflux, 12 h

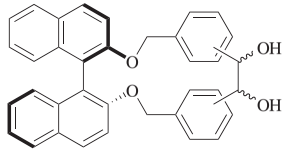


I

Isomer	**I**	**II**
2-	(52)	(8)
3-	(62)	(7)
4-	(15)	(50)

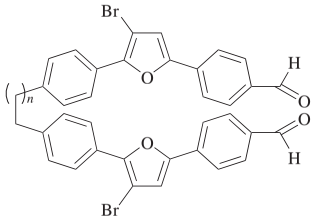
237

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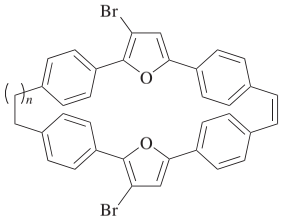


II

C_{36-46}



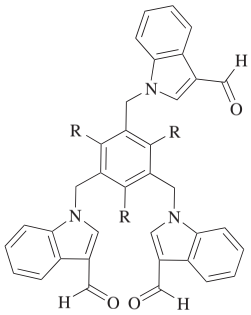
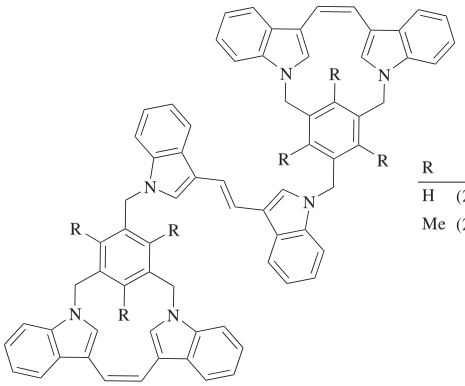
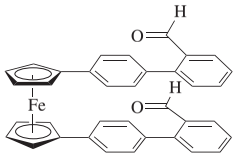
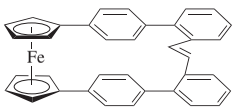
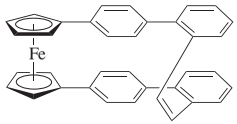
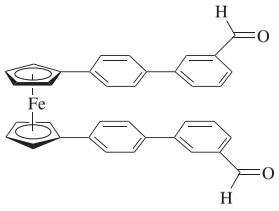
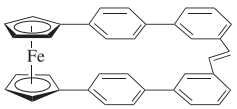
1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Py, reflux
3. Reflux, 16 h

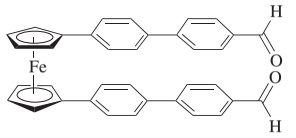


n	
1	(66)
2	(38)
3	(25)
4	(32)
5	(25)
11	(75)

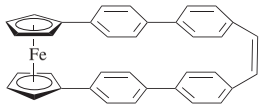
665

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{36-39} 	1. $TiCl_4$, Zn, py, THF, reflux, 1 h 2. Addition in one lot, reflux 3. Reflux, overnight	 R: H (24), Me (22)	666, 647
C_{36} 	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Py, reflux, 18 h 3. Reflux, 10 h	 (34) +  (25)	239
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Py, reflux, 18 h 3. Reflux, 10 h	 (28)	239

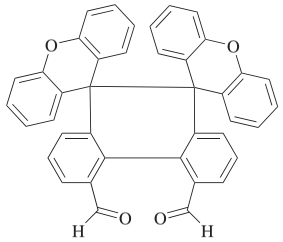


1. $TiCl_4$, Zn, THF, reflux, 2 h
2. Py, reflux, 18 h
3. Reflux, 10 h

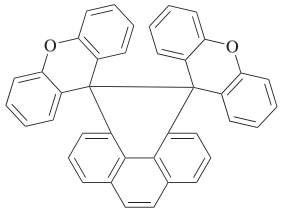


(32) 239

C_{40}

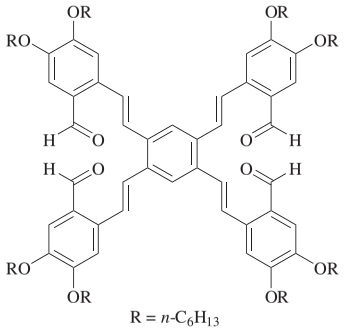


$TiCl_4$, Zn, THF



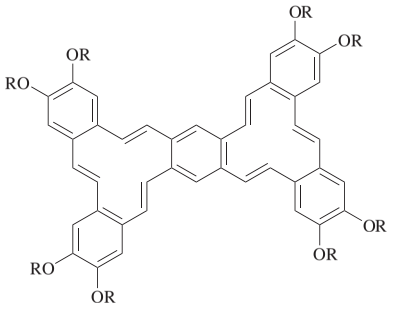
(22) 667

C_{42}



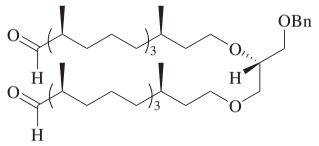
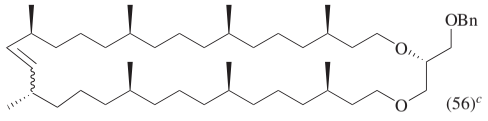
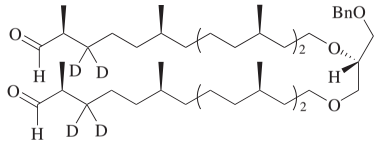
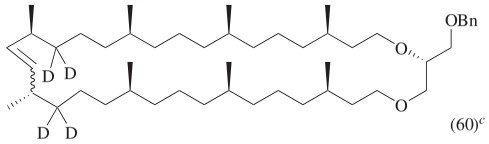
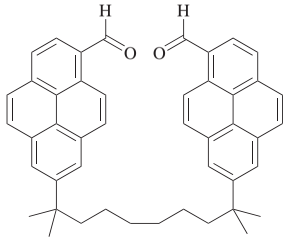
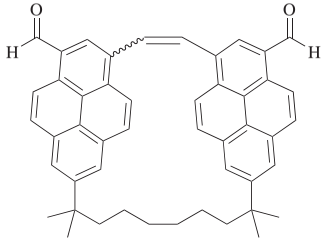
R = *n*-C_6H_{13}

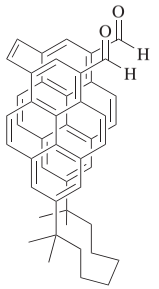
$TiCl_3$, Zn/Cu



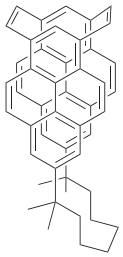
(13) 644

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{43} 	1. $TiCl_3$, Zn/Cu, DME, reflux, 1.5 h 2. Reflux, 50 h 3. Reflux, 18 h	 (56)[c]	668, 669
	1. $TiCl_3$, Zn/Cu, DME, reflux, 2 h 2 Reflux, 44 h 3. Reflux, 18 h	 (60)[c]	670
C_{46} 	$TiCl_4$, Zn, py, 0° to reflux, 5 h; then Rieche formylation	 (*E*) (11), (*Z*) (57)	671

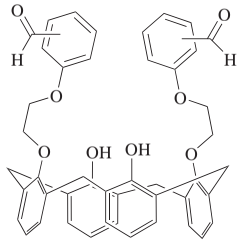


$TiCl_4$, Zn, py, 0° to reflux, 4 h

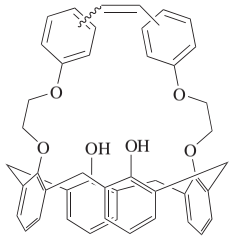


(41)

671



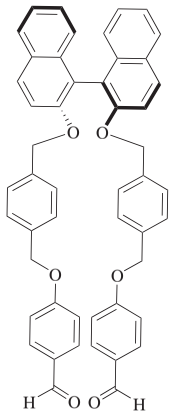
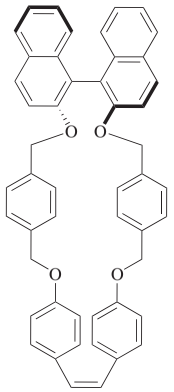
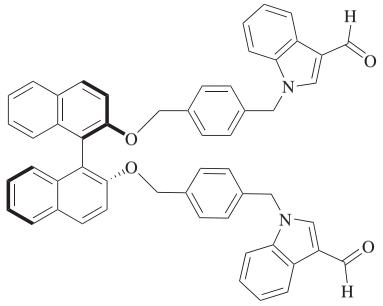
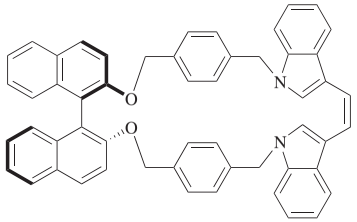
$TiCl_4$, Zn, THF



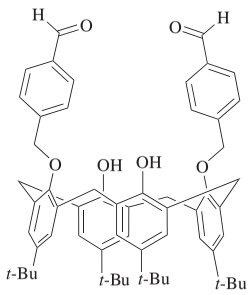
Isomer	(*E*)	(*Z*)
2-	(15)	(62)
3-	(37)	(37)
4-	(—)	(87)

242

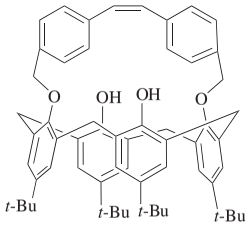
TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{50} 	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Addition in one lot, reflux 3. Reflux, 12 h	 (40)	237
C_{54} 	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Addition in one lot, reflux 3. Reflux, 12 h	 (15)	237

C_{60}



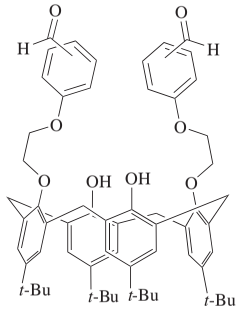
$TiCl_4(THF)_2$, Zn, THF, reflux, 20 h



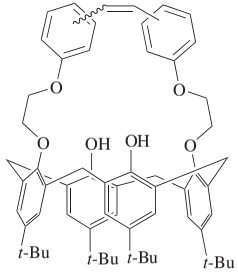
(42)

672

C_{62}



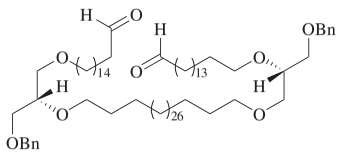
1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Dropwise addition, reflux
3. Reflux, 15 h



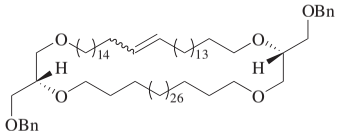
Isomer	(*E*)	(*Z*)
2-	(10)	(57)
3-	(8)	(20)
4-	(0)	(51)

673, 674

C_{70}



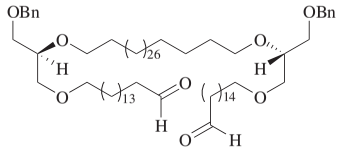
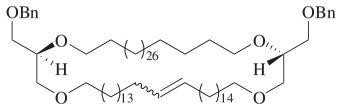
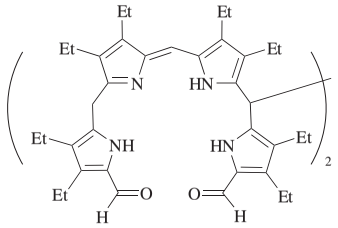
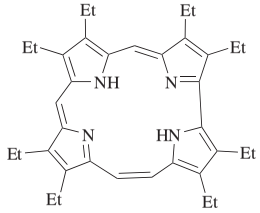
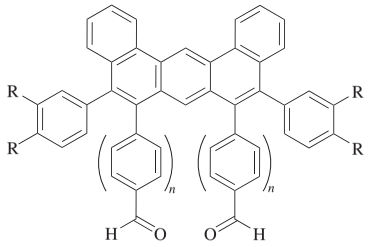
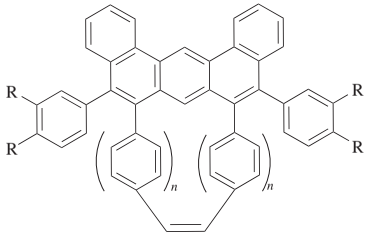
1. $TiCl_3$, Zn/Cu, DME, reflux, 4 h
2. Reflux, 50 h
3. Reflux, 11 h



(66), (*E*)/(*Z*) ~4:1

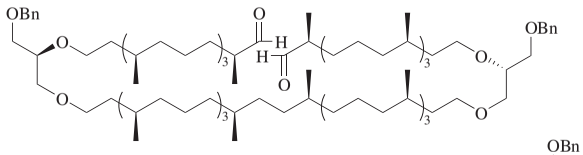
675, 147

TABLE 3A. INTRAMOLECULAR COUPLING OF DIALDEHYDES (*Continued*)

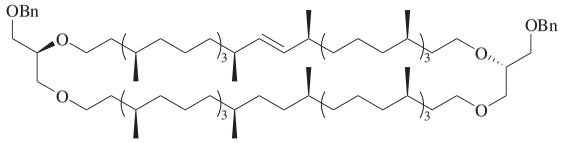
Dialdehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{70} 	1. $TiCl_3$, Zn/Cu, DME, reflux, 4 h 2. Reflux, 50 h 3. Reflux, 11 h	 (61), (*E*)/(*Z*) ~4:1	675, 147
C_{72} 	1. $TiCl_4$, Zn, CuCl, THF, reflux, 1 h 2. rt, 10 min; then oxidation with I_2	 (20)	676
 R = O*n*-C_6H_{13}	1. $TiCl_4$, Zn, THF, 80°, 1 h 2. Py, 80°, 10 h 3. Reflux, overnight		315

n	
1	(63)
2	(67)

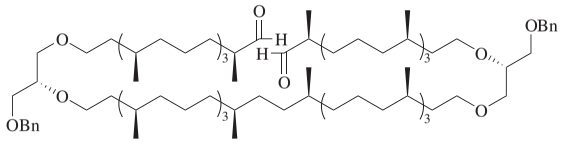
C_{86}



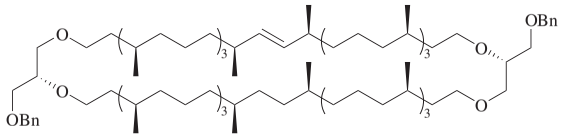
1. $TiCl_3$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 45 h
3. Reflux, 18 h



(59) 677



1. $TiCl_3$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 45 h
3. Reflux, 18 h



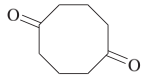
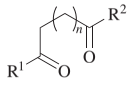
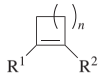
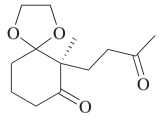
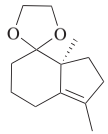
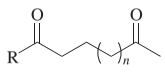
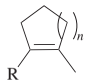
(66) 677

[a] The product was isolated as *trans*-1,2-dibromocyclohexane.

[b] This product was isolated as the diacetate.

[c] The product was a single isomer. The stereochemistry was not rigorously determined.

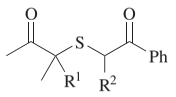
TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 18 h 3. Reflux, 24 h	 (32)	678
C_{11-19} 	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 30 h 3. Reflux, 14 h		61
C_{11} 	1. $TiCl_3$, C_8K, DME, reflux, 2 h 2. Reflux, 10 h 3. Reflux, 30 h	 (75)	84, 679
C_{12-15} 	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 9 h 3. Reflux, 12 h		27

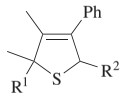
n	R^1	R^2	
1	Ph	Ph	(87)
2	Me	Ph	(70)
3	Me	Bu	(79)
3	Ph	Ph	(95)
3	Me	$Ph(CH_2)_2$	(50)
5	Bu	Bu	(67)
6	Bu	Bu	(68)
7	Bu	Bu	(75)
8	Bu	Bu	(76)

n	R	
1	Ph	(70)
2	n-C_7H_{15}	(79)
2	$Ph(CH_2)_2$	(50)

C_{12-18}

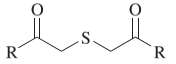


$TiCl_4$, Zn, THF, reflux, 5 h



R^1	R^2	
H	H	(82)
Me	H	(81)
H	Me	(63)
H	Ph	(76)

680

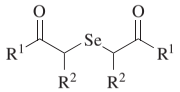


$TiCl_4$, Zn, dioxane, rt, 4 h; then 50°, 2 h

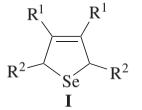


R	
Ph	(62)
2-C_4H_3S	(66)
4-MeC_6H_4	(68)
4-$MeOC_6H_4$	(70)
4-BrC_6H_4	(68)

680

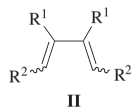


1. $TiCl_4$, Zn, THF
2. Dropwise addition, reflux
3. Reflux, time



I

+

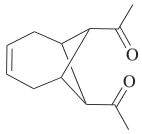


II

R^1	R^2	Time (h)	**I**	**II**
2-C_4H_3S	H	2	(24)	(28)
Ph	H	2	(16)	(31)
Ph	Me	4	(20)	(35)
4-ClC_6H_4	H	2	(30)	(36)
4-MeC_6H_4	H	2	(13)	(26)

681

C_{12}



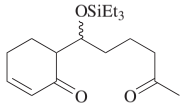
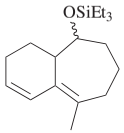
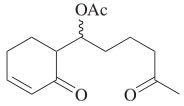
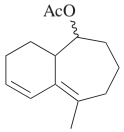
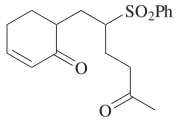
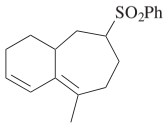
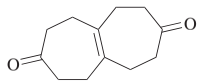
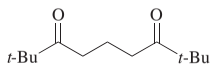
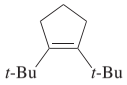
1. $TiCl_3(THF)_3$, K, DME, reflux, 1h
2. rt
3. Reflux, 15 h

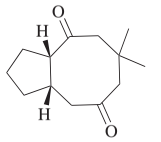


(13)

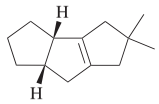
682, 222

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	1. $TiCl_3$, C_8K, DME, reflux, 2 h 2. Reflux, 10 h 3. Reflux, 3 h	 (74)	679, 84
	1. $TiCl_4$, Na-$C_{10}H_8$, THF, reflux, 30 min 2. rt, 10 h 3. Reflux, 4 h	 (58)	679, 84
	1. $TiCl_4$, Na-$C_{10}H_8$, THF, reflux, 30 min 2. rt, 10 h 3. Reflux, 4 h	 (39) single isomer	84
	1. $TiCl_3$, Zn/Cu, DME 2. Reflux, 48 h	 (50)[a]	223
C_{13}			
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 1.5 h 2. Reflux 3. Reflux, 92 h	 (85)	320

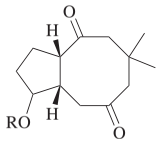


$TiCl_3$, K, THF, reflux, 6 d

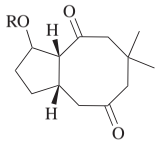


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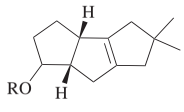
683



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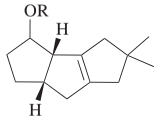


1. $TiCl_3$, K, THF, reflux, 1 h
2. rt
3. Reflux, 4 d



I

+

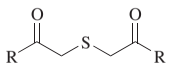


II

248

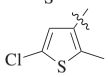
R	**I + II**	**I/II**
H	(—)	100:0
TBS	(59)	38:21

$C_{14–24}$



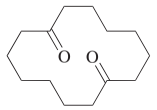
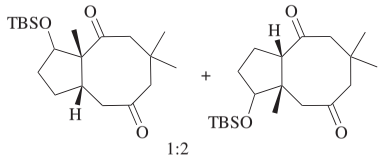
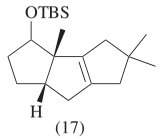
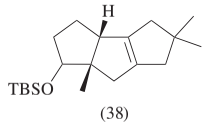
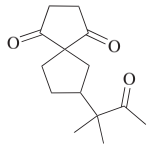
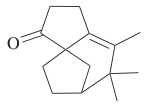
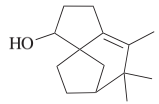
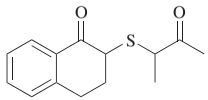
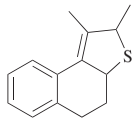
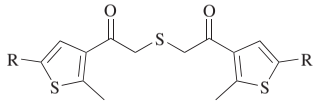
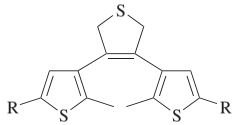
$TiCl_4$, Zn



R	
Ph	(—)
4-ClC_6H_4	(—)
4-BrC_6H_4	(—)
4-Tol	(—)
2-Np	(—)
	(—)
	(—)

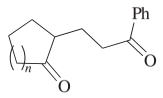
684, 685

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

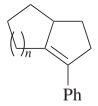
Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	1. $TiCl_3$, Zn/Cu, DME 2. Reflux, 24 h 3. Reflux, 6 h	 (72)	221
 1:2	$TiCl_3$, K, THF, reflux	 (17) +  (38)	686
	1. $TiCl_3$, Zn/Cu, DME, reflux, 4 h 2. Reflux, 50.5 h 3. Reflux, 84 h	 (57) +  (21)	255, 256
	$TiCl_4$, Zn, THF, reflux, 5 h	 (44)	680
C_{14-16}			
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Additive, temp 1, time 1 3. Temp 2, time 2		

R	Additive	Temp 1	Time 1 (h)	Temp 2	Time 2 (h)		
Cl	—	rt	24	rt	24	(70)	687
Me	py	20°	—	reflux	6	(11)	688

$C_{14–15}$

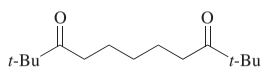


1. $TiCl_3$, C_8K, DME, reflux, 2 h
2. Reflux, 10 h
3. Reflux, 3 h

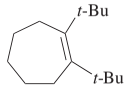


n		
1	(86)	84, 679
2	(87)	

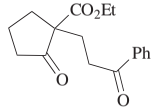
C_{15}



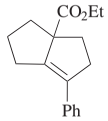
$TiCl_4$, $LiAlH_4$, THF, reflux, 15 h



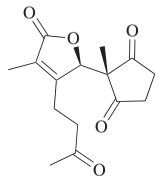
(10) — 148



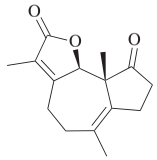
1. $TiCl_4$, Na/Hg, DME, reflux, 5 h
2. rt, 10 h
3. Reflux, 4 h



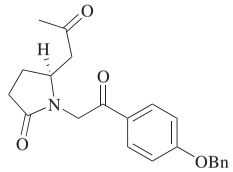
(73) — 84, 679



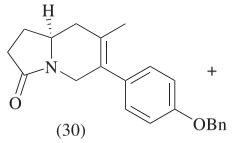
1. $TiCl_4$, Zn, THF, rt, 30 min
2. 0°
3. Reflux, 4 h



(45) — 689

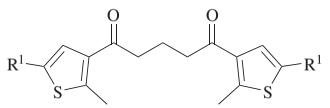
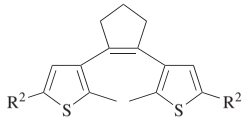


1. $TiCl_3(THF)_3$, Zn/Cu, DME, 80°, 4 h
2. 80°, 5 h
3. 80°, 40 h

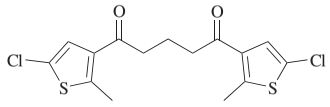
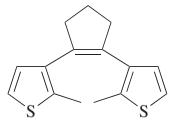


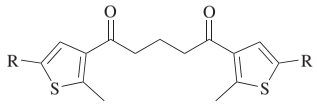
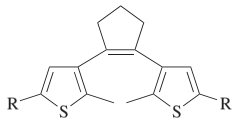
(30) + (30) — 252, 690

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

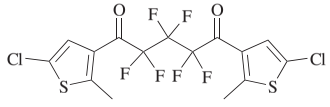
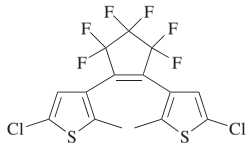
Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15-17} 	1. $TiCl_3(THF)_3$, Mg, THF, 40° 2. 40° 3. 40°, time		691

R^1	R^2	Time (h)	
Cl	H	0.5	(20)
Me	Me	2	(58)

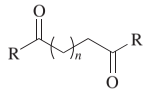
C_{15} 	1. $TiCl_4$, Zn, THF, reflux, 45 min 2. 0° 3. Reflux, 2 h	 (50)	691

C_{15-17} 	$TiCl_3(THF)_3$, M, THF, 40°		692

R	M	
H	Mg	(—)
Cl	Zn	(44)
Me	Zn	(—)

C_{15} 	$TiCl_3(THF)_3$, Zn, THF, 40°, 1 h	 (55)	693, 691

C_{16-24}

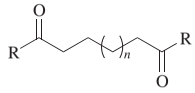


1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h
2. Reflux, 9 h
3. Reflux, 12 h



n	R	
1	Ph	(87)
5	*n*-C_5H_{11}	(67)
6	*n*-C_5H_{11}	(68)
7	Bu	(75)
8	Bu	(76)
9	Pr	(71)
10	Pr	(65)
11	Et	(75)
13	Me	(90)
19	Me	(83)

27

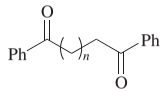


1. $TiCl_3$,Na/Al_2O_3, THF, reflux, 1 h
2. Reflux, 2 h
3. Reflux, time

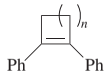


n	R	Time (h)	
1	Ph	1.5	(76)
7	Ph	3	(72)
9	Me	1	(39)

69



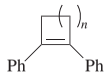
1. $TiCl_3$, $LiAlH_4$, THF, reflux, 15 min
2. Reflux, 0.5–1 h
3. Reflux, time



n	Time (d)	
1	1	(40–61)
2	6	(62)
3	1	(35)
3	5	(60)
5	6	(61)
6	6	(53)
7	6	(49)
9	6	(61)

146, 694
146
146, 694
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146
146
146

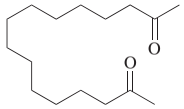
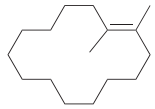
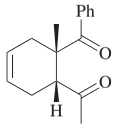
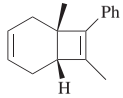
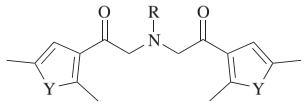
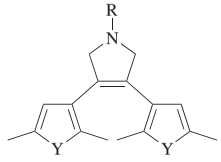
1. $TiCl_3$, C_8K, THF, reflux, 1.5 h
2. Reflux, 6–8 h
3. Reflux, 14 h



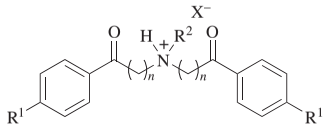
n	
1	(70)
3	(87)
9	(89)

73, 74

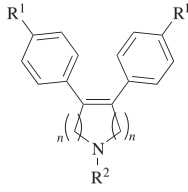
TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 5 h 2. Reflux, 35 h 3. Reflux, 8 h	 (82)	6
	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 19 h 3. Reflux, 12 h	 (97)	695
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Reflux, 8 h 3. Reflux, 24 h		696

Y	R	
S	Ph	(—)
S	4-$MeOC_6H_4$	(—)
S	4-ClC_6H_4	(—)
S	4-MeC_6H_4	(—)
S	Bn	(—)
O	Ph	(—)
O	4-$MeOC_6H_4$	(—)
O	4-ClC_6H_4	(—)

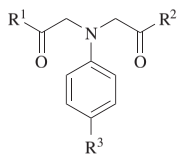
C_{16-20} 

1. $TiCl_4$, Zn, THF, reflux, 1 h
2. rt
3. Reflux, 6 d

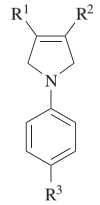


n	X	R^1	R^2		Refs.
1	Br	H	Bn	(90)	426
1	Br	H	4-MeC_6H_4	(91)	
2	Cl	H	Me	(63)	
2	Cl	H	Et	(60)	
2	Cl	H	Bu	(66)	
2	Cl	Me	Me	(56)	

C_{16}



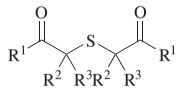
1. $TiCl_4$, Zn, THF, reflux, 1 h
2. rt
3. rt, 24 h



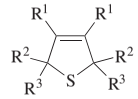
R^1	R^2	R^3	
Ph	Ph	H	(74)
Ph	Ph	MeO	(85)
Ph	Ph	Cl	(66)
Ph		MeO	(61)
		MeO	(80)

697

C_{16-24}



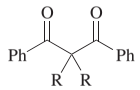
$TiCl_4$, Zn



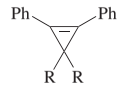
R^1	R^2	R^3	Solvent	Temp	Time (h)	
Ph	H	H	dioxane	rt	18	(67)
Ph	H	H	THF	reflux	5	(77)
Ph	Me	H	THF	reflux	5	(73)
Ph	Et	H	THF	reflux	5	(86)
Ph	Me	Me	THF	reflux	5	(75)
2-Np	H	H	THF	reflux	5	(71)

680

C_{17-19}



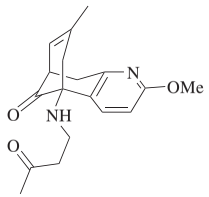
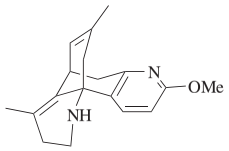
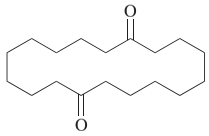
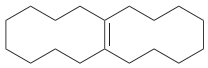
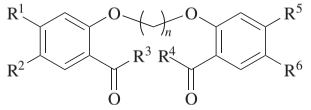
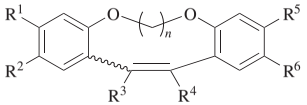
1. $TiCl_3$, $LiAlH_4$, THF, reflux, 15 min
2. Reflux, 0.5–1 h
3. Reflux, 6 d



R	
Me	(46)
Et	(40)

146

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	$TiCl_4$, Zn, py, THF, reflux, 20 h	 (62)	253
C_{18} 	$TiCl_3$, Li	 (34–70)	698
C_{18-20} 	1. $TiCl_4$, Zn, solvent, reflux, 2.5 h 2. rt 3. Reflux, time		

n	R^1	R^2	R^3	R^4	R^5	R^6	Solvent	Time (h)	(*E*)/(*Z*)		Refs.
2	H	H	Me	Me	H	H	DME	16	2:98	(80)	618
2	H	H	Me	Me	EtO	H	DME	16	10:90	(56)	618
2	H	H	Me	Et	H	H	DME	16	5:95	(56)	618
2	H	H	Me	Me	H	Me	DME	16	4:94	(76)	618
2	H	H	Me	Me	H	H	THF	1	1:3	(70)	619
2	H	MeO	Me	Me	H	MeO	THF	1.5	1:3	(65)	619
2	H	H	Et	Et	H	H	THF	1.5	3:8	(75)	619
2	Me	H	Me	Me	H	H	THF	1.5	3:7	(63)	619
4	H	H	Me	Me	H	H	DME	16	8:92	(75)	618
4	H	H	Me	Me	H	H	THF	6	1:3	(52)	619

C_{18}

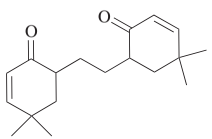
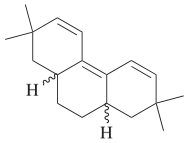
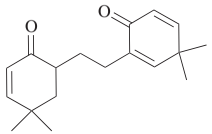
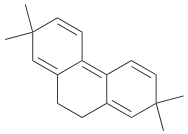
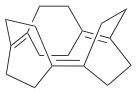
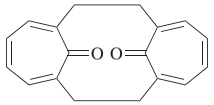
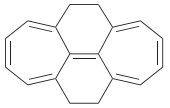
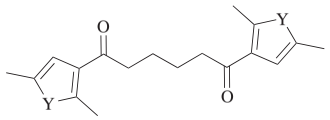
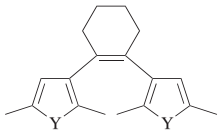
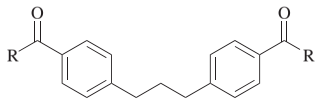
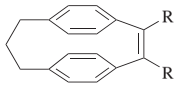
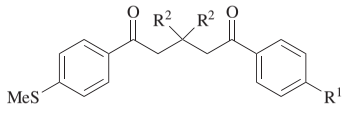
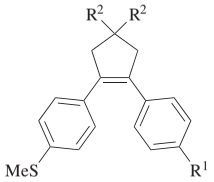
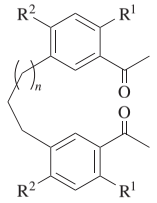
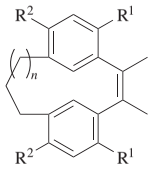
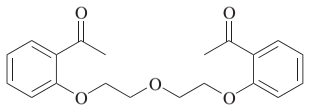
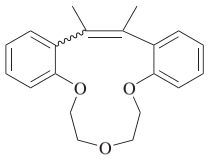
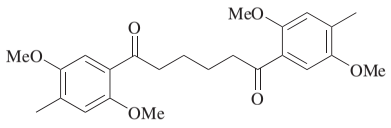
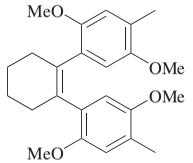
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux, 10 h 3. Reflux, 12 h		(51) dr 1:1.7	200
	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux, 10 h 3. Reflux, 12 h		(55)	200
	1. $TiCl_3$, Zn/Cu, DME, reflux, 5 h 2. 68°, 45 h 3. 68°, 2 h		(24)	699, 230
	$TiCl_4$, Zn, THF		(90–95)	700
	1. $TiCl_4$, Zn, THF or dioxane, reflux, 1 h 2. 20° 3. Reflux, 20 h		Y O (33) S (25)	688

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

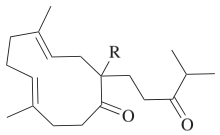
Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{19–21}$ 	1. $TiCl_4$, Zn, py, THF, reflux, 2 h 2. Reflux, 80 h 3. Reflux, 10–12 h	 R: Me (82), Et (60)	234
	$TiCl_4$, Zn, THF	 R^1: F, Me, (—); Cl, Me, (—); F, CF_3, (—); F, Et, (—)	701
$C_{19–22}$ 	1. $TiCl_4$, Zn, THF 2. Py, reflux, 60 h 3. Reflux, 8 h	 *n*, R^1, R^2: 1, MeO, H, (40); 1, H, MeO, (80); 2, MeO, H, (69); 2, H, MeO, (83); 3, H, MeO, (77); 4, H, MeO, (19)[b]	621 702, 703 621 702, 703 702, 703 702, 703
C_{20} 	1. $TiCl_4$, Zn, dioxane, reflux, 1 h 2. Dropwise addition, reflux 3. 16 h	 (81.9), (*E*)/(*Z*) = 41:59	626



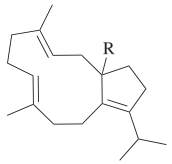
$TiCl_4$, Zn, THF, reflux, 16 h



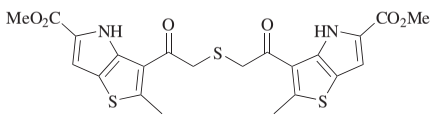
(42) 704



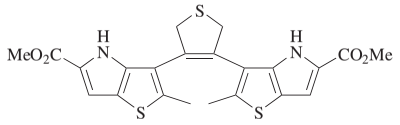
1. $TiCl_3$, Zn/Cu, DME, reflux, time 1
2. Reflux, 12 h
3. Reflux, time 2



R	Time 1 (h)	Time 2 (h)		
t-Bu(Ph)$_2$SiOCH$_2$	6	6	(90)	705
Me	6	6	(91)	705
Me	2	5	(90)	250

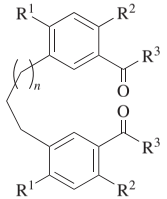


1. $TiCl_4$, Zn, THF, heat, 1 h
2. Py, 20°
3. Reflux, 6 h

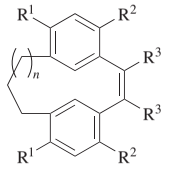


(51) 706

$C_{21–30}$

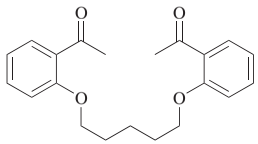
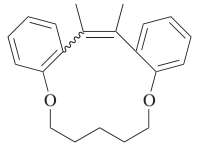
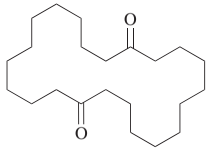
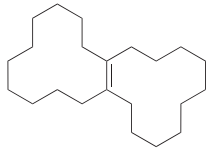
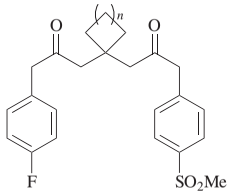
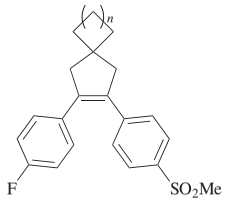


1. $TiCl_4$, Zn, THF
2. Py, reflux, 60 h
3. Reflux, 8 h

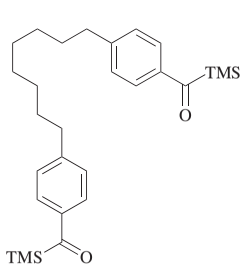


n	R^1	R^2	R^3		
1	H	Me	Me	(26.5)[b]	629
1	H	H	Ph	(55)	707
2	MeO	H	Ph	(40)	707

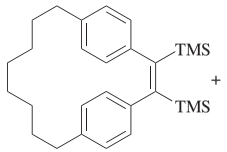
TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21} 	1. $TiCl_3$, Zn, dioxane, reflux 2. Reflux, 20 min 3. Reflux, 30 h	 (91), (*E*)/(*Z*) = 24:76	626
C_{22} 	$TiCl_3$, Li	 (62–73)	698
C_{22-24} 	$TiCl_4$, Zn, THF	 *n*: 1 (76); 2 (71); 3 (81)	708

C_{22}

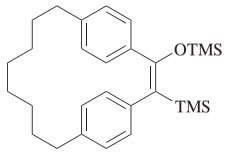


1. $TiCl_3$, Na/Al_2O_3, DME, reflux, 1 h
2. Reflux, 2 h
3. Reflux, 2.5 h



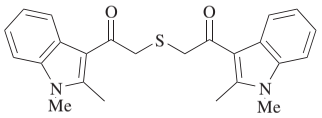
(49)

+

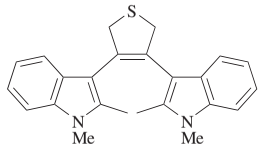


(44)

70



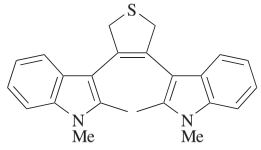
1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Py, 20°
3. Reflux, 6 h



(18)

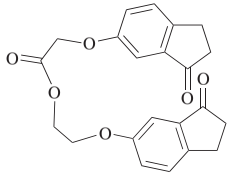
688

1. $TiCl_4$, $NaAlH_4$, THF, 0–2°, 1 h
2. 0–2°
3. rt, 1 h; then 60°, 8 h

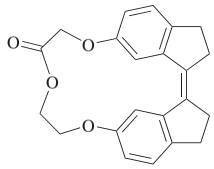


(11)

709



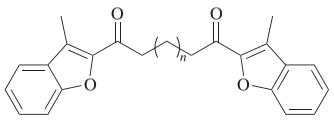
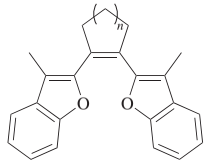
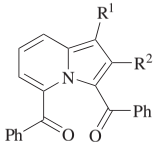
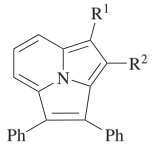
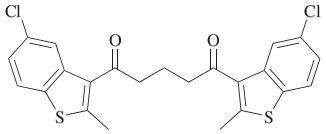
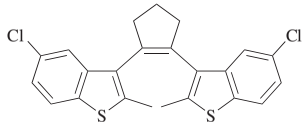
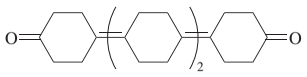
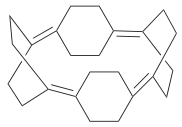
1. $TiCl_4$, Zn, THF, reflux, 1.5 h
2. Reflux, 3–6 h
3. Reflux, 20–40 min

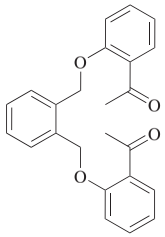


(52)

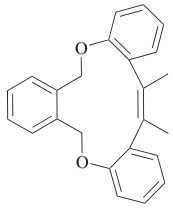
710

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{23–24}$ 	1. $TiCl_4$, $NaAlH_4$, THF, 0–2°, 1 h 2. Dropwise addition, 0-2° 3. rt, 1 h; then 60°, 4 h		711
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. rt, 40 min 3. rt, 30 min		712
		R^1 / R^2 / (%) NC / H / (95) MeO_2C / H / (90) EtO_2C / EtO_2C / (90)	
C_{23} 	$TiCl_4$, Zn, THF, reflux, 30 h	 (53)	713
C_{24} 	$TiCl_3$, Zn/Cu, DME, reflux, 48 h	 (90)	231

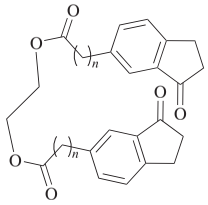


1. $TiCl_3$, Zn, dioxane, reflux
2. Reflux, 20 min
3. Reflux, 3 h

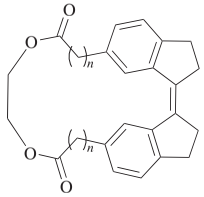


(60) 626

$C_{24–26}$



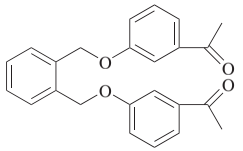
1. $TiCl_4$, Zn, THF, reflux, 1.5 h
2. Reflux, 3–6 h
3. Reflux, 20–40 min



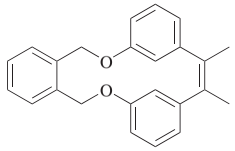
n	
1	(70)
2	(76)

710

C_{24}

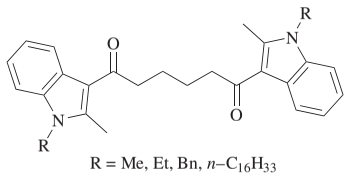
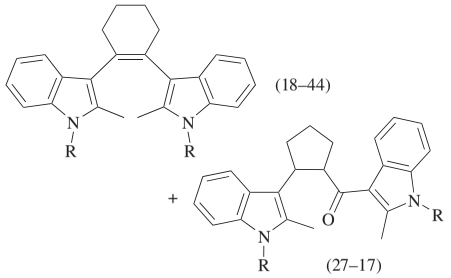
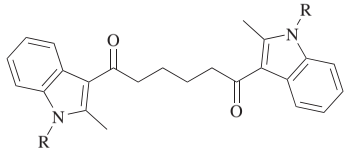
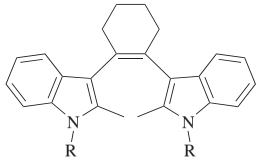
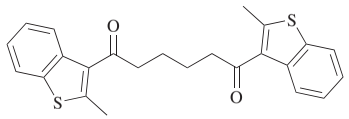
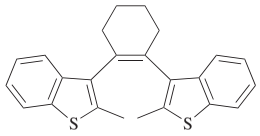
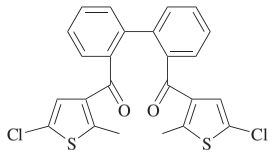
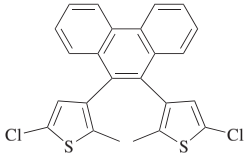


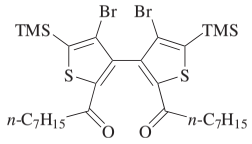
1. $TiCl_3$, Zn/Cu, THF, reflux, 1 h
2. Reflux, 8 h
3. Reflux, 13 h



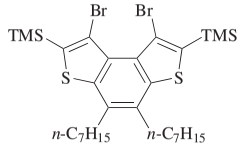
(78) 637

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

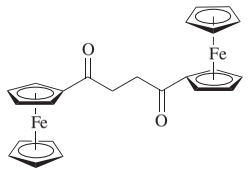
Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24}  R = Me, Et, Bn, *n*–$C_{16}H_{33}$	$TiCl_4$, Zn, THF, reflux, 20–48 h	 (18–44) + (27–17)	714
	1. $TiCl_4$, Zn, THF or dioxane, reflux, 1 h 2. 20° 3. Reflux, 20 h	 R: Et (26); Bn (23); *n*-$C_{16}H_{33}$ (44)	688
	1. $TiCl_4$, Zn, THF or dioxane, reflux, 1 h 2. 20° 3. Reflux, 20 h	 (40)	688
	$TiCl_4$, Zn, THF, reflux	 (—)	715



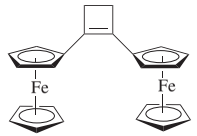
$TiCl_3$, Zn, DME, rt, 1 h;
then 85–90°, 20 h



(77) 716

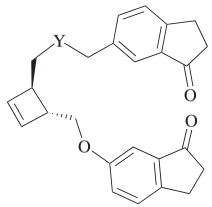


$TiCl_4$, Zn, py, THF, rt, 5 h

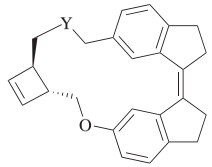


(56) 717

C_{25}



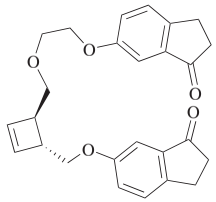
1. $TiCl_4$, Zn, THF, reflux, 1.5 h
2. Reflux, 3–6 h
3. Reflux, 20–40 min



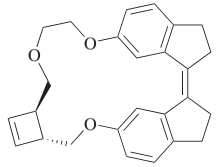
Y	
O	(—)
S	(—)

718

C_{26}

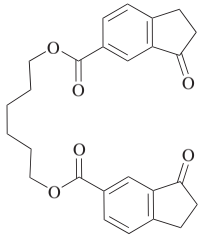
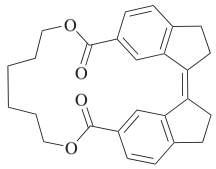
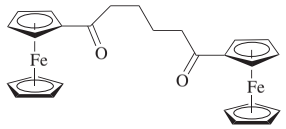
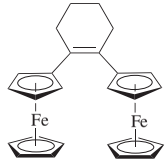
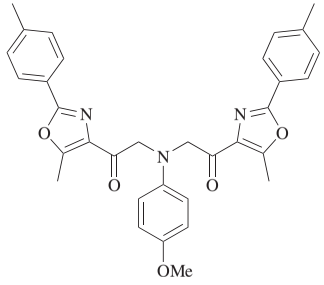
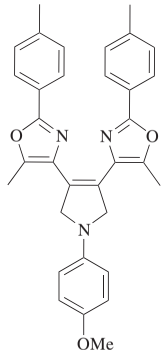


1. $TiCl_4$, Zn, THF, reflux, 1.5 h
2. Reflux, 3–6 h
3. Reflux, 20–40 min

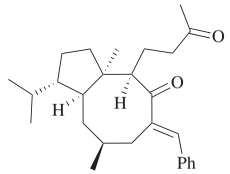


(—) 718

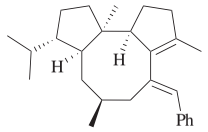
TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}			
	1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. Reflux, 3–6 h 3. Reflux, 20–40 min	 (65)	710
	1. $TiCl_4$, $LiAlH_4$,THF, reflux, 3 h 2. Reflux, 5 h 3. Reflux, 30 min	 (53)	456
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. rt 3. rt, 24 h	 (78)	697

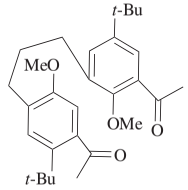
C_{27}



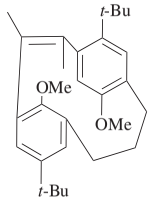
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 1.5 h
2. Reflux
3. Reflux, 3.5 h



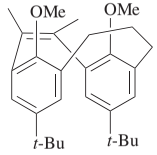
(73) 249, 719



1. $TiCl_4$, Zn, THF
2. Py, reflux, 60 h
3. Reflux, 8 h

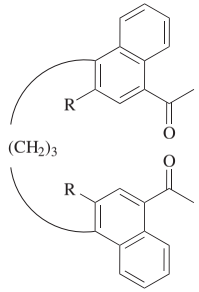


(17) +

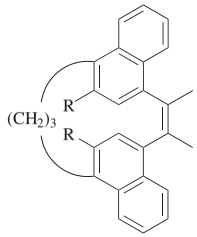


(13) 720

C_{27-29}



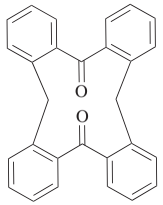
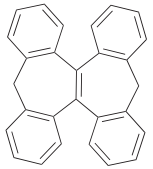
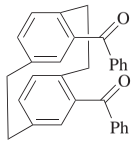
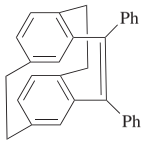
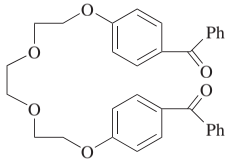
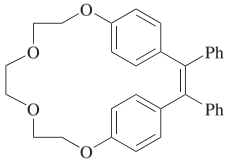
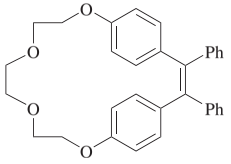
1. $TiCl_4$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 72 h
3. Reflux, 12 h

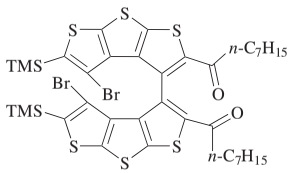


R	
H	(41)
Me	(50)

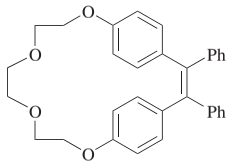
150

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28} 	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux 3. Reflux, 3 d	 (81)	224
C_{30} 	1. $TiCl_4$, Zn, py, THF 2. 0°, 20 min 3. Reflux, 4 h	 (79)	235
C_{32} 	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 0.5 h 3. Reflux, 0.5 h	 (81)	69, 85
	1. $TiCl_3$, Na/Al_2O_3, THF, reflux, 1 h 2. Reflux, 2 h 3. Reflux, 1 h	 (83)	69, 85



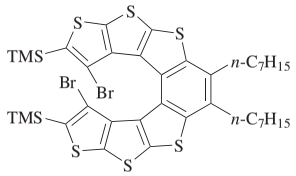
1. Ti, TMSCl, DME, reflux, 48 h
2. Addition in one lot, reflux
3. Reflux, 8 h



(57)

69, 85

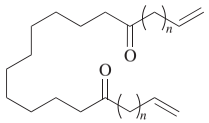
$TiCl_3$, Zn, DME, rt, 1 h; then 85–90°, 24 h



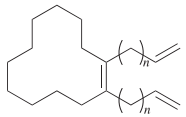
(38)[c]

246

$C_{34–38}$



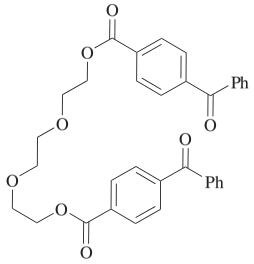
1. $TiCl_3$, Li, DME, heat
2. 20 h



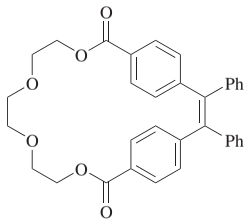
n	
9	(78)
11	(82)

659

C_{34}



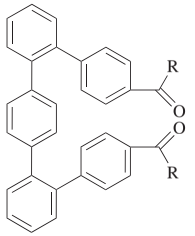
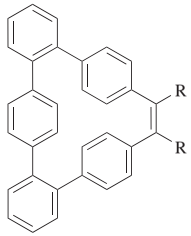
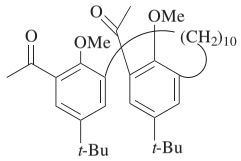
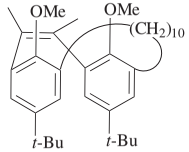
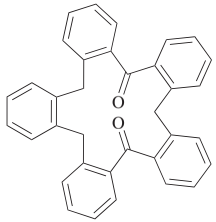
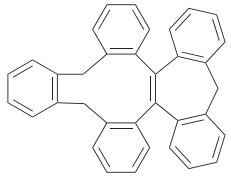
1. $TiCl_3$, C_8K, THF, reflux, 1.5 h
2. Reflux, 30 min
3. Reflux, 30 min



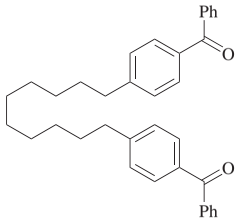
(40)

85

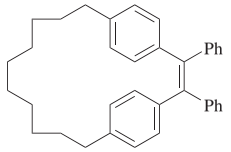
TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{34-44} 	1. $TiCl_4$, Zn, THF, py, reflux, 2 h 2. Reflux, 20 h 3. Reflux, 12 h	 R: Me (91); n-C_5H_{11} (93); Ph (98); 4-$MeOC_6H_4$ (96)	236
C_{34} 	1. $TiCl_4$, Zn, THF 2. Reflux, 60 h 3. Reflux, 8 h	 (90)	721
C_{35} 	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 20 min 2. Reflux 3. Reflux, 2 d	 (94)	224

C_{36}



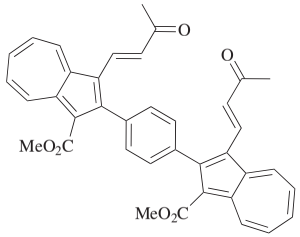
1. $TiCl_3$, M, THF, reflux, time 1
2. Reflux, time 2
3. Reflux, time 3



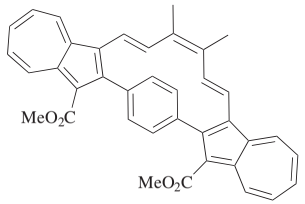
(86)

85

M	Time 1 (h)	Time 2 (h)	Time 3 (h)
C_8K	1.5	7	12
Na/Al_2O_3	1	2	1



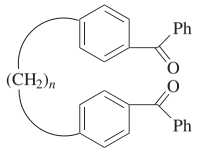
$TiCl_3$, $LiAlH_4$, THF, reflux



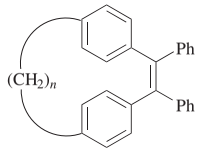
(20)

772

C_{36-52}



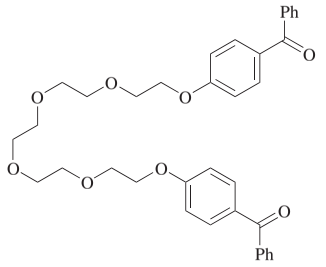
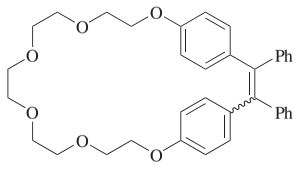
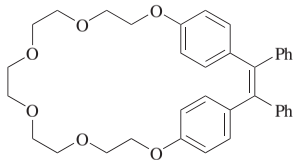
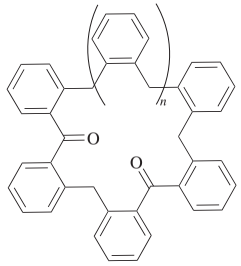
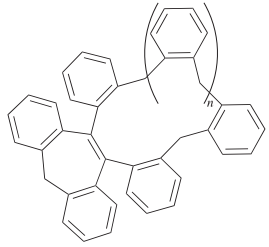
1. $TiCl_3$, Na/Al_2O_3, THF, reflux, 1 h
2. Reflux, 2 h
3. Reflux, 2 h



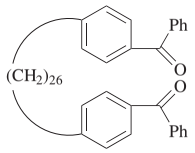
n	
10	(86)
26	(83)

69

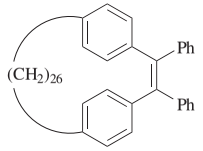
TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{36} 	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 30 min 3. Reflux, 30 min	 (63)	85
	1. Ti, TMSCl, DME, reflux, 40 h 2. Addition in one lot, reflux 3. Reflux, 6 h	 (60), (*E*)/(*Z*) = 0:100	85
C_{42-49} 	1. $TiCl_3$, $LiAlH_4$, THF, reflux, 30 min 2. Reflux 3. Reflux, 1 d	 *n*: 1 (92); 2 (87)	723 724

C_{52}



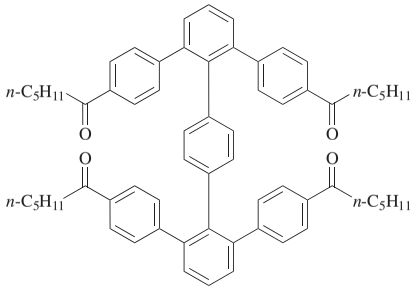
1. Ti powder, TMSCl, DME, reflux, 67 h
2. Addition in one lot, reflux
3. Reflux, 6 h



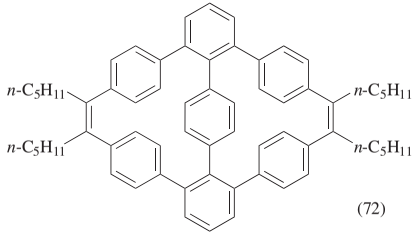
(90)

83

C_{66}



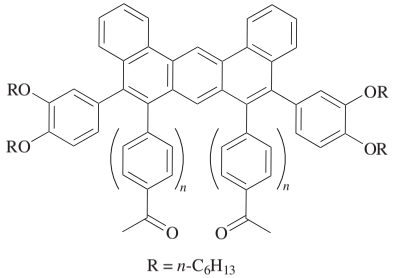
1. $TiCl_4$, Zn, py, THF, reflux, 2 h
2. Reflux, 4 h
3. Reflux, 12 h



(72)

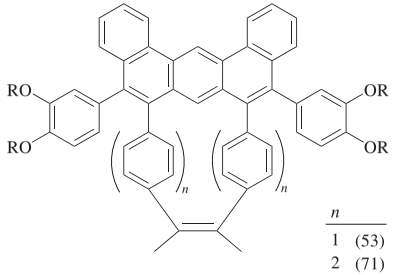
725

$C_{48–60}$



R = *n*-C_6H_{13}

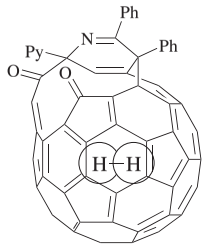
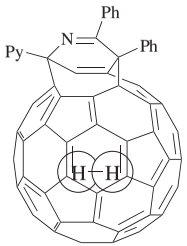
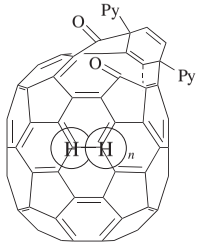
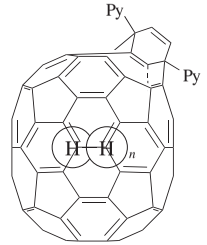
1. $TiCl_4$, Zn, THF, 80°, 1 h
2. Py, 80°, 10 h
3. Reflux, overnight



n	
1	(53)
2	(71)

315

TABLE 3B. INTRAMOLECULAR COUPLING OF DIKETONES (*Continued*)

Diketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{80} 	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. rt 3. 1,2-dichlorobenzene, 80°, 2 h	 (88)	726, 727 728, 729
C_{82}  $(n = 1)/(n = 2) = 97:3$	1. $TiCl_4$, Zn, THF, reflux, 1.5 h 2. rt 3. 1,2-dichlorobenzene, 80°, 45 min	 (61)	316

[a] This is produced by the Cope rearrangement of the McMurry product.

[b] This is the yield in the absence of pyridine.

[c] This is the yield of *rac*-**II** from *rac*-I. (*M*)-**II** (er 87.0:13.0) and (*P*)-**II** (er 75.0:25.0–95.0:5.0) were obtained from (*R*)-**I** (er 78.0:22.0) and (*S*)-I (er 85.5:14.5–95.5:4.5) in 28 and 17–63% yields, respectively.

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES

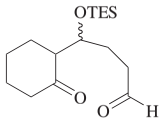
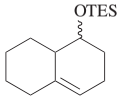
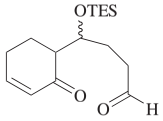
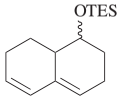
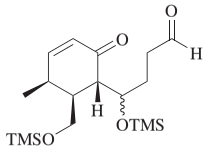
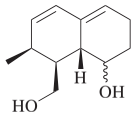
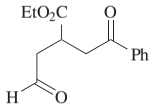
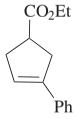
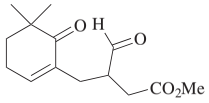
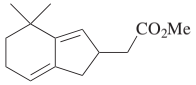
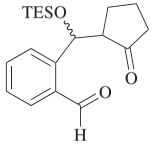
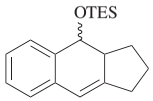
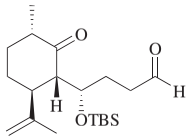
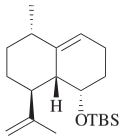
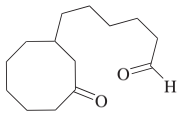
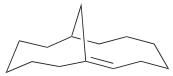
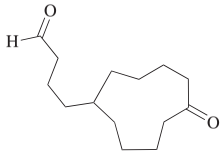
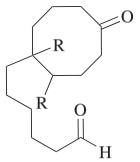
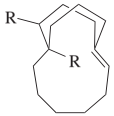
Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. $TiCl_3$, C_8K, DME, reflux, 2 h 2. Reflux, 10 h 3. Reflux, 30 h	 (64)	84, 679
	1. $TiCl_3$, C_8K, DME, reflux, 2 h 2. Reflux, 10 h 3. Reflux, 3 h	 (82)	84, 679
C_{12}			
	$TiCl_3$, Zn/Cu, DME, reflux	 (72) dr 1.3:1	730
	1. $TiCl_4$, Zn, py, THF, rt, 1.5 h 2. rt 3. Reflux, overnight	 (64)	731
C_{13}			
	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 97 h	 (52)	247

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	1. $TiCl_3$, C_8K, dioxane, reflux, 2 h 2. Reflux, 10 h 3. Reflux, 30 h	 Isomer (*R**,*S**) (64) (*R**,*R**) (67)	84, 679
C_{14}			
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, reflux 2. Reflux, 12 h	 (60)	732
	1. $TiCl_3$, Zn/Cu, DME, reflux, 4 h 2. Reflux, 24 h 3. Reflux, 2 h	 (38)	733
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 3 h 2. Reflux, 35 h	 (30)	734, 735

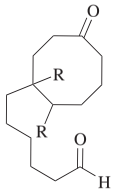


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 3 h
2. Reflux, 35 h

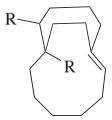


R	
H	(35)
D	(—)

220

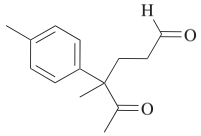


1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 3 h
2. Reflux, 40 h

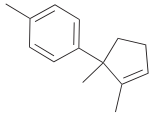


R	
H	(36)
D	(—)

220



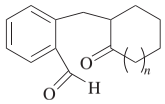
1. $TiCl_3$, K, THF, reflux, 45 min
2. Reflux
3. Reflux, 12 h



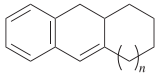
(55)

62

$C_{14–15}$



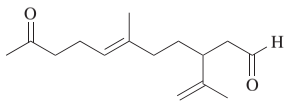
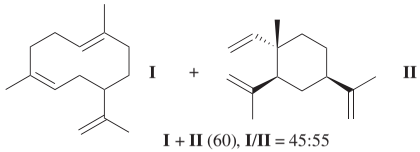
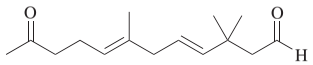
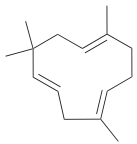
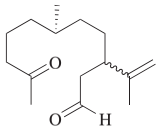
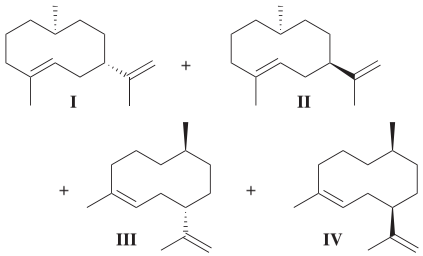
1. $TiCl_3$, C_8K, DME, reflux, 2 h
2. Reflux, 10 h
3. Reflux, 11–14 h

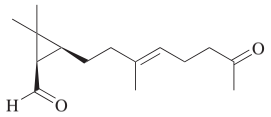


n	
1	(81)
2	(86)

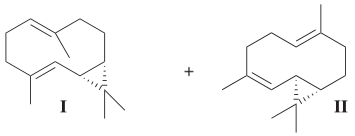
84, 679

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	$TiCl_3$, Zn/Cu, DME, reflux, 34 h	 **I** + **II** **I + II** (60), **I/II** = 45:55	268
	$TiCl_3$, Zn/Cu, DME, reflux, 18 h	 (60)	270
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 5 h 2. Reflux, 30 h 3. Reflux, 5 h	 **I** + **II** + **III** + **IV** **I + II + III + IV** (45), **I/II/III/IV** = 1.0:1.1:1.6:2.0	267

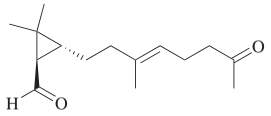


1. $TiCl_3$, Zn/Cu, DME, reflux, 7 h
2. Reflux, 42 h
3. Reflux, 2 h

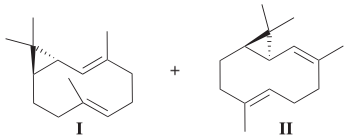


I + **II** (60), **I**:**II** = 3:1

266

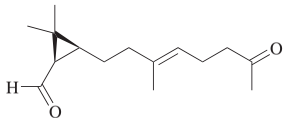


1. $TiCl_3$, Zn/Cu, DME, reflux, 3 h
2. Reflux, 46 h
3. Reflux, 2.5 h

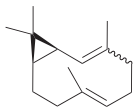


I + **II** (78), **I**/**II** = 2:3

266

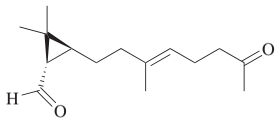


1. $TiCl_3$, Zn/Cu, DME
2. Reflux, 30 h

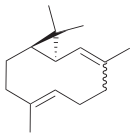


(61), (*E*)/(*Z*) = 80:20

265



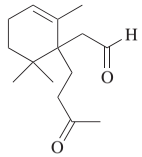
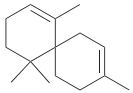
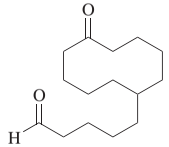
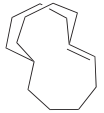
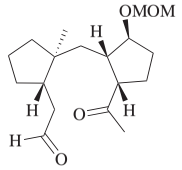
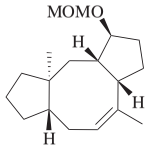
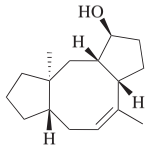
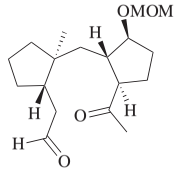
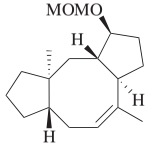
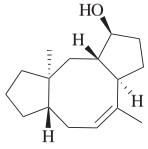
1. $TiCl_3$, Zn/Cu, DME
2. Reflux, 30 h

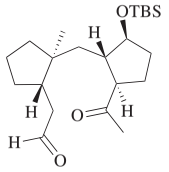


(75), (*E*)/(*Z*) = 40:60

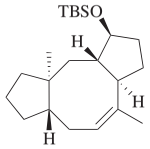
265

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

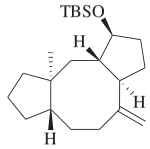
Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 25 h 3. Reflux, 14 h	 (45)	254
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 3 h 2. Reflux, 35 h	 (22)	220
C_{16}			
	1. $TiCl_3$, Zn/Cu, DME, reflux, 3 h 2. Reflux, 21 h 3. Reflux, 12 h	 (29) +  (16)	263
	1. $TiCl_3$, Zn/Cu, DME, reflux, 6 h 2. Reflux, 40 h 3. Reflux, 2.5 h	 (18) +  (31)	263



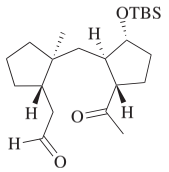
1. $TiCl_3(DME)_{1.5}$, Zn/Cu,
   DME, reflux, 10 h
2. Reflux, 12 h
3. Reflux, 2 h



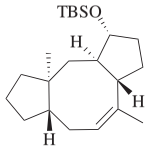
(31) +



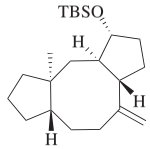
(29) 264



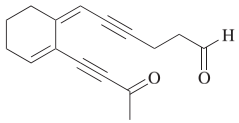
1. $TiCl_3(DME)_{1.5}$, Zn/Cu,
   DME, reflux, 10 h
2. Reflux, 12 h
3. Reflux, 2 h



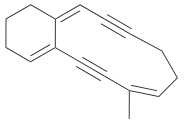
(40) +



(29) 264

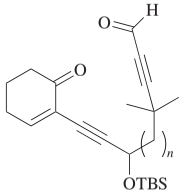


1. $TiCl_3(DME)_{1.5}$, Zn/Cu,
   DME, reflux, 5 h
2. –5°, 6 h
3. –5°, 15 h

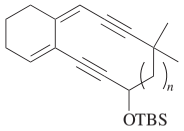


(47) 228

$C_{16–17}$



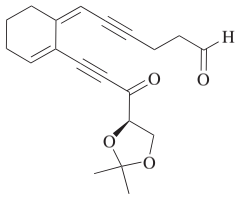
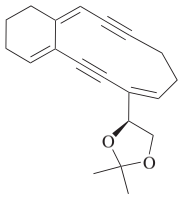
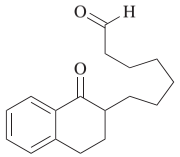
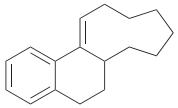
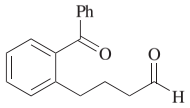
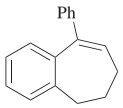
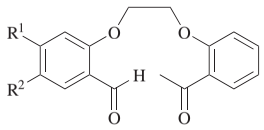
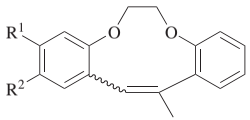
1. $TiCl_3(DME)_2$, Zn/Cu,
   DME, reflux, 3 h
2. rt, 14 h
3. rt, 1 h



n	
1	(41)
2	(18)

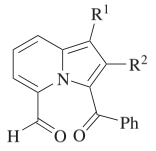
736

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

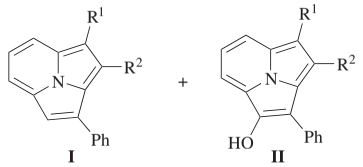
Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 5 h 2. 30–35°, 3 h 3. 30–35°, 1.5 h	 (>45)[a]	737, 228
	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 16 h 3. Reflux, 12 h	 (31.2)	738
 C_{17-19}	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 9 h 3. Reflux, 12 h	 (80)	61, 27
	1. $TiCl_4$, Zn, solvent, reflux, 2.5 h 2. rt 3. Reflux, time		

R^1	R^2	Solvent	Time (h)		$(E)/(Z)$	
H	H	THF	20	(25)	2:1	619
H	H	DME	16	(41)	45:55	618
Me	MeO	THF	1.5	(70)	1:3	619
Et	H	THF	1	(65)	1:4	618

$C_{17–18}$



1. $TiCl_4$, Zn, THF, reflux, 2 h
2. rt, 40 min
3. rt, 30 min

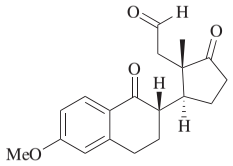


I **II**

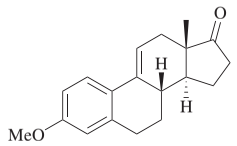
R^1	R^2	**I**	**II**
NC	H	(30)	(29)
MeO_2C	H	(38)	(41)
EtO_2C	EtO_2C	(20)	(55)

712

C_{18}

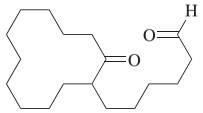


1. $TiCl_3$, Zn/Ag, DME, reflux, 2 h
2. Reflux
3. Reflux, 2 h

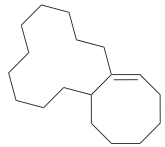


(56)[b]

257, 739
258, 740



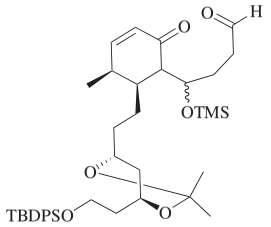
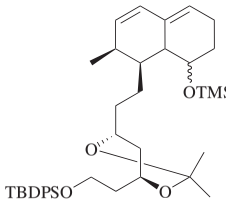
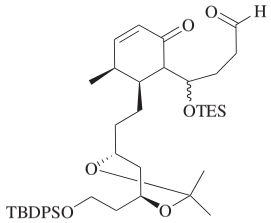
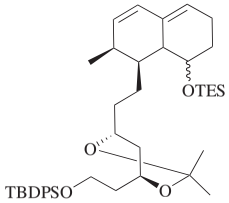
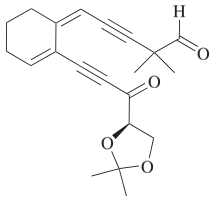
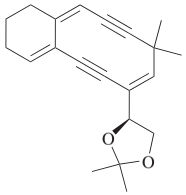
1. $TiCl_3$, Zn/Cu, DME, reflux, 4.6 h
2. Reflux, 25.5 h
3. Reflux, 5.8 h



(—)

741

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	$TiCl_4$, Na, naphthalene, THF	 (71)	84
	1. $TiCl_3$, C_8K, DME 2. 9 h 3. rt, 15 h; then reflux, 3 h	 (85)	251
	1. $TiCl_3(DME)_2$, Zn/Cu, DME, reflux, 5 h 2. 35°, 3 h	 (42)	742

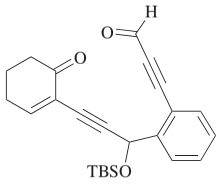
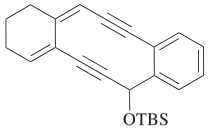
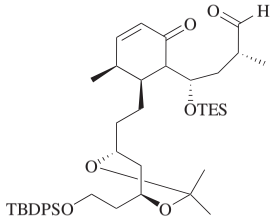
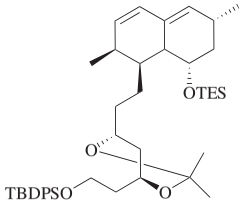
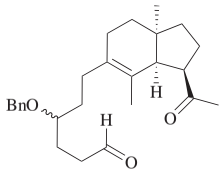
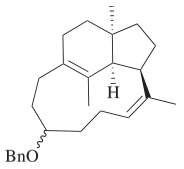
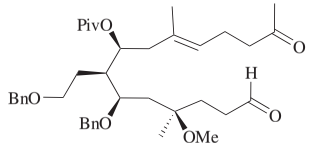
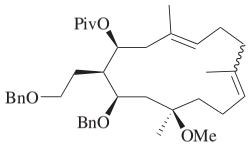
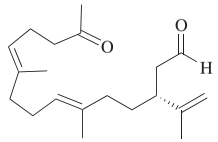
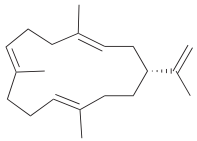
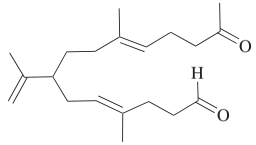
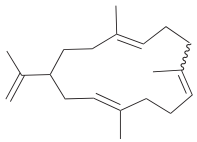
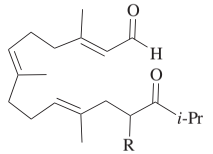
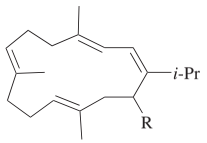
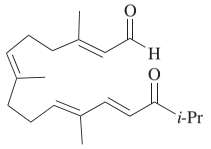
	1. $TiCl_3$, Zn/Cu, DME, reflux, 6 h 2. 30°, 4 h		(17)	742a
C_{19}				
	1. $TiCl_3$, C_8K, DME, reflux, 2 h 2. rt, 9 h 3. rt, 14 h; then reflux, 4 h		(86)[b]	75, 251
	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux 2. Reflux, "several hours"		(11)	269

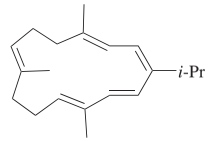
TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	$TiCl_3$, Zn/Cu, DME, reflux	 (65), (*E*)/(*Z*) = 4:3	286
C_{20}			
	1. $TiCl_4$, Zn, DME, reflux, 1.5 h 2. Reflux, 30 h 3. Reflux, 3 h	 (81)	278, 743
	1.$TiCl_3$, $AlCl_3$, Zn/Cu, DME, reflux, 3.5 h 2. Reflux, 30 h 3. Reflux, 6 h	 (82), (*E*)/(*Z*) >96:<4	273
	1. $TiCl_3/AlCl_3$, Zn/Cu, solvent, reflux, time 1 2. Reflux, time 2 3. Reflux, time 3		

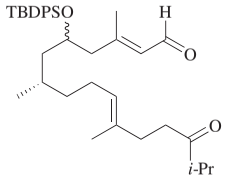
R	Solvent	Time 1 (h)	Time 2 (h)	Time 3 (h)		
H	DME	1.5	36	3	(40)	274
BnO	THF	3	28	5	(62)	285



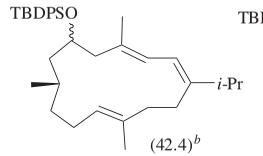
1. $TiCl_4$, Zn, py, solvent, reflux, 2 h
2. Reflux, time
3. Reflux, 3 h



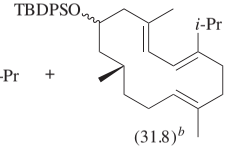
Solvent	Time (h)		
THF	17	(82)	275
DME	13	(72)	276



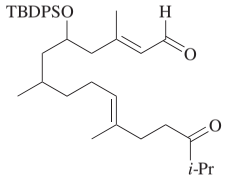
1. $TiCl_4$(DME), Zn, py, DME, reflux, 2.5 h
2. Reflux, 20 h
3. Reflux, 3 h



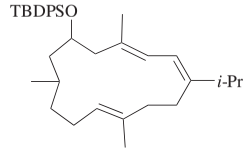
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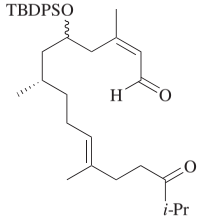
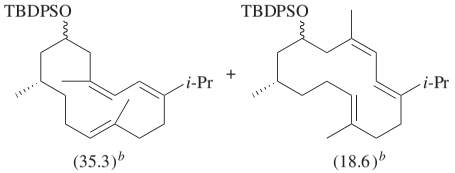
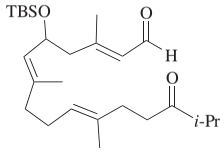
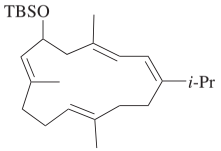
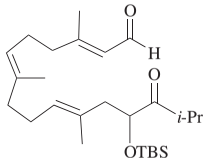
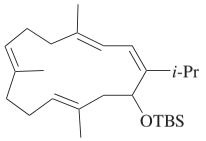
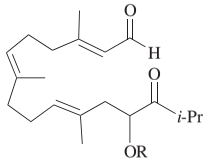
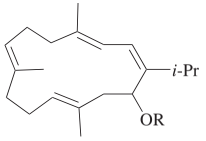


$TiCl_4$, Zn, py, DME, reflux, 30 h



(62) 287

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	1. $TiCl_4$(DME), Zn, py, DME, reflux, 2.5 h 2. Reflux, 20 h 3. Reflux, 3 h	 (35.3)[b] + (18.6)[b]	744
	1. $TiCl_4$(DME), Zn, py, DME, reflux, 2.5 h 2. Reflux, 24 h 3. Reflux, 3 h	 (66)	288, 745
	1. $TiCl_4$, Zn, py, THF 2. Reflux, 20 h	 (62)	284
	1. $TiCl_4$(THF), Zn, py, THF, reflux, 2.5 h 2. Reflux, 26 h 3. Reflux, 4 h	 R: TBS (78); TBDPS (78)	746, 280

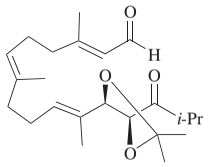
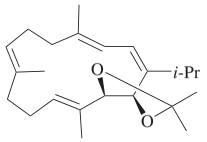
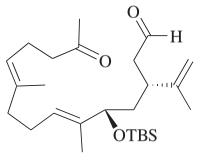
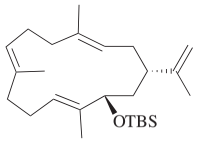
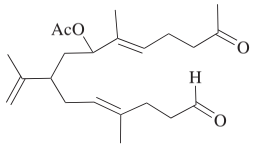
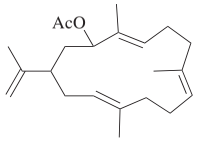
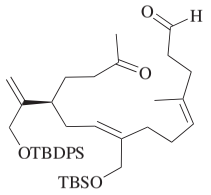
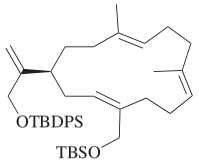
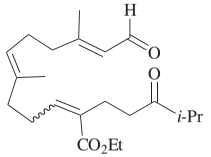
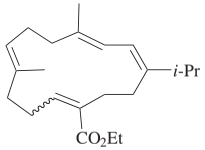
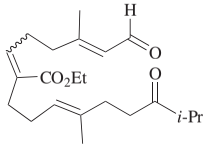
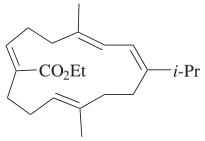
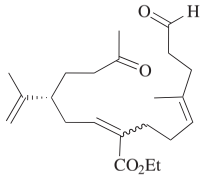
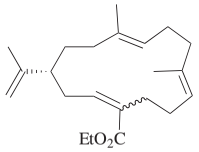
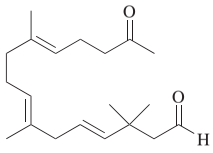
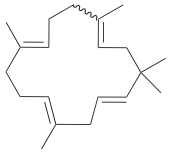
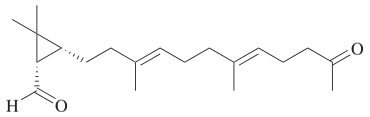
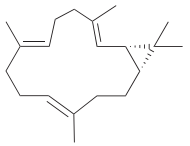
	1. $TiCl_4$, Zn, py, THF 2. Reflux, 20 h		(58)	284
	1. $TiCl_4$, Zn, py, DME, reflux, 2 h 2. Reflux, 8 h 3. Reflux, 2 h		(81)[b]	281, 283
	1. $TiCl_4$, Zn/Cu, THF, reflux, 2 h 2. Reflux, 30 h 3. Reflux, 3 h		(38)	282
	$TiCl_4$, Zn, py, DME, reflux		(69)[b]	289

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 6 h 3. Reflux, 2 h		(48), (*E*)/(*Z*) = 1:1	279, 747
	1. $TiCl_4$, Zn, THF, reflux, 2 h 2. Reflux, 6 h 3. Reflux, 2 h		(42)	747
	1. $TiCl_3$, Zn/Cu, DME, reflux, 2 h 2. Reflux, 6 h 3. Reflux, 2 h		(41)[b], (*E*)/(*Z*) = 1:2	277
	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 32 h 3. Reflux, 8 h		(79), (*E*)/(*Z*) = 2:1	290, 291

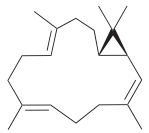


1. $TiCl_3$, Zn/Cu, DME, reflux, 4 h
2. Reflux, 38 h
3. Reflux, 3 h



I

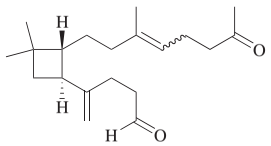
+



II

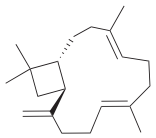
I + **II** (75)[b], **I**/**II** = 2:1

266

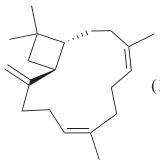


(*E*)/(*Z*) = 5:11

1. $TiCl_3$, Zn/Cu, DME, reflux, 17 h
2. Reflux, 4 d
3. Reflux, 4 h

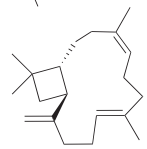


(16) +



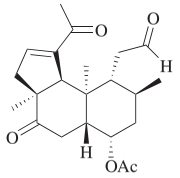
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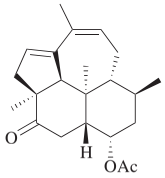


(19)

748



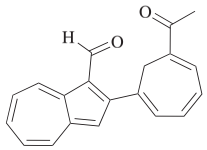
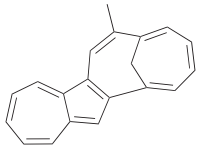
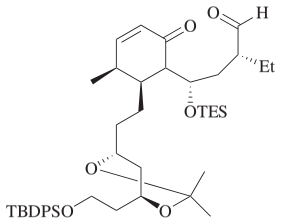
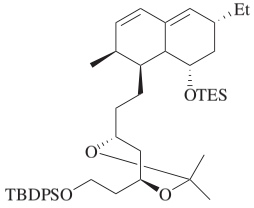
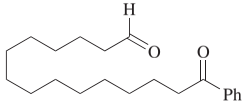
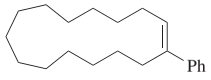
1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME, reflux, 4 h
2. Reflux, 12 h
3. Reflux, 2 h

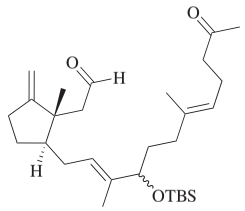
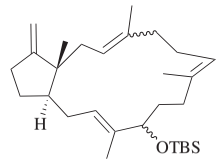
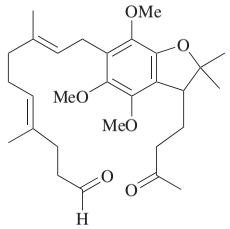
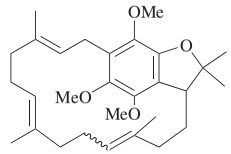


(32)

260

TABLE 3C. INTRAMOLECULAR COUPLING OF KETO ALDEHYDES (*Continued*)

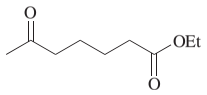
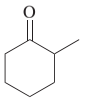
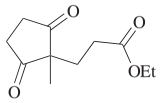
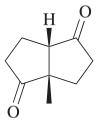
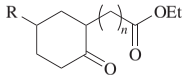
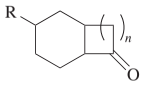
Keto Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	$TiCl_3$, $LiAlH_4$, DME, reflux, 8 h	 (3–5)	630
	1. $TiCl_3$, C_8K, DME, reflux, 2 h 2. rt, 9 h; then reflux, 5 h 3. rt, 5 h	 (89)[b]	749
C_{21}			
	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 9 h 3. Reflux, 12 h	 (80)	61, 27

C_{23}		1. $TiCl_3$, Zn/Cu, DME, 80° 2. 80°, 24 h		(54), (*E*)/(*Z*) = 64:36 292
C_{26}		1. $TiCl_3$, C_8K, DME, reflux, 2 h 2. Reflux, 20 h 3. Reflux, 3 h		(11) 293

[a] The product was isolated after acetonide deprotection.

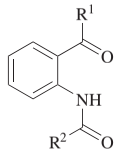
[b] Optically active starting material was employed.

TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS

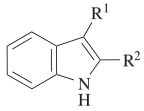
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 8 h 3. Reflux, 6 h	 (77)[a]	73, 74 79
C_9			
	$TiCl_3(DME)_{1.5}$, Zn/Cu, DME, heat	 (18)[a]	750
C_{9-18}			
	1. $TiCl_3$, $LiAlH_4$, Et_3N, DME, reflux, 1.5 h 2. Reflux, 24 h 3. Reflux, 3 h		63

R	*n*	
t-Bu	1	(57)[a]
H	2	(75)[a]
H	3	(80)[a]
H	4	(82)[a]
H	5	(52)[a]
H	7	(50)[a]
H	11	(54)[a]

C_{9-29}

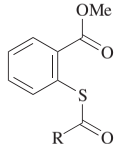


1. $TiCl_3$, C_8K, THF, reflux, 1.5 h
2. Reflux, time 1
3. Reflux, time 2

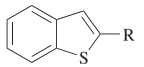


R^1	R^2	Time 1 (h)	Time 2 (h)		
Me	H	0	3	(69)	
Me	Me	8	0	(70)	79, 78
H	Ph	0	2	(90)	
Ph	H	8	0	(92)	
Me	Ph	8	0	(75)	
Ph	Me	8	0	(87)	
Ph	*t*-Bu	0	3	(84)	
Ph	2-C_4H_3S	0	2	(79)	
Ph	Ph	8	0	(90)	
Ph	*n*-$C_{15}H_{32}$	3	0	(92)	

C_{9-15}

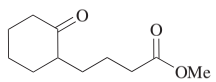
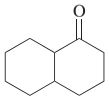
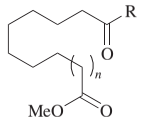
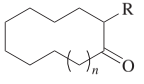
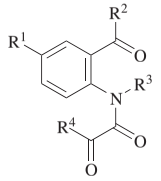
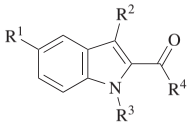


1. $TiCl_4$, Zn, $LiAlH_4$, CH_2Cl_2, rt, 1 h
2. rt
3. Reflux, time

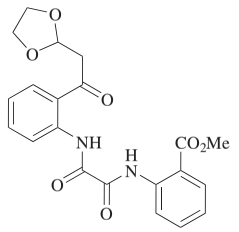


R	Time (h)			
Me	1	(70)		
2-C_4H_3O	0.25	(85)		133
2-C_4H_3S	5	(85)		
3-C_5H_4N	1	(60)		
Ph	2	(87)		
4-ClC_6H_4	0.25	(80)		
2,4-$Cl_2C_6H_3$	0.5	(80)		
2-$MeOC_6H_4$	2	(80)		
n-C_7H_{15}	4	(65)		
Bn	5	(85)		
4-MeC_6H_4	0.5	(75)		

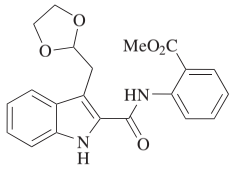
TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 8 h 3. Reflux, 6 h	 (91)[a]	73, 74 79
$C_{11–14}$ 	1. $TiCl_3$, $LiAlH_4$, Et_3N, DME, reflux, 1.5 h 2. Reflux, 24 h 3. Reflux, 3 h	 R n Me 1 (50)[a] Et 2 (45)[a] Et 3 (63)[a] Me 4 (60)[a]	63
$C_{11–15}$ 	Ti/graphite, DME, reflux, 0.5–1 h	 R^1 R^2 R^3 R^4 H Me H Me (60) Cl Ph H EtO (93) Cl Ph Me EtO (94)	80

C_{11}

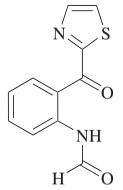


1. $TiCl_3$, C_8K, THF, reflux, 1.5 h
2. 0°
3. 0°, 21 h; then reflux, 5 h

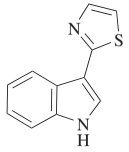


(—)

751



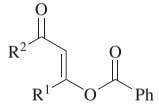
$TiCl_3$, Zn, DME, reflux, 20 min



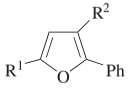
(71)

752, 471

$C_{12–22}$



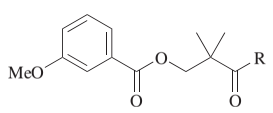
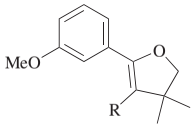
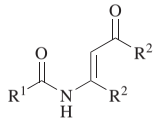
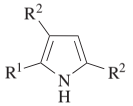
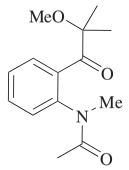
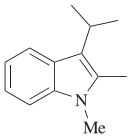
1. $TiCl_3$, C_8K, THF, reflux, 1.5 h
2. Reflux, 8 h



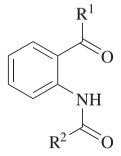
R^1	R^2	
Me	Me	(58)
Ph	Ph	(92)

79, 78

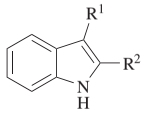
TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-16} 	—	 R: H (—); Me (—); *i*-Pr (—); *t*-Bu (—)	753
C_{12-26} 	$TiCl_3$, Zn, THF, reflux	 R^1 / R^2 / Time (h): Ph / Ph / 3 (78); *t*-Bu / Ph / 0.5 (60); *n*-C_3F_7 / Ph / 2 (54); 2-Np / Ph / 1 (77); Ph / Me / 3 (38)	754
C_{12} 	$TiCl_3$, Zn, DME, reflux, 1 h	 (54)	755

$C_{13–23}$

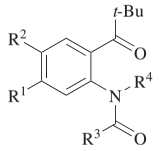


$TiCl_3$, Zn, DME, reflux

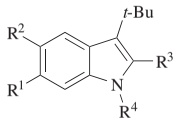


R^1	R^2	Time (h)		
EtO_2C	*t*-Bu	2	(58)	
c-C_3H_5	Ph	96	(78)	751
2-C_4H_3N	Ph	4	(58)	
	Ph	15	(57)	
n-C_9H_{19}	Ph	72	(73)	
Ph	Ph—≡—	0.8	(77)	

$C_{13–19}$

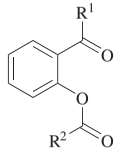


$TiCl_3$, Zn, DME,
reflux, 1 h

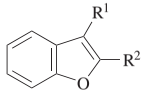


R^1	R^2	R^3	R^4		
H	Cl	Me	Me	(77)	
MeO_2C	H	Ph	Me	(81)	755
H	H	Ph	Me	(82)	
H	H	Me	Bn	(68)	

$C_{14–20}$

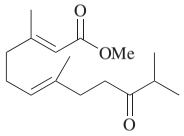
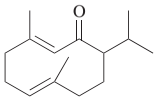
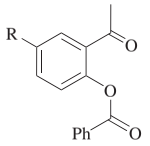
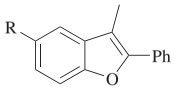
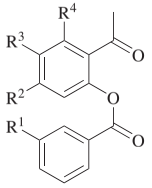
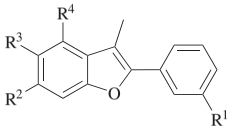
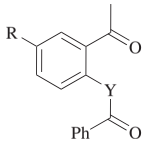
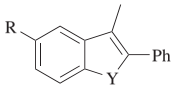


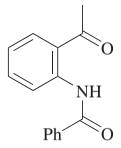
1. $TiCl_3$, C_8K, THF,
reflux, 1.5 h
2. Reflux, 8 h



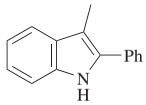
R^1	R^2		
H	Ph	(89)	
Ph	Me	(85)	78, 79
Me	Ph	(80)	
Ph	Ph	(88)	

TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	1. $TiCl_4$, $LiAlH_4$, Et_3N, DME, reflux, 2 h 2. Reflux, 20 h 3. Reflux, 4 h	 (62)	756, 322
	1. $TiCl_3$, Li, THF, reflux, 3 h; then I_2, 5 min 2. rt 3. rt, 8 h		R: H (62); MeO (55)	115
	$TiCl_4$, Zn, dioxane, reflux, 6 h		R^1 / R^2 / R^3 / R^4: H H H H (55); MeO H H H (60); H MeO H H (58); H H MeO H (56); H H H MeO (45); H H MeO MeO (24)	757
	1. $TiCl_3$, Li, naphthalene, THF, reflux, 3 h 2. rt 3. rt, 14 h		R / Y: H O (55); MeO O (52); H HN (60)	67

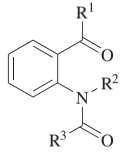


1. Ti powder, $(i\text{-PrO})_3TiCl$, TMSCl, DME, reflux, 68 h
2. Addition in one lot, reflux
3. Reflux, 2.5 h

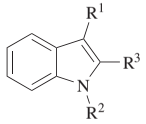


(97) 83

C_{15-18}



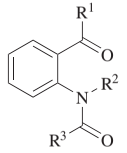
1. $TiCl_3$, C_8K, reflux, DME, 1.5 h
2. Addition in one lot, reflux
3. Reflux, time



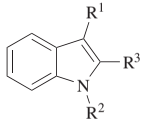
R^1	R^2	R^3	Time (h)	
Me	H	Ph	—	(75)
Me	Me	Ph	0.5	(92)
t-Bu	Me	Ph	3	(62)
t-Bu	Me	*i*-Pr	22	(36)
t-Bu	Me	*t*-Bu	1	(35)

7

C_{15-21}



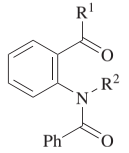
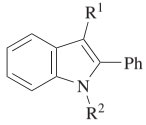
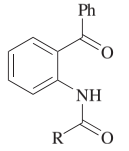
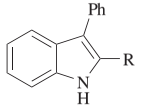
$TiCl_3$, Zn, DME, reflux

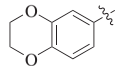


R^1	R^2	R^3	Time (h)	
Me	H	Ph	0.75	(76)
n-Bu	Me	Ph	4	(70)
t-Bu	H	Ph	69	(86)
t-Bu	Me	Ph	4	(75)
t-Bu	Me	mesityl	67	(88)
Bn	H	Ph	22	(88)
Bn	H	*t*-Bu	92	(95)

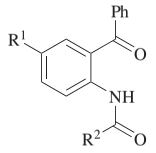
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TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

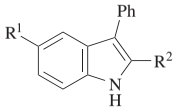
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{15–18}$ 	$TiCl_3$ (8 mol %), Zn, $Me_2ClSi(CH_2)_3CN$, DME, reflux, 30 min	 R^1 R^2 Me H (82); Bu Me (67)	83
$C_{15–29}$ 	$TiCl_3$, Zn, reflux		7

R	Solvent	Time (h)	
Ph	DME	1.5	(98)
n-$C_{15}H_{31}$	DME	1.25	(93)
$H_2C{=}CH(CH_2)_8$	THF	2	(85)
$ClCH_2(CH_2)_3$	THF	2	(86)
CF_3	THF	4	(82)
$HO_2C(CH_2)_2$	THF	1.5	(51)
c-C_3H_5	THF	3	(84)
2-BrC_6H_4	DME	5	(88)
2-IC_6H_4	THF	2.5	(85)
2-C_4H_3O	THF	7	(78)
2-Py	DME	1	(63)
2-benzofuranyl	THF	3	(94)
t-Bu	DME	2	(97)
	THF	4	(99)

C_{15-20}



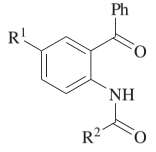
1. $TiCl_3$, Na/Al_2O_3, THF, reflux, 1 h
2. Reflux, 2 h
3. Reflux, 1 h



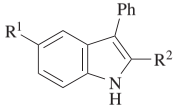
R^1	R^2	
H	Ph	(75)
Cl	EtO_2C	(72)

69

C_{15-29}



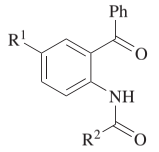
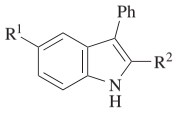
$TiCl_3$ (10 mol %), Zn, TMSCl, MeCN, reflux, 30 min



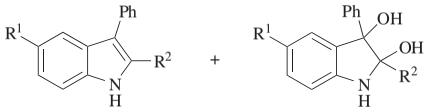
R^1	R^2	
H	Ph	(80)
H	CF_3	(88)
H	n-C_3F_7	(73)
Cl	EtO_2C	(79)
H	n-$C_{15}H_{31}$	(77)
H		(69)

83

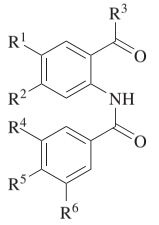
TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15-21} 	1. $TiCl_4$, Sm, THF, reflux, 2h 2. rt 3. Reflux, 1 h		758a

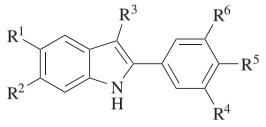
R^1	R^2	
H	Ph	(89)
H	4-MeC_6H_4	(91)
H	4-FC_6H_4	(94)
H	Me	(83)
H	Et	(81)
Cl	Ph	(90)
Cl	4-MeC_6H_4	(86)
Cl	4-ClC_6H_4	(83)
Cl	4-FC_6H_4	(88)
Cl	Me	(78)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI_2, THF, 65°	 **I** + **II**	758

R^1	R^2	Time (min)	**I**	**II**
H	Ph	30	(85)	(0)
H	4-MeC_6H_4	30	(84)	(0)
H	4-ClC_6H_4	50	(88)	(0)
Cl	Ph	30	(88)	(0)
Cl	4-MeC_6H_4	30	(84)	(0)
Cl	4-ClC_6H_4	40	(87)	(0)
Cl	4-FC_6H_4	50	(85)	(0)
H	Et	60	(40)	(32)
H	Me	60	(38)	(35)
Cl	Et	60	(43)	(32)
Cl	Me	60	(43)	(30)



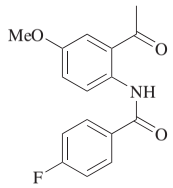
1. $TiCl_3$, C_8K, DME, reflux, 1.5 h
2. Reflux
3. Reflux, time



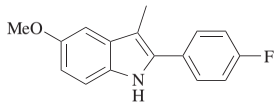
R^1	R^2	R^3	R^4	R^5	R^6	Time (h)	
MeO	MeO	Me	H	MeO	H	~2	(66)
H	Me	Ph	H	MeO	H	8	(79)
MeO	MeO	Me	MeO	H	MeO	0.5	(86)

82

C_{15}



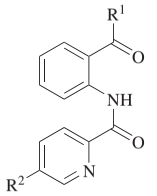
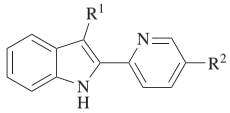
1. $TiCl_3$, C_8K, DME, heat, 1.5 h
2. Heat
3. Heat, 1 h



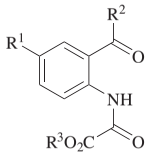
(96)

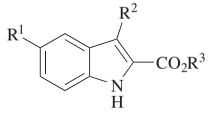
82

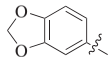
TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15-17} 	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, time 1 3. Reflux, time 2		

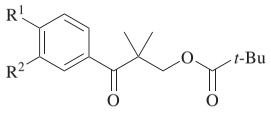
R^1	R^2	Time 1 (h)	Time 2 (h)		
$MeO(CH_2)_2$	H	3	1	(62)	752
$MeO(CH_2)_2$	Et	3	1	(52)	752
	H	3.5	3	(57)	751

C_{15} 

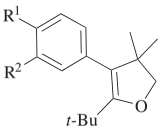
$TiCl_3$, Zn, DME, reflux 

R^1	R^2	R^3	Time		
Cl	Ph	Et	2 h	(78–81)	471
H		Me	80 min	(73–85)	751

C_{16}

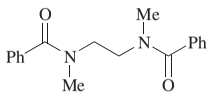


1. $TiCl_3$, $LiAlH_4$, Et_3N, THF, reflux, 30 min
2. Reflux, 1 h
3. Reflux, 1 h

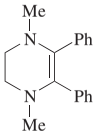


R^1	R^2	
H	MeO	(75.4)
MeO	H	(79.0)

759



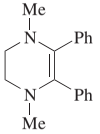
Sm, SmI_2, THF, 67°, 2–4 h



(62)

105, 760

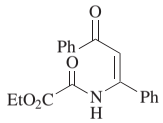
1. Yb, ICH_2CH_2I, THF, 67°, 1 h
2. 67°, 4 h



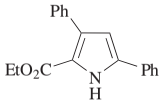
(23)

108

C_{17}



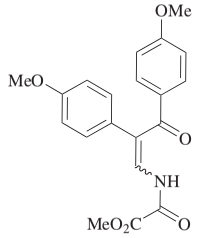
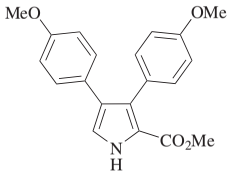
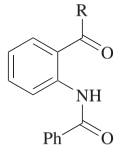
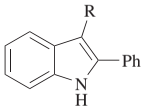
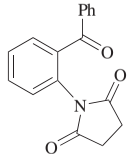
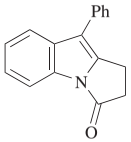
1. $TiCl_3$, C_8K, DME, reflux, 1.5 h
2. Reflux
3. Reflux, 15 min



(60)

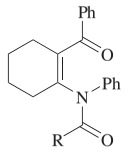
754

TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

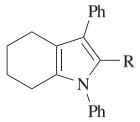
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	1. $TiCl_3$, C_8K, DME, reflux, 1.5 h 2. Reflux, 2.5 h 3. Reflux, 15 min	 (52)	754
C_{17-18} 	1. $TiCl_3$, C_8K, DME, reflux, 1.5 h 2. Reflux 3. Reflux, time		751
C_{17} 	1. $TiCl_3$, C_8K, THF, reflux, 1.5 h 2. Reflux, 3 h	 (61)	79

R	Time (h)	
c-C_3H_5	48	(70)
2-C_4H_3N	1	(92)

$C_{18–20}$



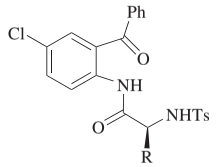
$TiCl_3$, Zn, THF, reflux



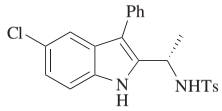
R	Time (min)	
Ph	15	(85)
t-Bu	30	(58)

754

$C_{18–22}$



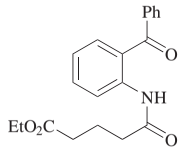
$TiCl_3$, Zn, TMSCl, MeCN



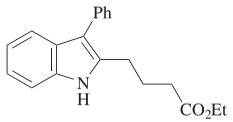
R	
i-Pr	(46)
Bn	(48)

761

C_{18}

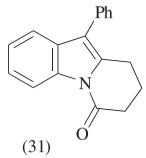


1. $TiCl_3$, C_8K, THF, reflux, 1.5 h
2. Reflux, 8 h



(63)

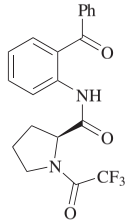
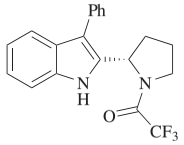
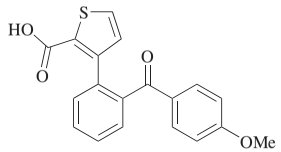
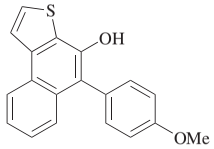
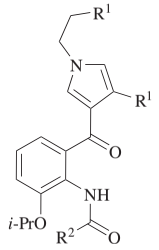
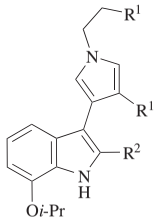
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(31)

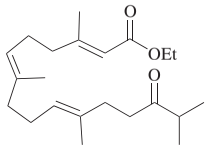
79

TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

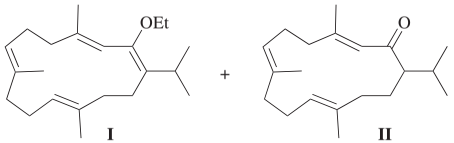
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	$TiCl_3$, Zn, THF, reflux, 1 h	 (90)	7
	$TiCl_3$, Zn, DME, reflux	 (85)	137
$C_{19–26}$  $R^1 = 4\text{-}MeOC_6H_4$	$TiCl_3$, C_8K, DME, reflux		137

R^2	
Me	(77)
$4\text{-}MeOC_6H_4$	(89)
$4\text{-}MeOC_6H_4(CH_2)_2$	(20)
$4\text{-}MeOC_6H_4CH{=}CH$	(73)

C_{20}

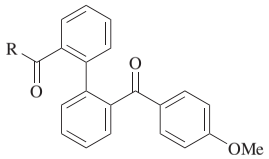


1. $TiCl_3$, $LiAlH_4$, DME
2. Et_3N, reflux, 24 h

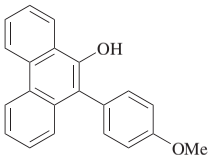


I + **II** (81), **I/II** = 4:1

762

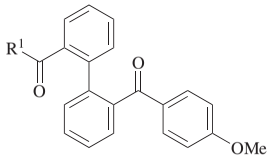


1. $TiCl_3$, C_8K, DME, reflux, 1.5 h
2. Reflux
3. Reflux

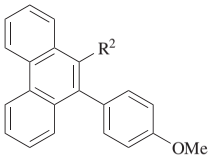


R		
HO	(89)	
F	(85)	

137

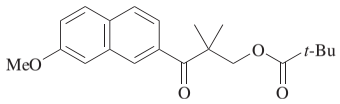


$TiCl_3$, Zn, DME, reflux

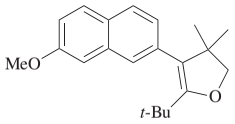


R^1	R^2	
HO	HO	(86)
F	HO	(90)
H_2N	H_2N	(58)

137



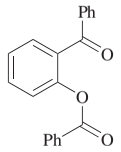
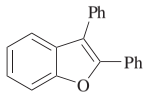
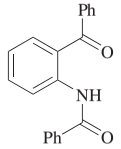
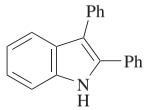
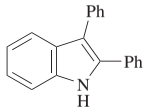
1. $TiCl_3$, $LiAlH_4$, Et_3N, THF, reflux, 30 min
2. Reflux, 1 h
3. Reflux, 1 h



(66.3)

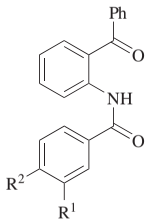
759

TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

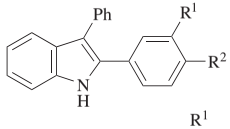
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	$TiCl_3$, Zn, DME, reflux, 1 h	 (76)	7
	Ti powder, TMSCl, DME, reflux, 19 h	 (92)	83
	See table.		7

	Solvent	Temp	Time (h)	
SmI_2	THF	rt	1	(31)
$NbCl_3$(DME)	DME	reflux	21	(77)
$NbCl_5$, Zn	THF	reflux	3	(79)
WCl_4, BuLi	THF	reflux	26	(97)
Mg-graphite	—	reflux	4	(27)
VCl_3, Zn	THF	reflux	20	(55)
$ZrCl_4$, Zn	DME	reflux	1.5	(39)

C_{20-21}



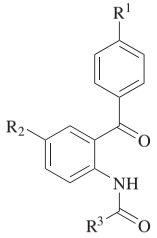
1. $TiCl_3$, C_8K, THF, reflux, 1.5 h
2. Reflux, time 1
3. Reflux, time 2



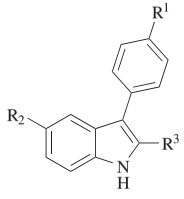
79

R^1	R^2	Time 1 (h)	Time 2 (h)	
F	H	8	0	(94)
H	Cl	8	0	(86)
Br	H	8	0	(81)
H	I	0	1	(80)
MeO	H	3	0	(86)
H	CF_3	8	0	(83)
H	NC	3	0	(76)

C_{20}

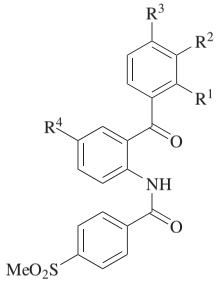
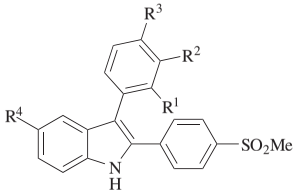


$TiCl_4$, Zn, THF, reflux

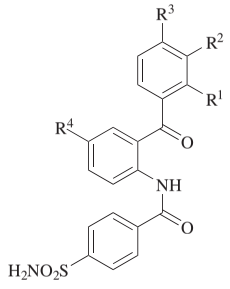


R^1	R^2	R^3		
H	F	4-$H_2NO_2SC_6H_4$	(76.9)	
H	Cl	4-$H_2NO_2SC_6H_4$	(72.3)	
H	Cl	4-$MeO_2SC_6H_4$	(75.4)	763
MeO_2S	Cl	2-FC_6H_4	(78.1)	
MeO_2S	Cl	Ph	(82.4)	
MeO_2S	Cl	4-ClC_6H_4	(77.1)	

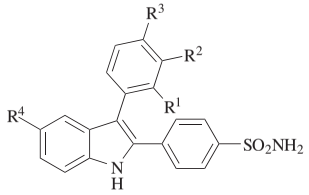
TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20-22} 	$TiCl_4$, Zn, THF, reflux, 1.5 h	 (—)	764

R^1	R^2	R^3	R^4
H	H	H	H
H	H	F	H
H	H	Cl	H
H	H	Br	H
H	H	MeO	H
H	H	Me	H
H	Me	Me	H
H	H	Cl	Cl
H	Cl	H	Cl
Cl	H	H	Cl
H	H	H	F
H	H	H	Cl
H	H	H	Br
H	H	H	Me



$TiCl_4$, Zn, THF,
reflux, 1.5 h

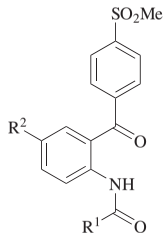
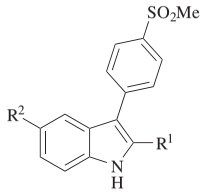


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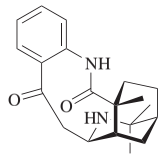
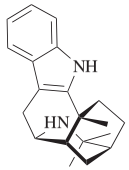
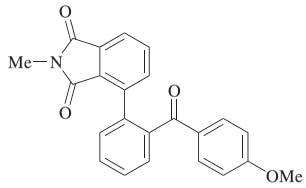
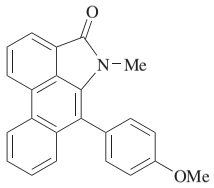
764

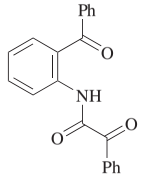
R^1	R^2	R^3	R^4
H	H	H	H
H	H	F	H
H	H	Cl	H
H	H	Br	H
H	H	MeO	H
H	H	Me	H
H	Me	Me	H
H	H	Cl	Cl
H	Cl	H	Cl
Cl	H	H	Cl
H	H	H	F
H	H	H	Cl
H	H	H	Br
H	H	H	Me

TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

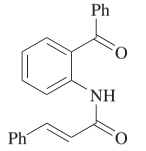
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20-21} 	$TiCl_4$, Zn, THF, reflux, 1.5 h	 (—)	765

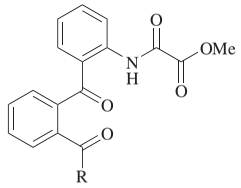
R^1	R^2
Ph	Cl
2-FC_6H_4	Cl
4-ClC_6H_4	Cl
4-MeC_6H_4	Cl
4-$MeOC_6H_4$	Cl
2-$MeO_2CC_6H_4$	Cl
4-$MeO_2CC_6H_4$	Cl
4-$MeO_2SC_6H_4$	Cl
4-$MeO_2SC_6H_4$	Me

C_{20} 	$TiCl_3$, Zn, THF, reflux, 4 h	 (75)[b]	7
C_{21} 	$TiCl_3$, C_8K, DME, reflux	 (86)	137

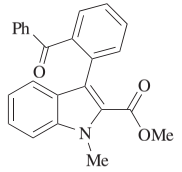


C_{22}

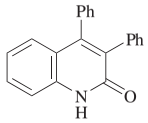




R = 4-$MeOC_6H_4$

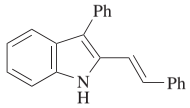


1. Ti powder, TMSCl, DME, reflux, 67 h
2. Addition in one lot, reflux
3. Reflux, 2.5 h



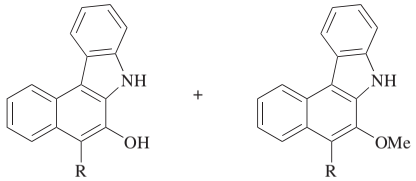
(73) 83

1. $TiCl_3$, C_8K, THF, reflux, 1.5 h
2. Reflux, 8 h



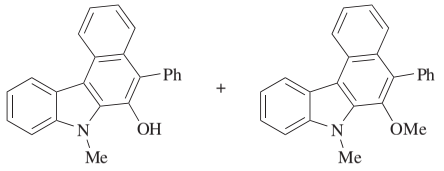
(68) 79

$TiCl_3$, C_8K, DME, reflux, 40 min



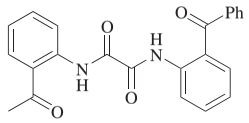
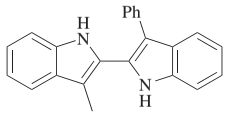
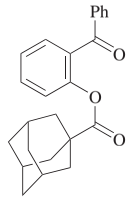
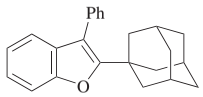
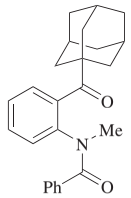
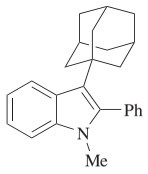
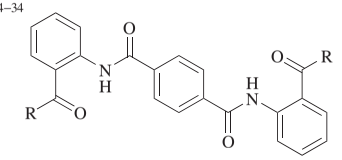
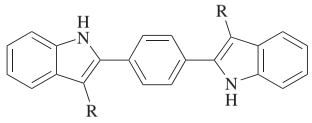
I **I** + **II** (54), **I**/**II** = 9:1 **II** 137

$TiCl_3$, C_8K, py, DME, reflux

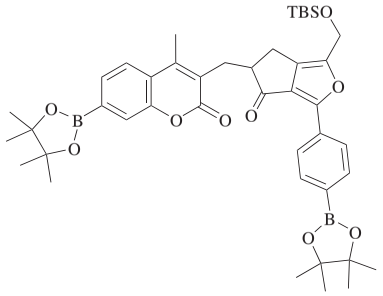


I **I** + **II** (89), **I**/**II** = 5:1 **II** 137

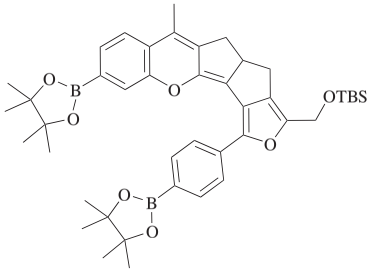
TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23} 	$TiCl_4$, Zn, DME, reflux, 20 h	 (76)	766
C_{24} 	Ti powder, TMSCl, DME, reflux, 16 h	 (91)	83
	$TiCl_3$, Zn, DME, reflux, 1 h	 (79)	755
C_{24-34} 	$TiCl_4$, Zn, DME, reflux	 R Time (h): Me 23 (77); Ph 2 (88)	766

C_{25}

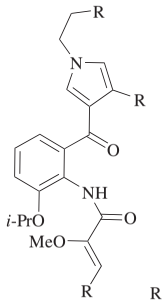


$TiCl_3$, $LiAlH_4$



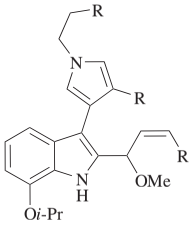
(—) 767

C_{34}



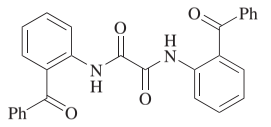
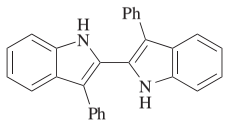
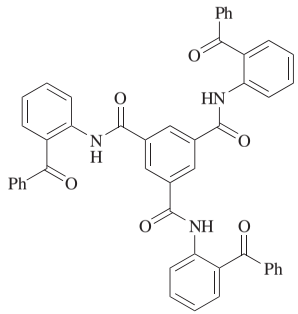
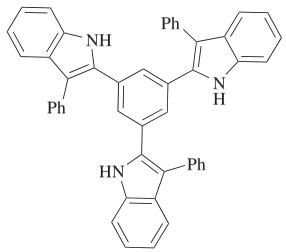
$R = 4\text{-}MeOC_6H_4$

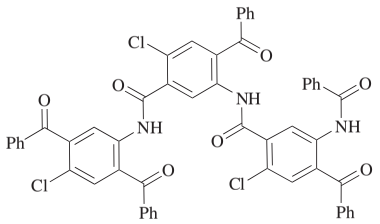
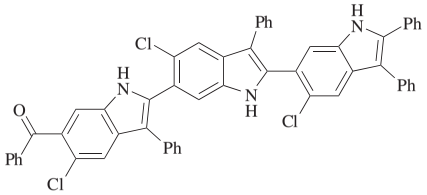
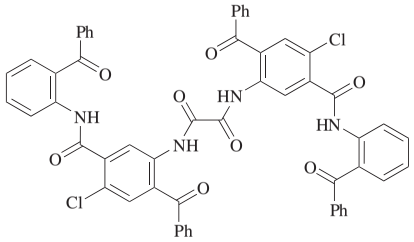
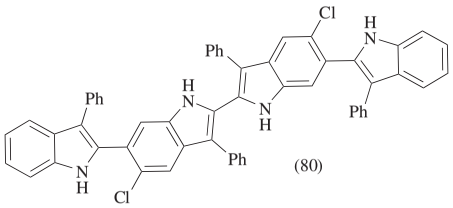
1. $TiCl_3$, C_8K, DME, reflux, 1.5 h
2. Py, reflux, 15 min
3. Reflux, 1.5 h



(71–93) 768, 769

TABLE 3D. INTRAMOLECULAR COUPLING OF OXO ESTERS, OXO AMIDES, AND RELATED COMPOUNDS (*Continued*)

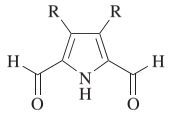
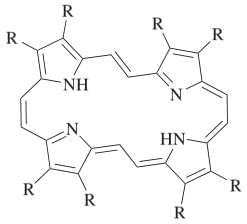
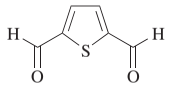
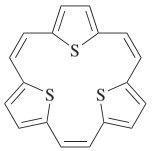
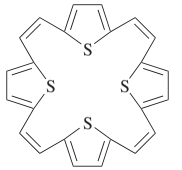
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28} 	$TiCl_3$, M 		
		M Solvent Temp Time (h) Zn DME reflux 3 (81)	766, 471
		C_8K THF — 3.5 (65)	766
C_{48} 	$TiCl_4$, Zn, DME, reflux, 2 h 	(95)	766

C_{55}		$TiCl_4$, Zn, DME, reflux, 1.5 h		(86) 766
C_{56}		$TiCl_4$, Zn, DME, reflux, 2.5 h	 (80)	766

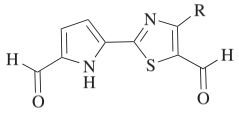
[a] The product was isolated after acid hydrolysis.

[b] Optically active starting material was employed.

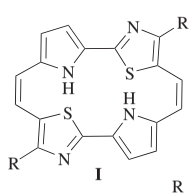
TABLE 4A. TANDEM HOMOCOUPLING

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-10} 	$TiCl_4$, Zn/Cu, THF	 R: H (0.1–0.2); Et (1)	770
C_6 	1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 1 h 2. Py, reflux 3. Reflux, 18 h	 (38) +  (4.7)	149

C_{9-15}

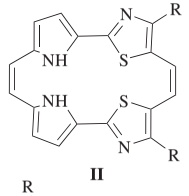


1. $TiCl_4$, Zn/Cu, py, THF, reflux, 2 h
2. Reflux, 60 h
3. Reflux, 5 h



I

+

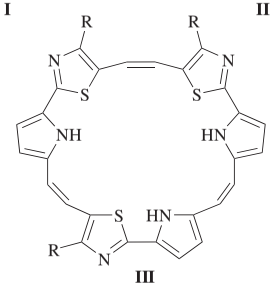


II

771

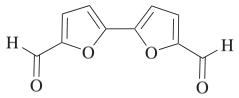
R	**I**	**II**	**III**
H	(7)	(0)	(0)
t-Bu	(18)	(3)	(5)
Ph	(14)	(2)	(—)

+

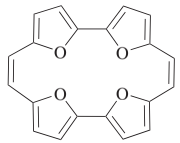


III

C_{10}



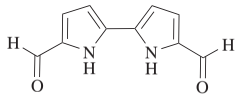
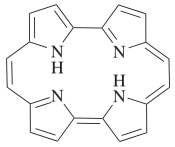
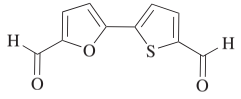
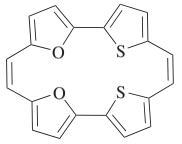
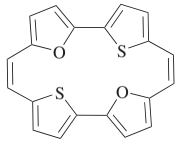
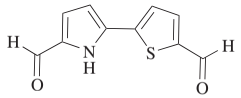
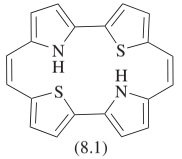
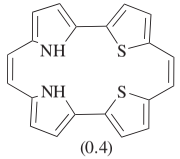
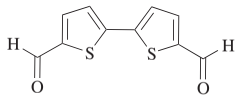
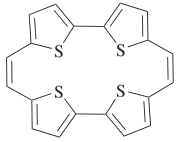
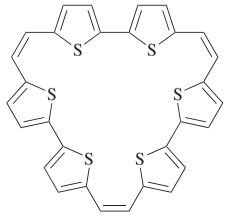
$TiCl_4$, Zn

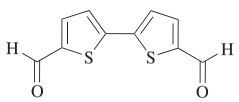


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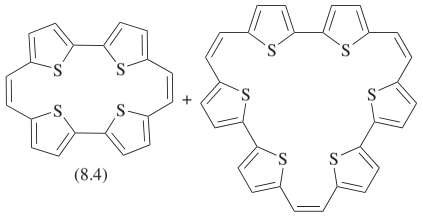
772

TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. $TiCl_4$, Zn, py, THF 2. Reflux 3. Reflux, 4 h	 (2–3)[a]	773
	$TiCl_4$, Zn, py, THF, reflux, 2.5 h	 (7.2) +  (2.6)	151
	1. $TiCl_4$, Zn, py, THF 2. Slow addition, reflux 3. Reflux, 1 h	 (8.1) +  (0.4)	774
	1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 1 h 2. Dropwise addition, py, reflux 3. Reflux, 18 h	 (10.5) +  (13.6)	149

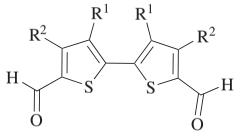


1. $TiCl_4$, Zn/Cu, py, THF
2. Reflux, 13 h
3. Reflux, 1 h

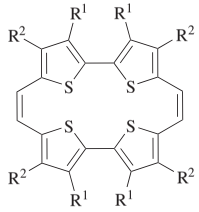


(8.4) + (2.9)

775



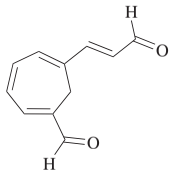
1. $TiCl_4$, Zn/Cu, THF, reflux, 2 h
2. Reflux, 42 h
3. Reflux, 30 h



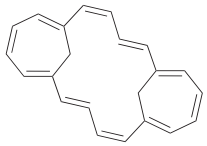
R^1	R^2	
H	Br	(26)
Br	H	(8.8)

776

C_{11}



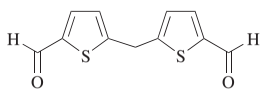
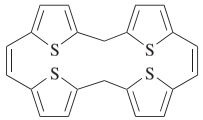
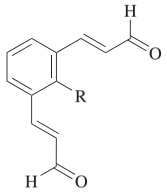
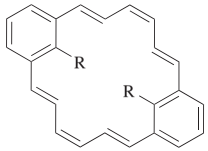
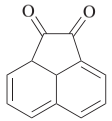
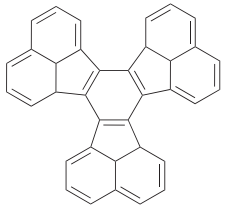
1. $TiCl_3$, $LiAlH_4$, DME, reflux, 30 min
2. Dropwise addition, reflux
3. Reflux, 6 h

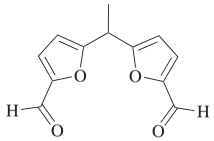


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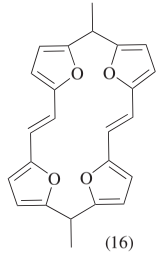
226

TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 1 h 2. Py, reflux, 30 min 3. Reflux, 18 h	 (75)	777, 149
$C_{12–13}$ 	1. $TiCl_4$, Zn, py, dioxane, reflux, 2.5 h 2. Reflux, 5 h 3. Reflux, 1 h	 R: H (11), Me (18)	778
C_{12} 	Bis(η^6-biphenyl)Ti(0), toluene, reflux, 2h	 (12–15)	779

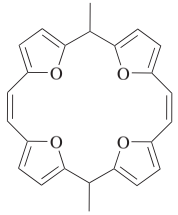


1. $TiCl_4$, Zn/Cu, THF, reflux, 1 h
2. Reflux, 60 h
3. Reflux, 2 h



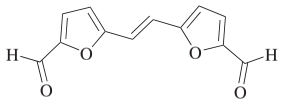
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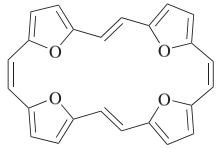


(10)

780



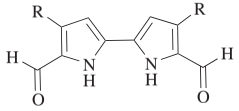
$TiCl_4$, Zn/Cu, THF



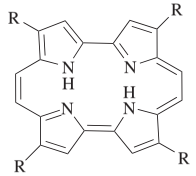
(7)

781

$C_{12–16}$



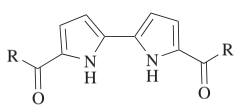
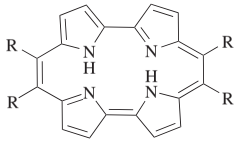
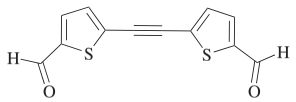
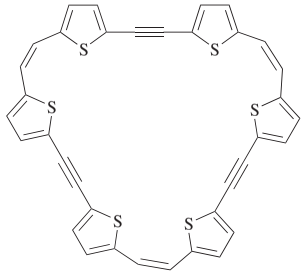
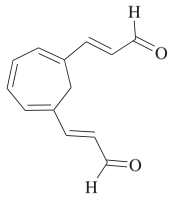
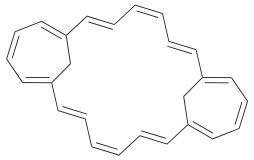
1. $TiCl_4$, Zn, py, THF
2. Reflux
3. Reflux, 30 min



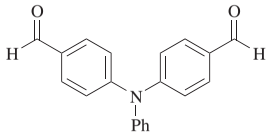
R	
Me	(2)
Et	(4)
Pr	(10)

782

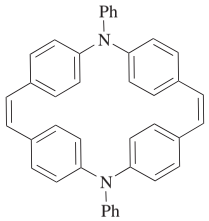
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-16} 	1. $TiCl_4$, Zn, py, THF 2. Addition in one lot 3. Reflux, 3 h	 R: Me (2.5); Et (5); Pr (7)	783
C_{12} 	1. $TiCl_3(DME)_{1.5}$, Zn/Cu, DME 2. rt, 12 h 3. Reflux, 6 h	 (10–15)	784
C_{13} 	1. $TiCl_3$, $LiAlH_4$, DME, reflux, 30 min 2. Reflux, 6 h 3. Reflux, 6 h	 (4.8)	226

C_{14}

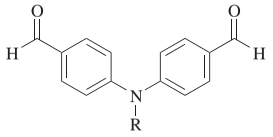


1. $TiCl_4$, Zn, CH_2Cl_2, reflux, 1 h
2. Dropwise addition, py, reflux
3. Reflux, 8 h



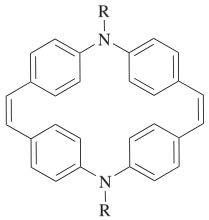
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785



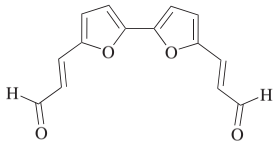
R = 4-BuC_6H_4

$TiCl_4$, Zn, py, THF, reflux, 8 h

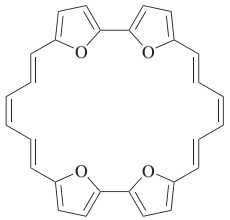


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786



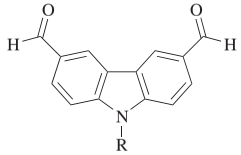
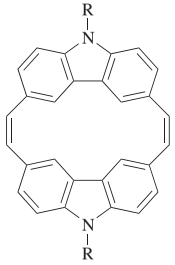
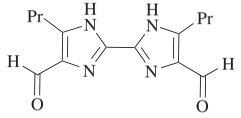
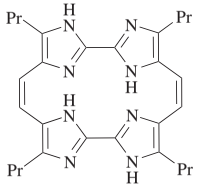
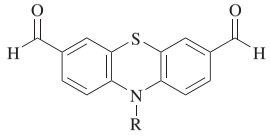
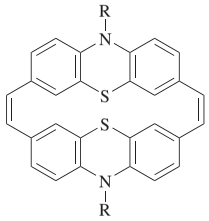
1. $TiCl_4$, Zn/Cu, py, THF, reflux, 1 h
2. Reflux, 24 h
3. Reflux, 6 h

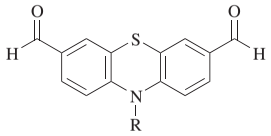


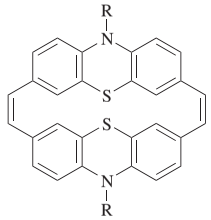
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787

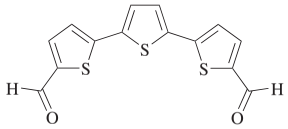
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 1 h 2. Dropwise addition, py, reflux 3. Reflux, 10 h	 R: Bu (8.1); Ph (5.6)	377
	1. $TiCl_4$, Zn, py, THF, reflux, 3 h 2. Addition in one lot, reflux 3. Reflux, 4 h	 (2)	788
	$TiCl_4$, Zn	 R: Solvent, Temp, Time allyl: dioxane, heat, 2–3 d (84) $(CH_2)_4$: dioxane, heat, 2–3 d (49)	789 789

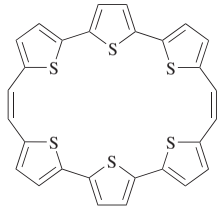




R	Additive	Solvent	Temp	Time		
n-C_6H_{13}	—	dioxane	heat	2–3 d	(78)	789
Bn	—	dioxane	heat	2–3 d	(54)	789
n-C_7H_{15}	py	THF	reflux	12 h	(26)	790

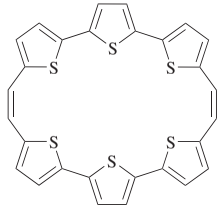


1. $TiCl_4$, Zn, THF/CH_2Cl_2,
   reflux, 1 h
2. Py, reflux
3. Reflux, 18 h



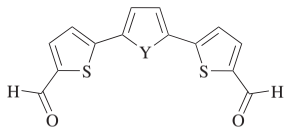
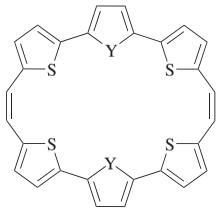
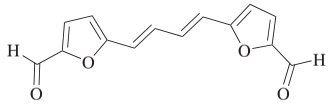
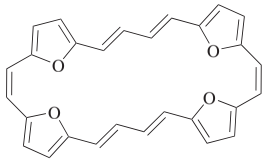
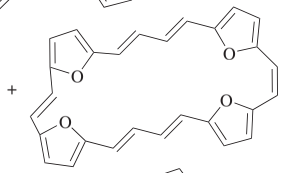
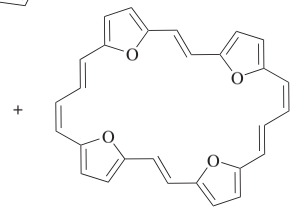
(64) 149

$TiCl_3$, $LiAlH_4$, THF ,
reflux, 12 h

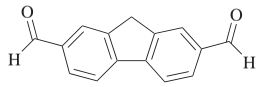


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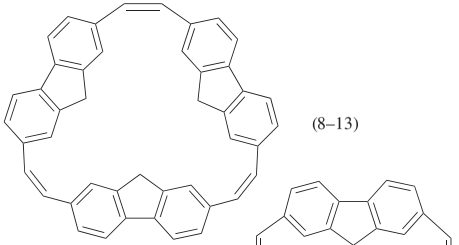
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	$TiCl_4$, Zn, py, THF	 Y: S (64); MeN (>69); *n*-$C_{12}H_{25}N$ (>69)	791
	1. $TiCl_4$, Zn/Cu, THF, reflux, 3 h 2. Reflux, 36 h 3. Reflux, 4 h	 (—) +  (—) +  (—)	792

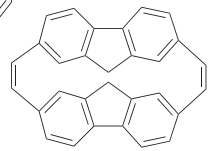
C_{15}



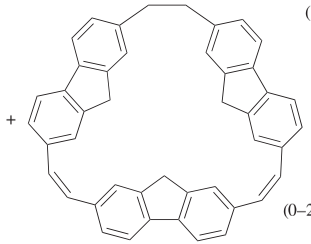
1. $TiCl_4$, Zn, CuI, DME, reflux, 4 h
2. 0°, 2 h
3. rt, overnight; then reflux, 6 h



(8–13)



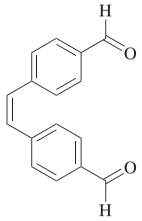
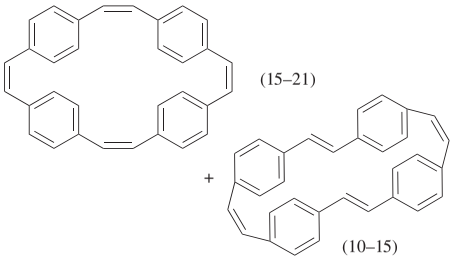
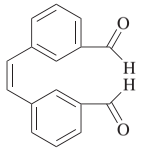
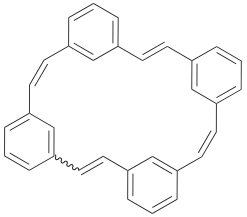
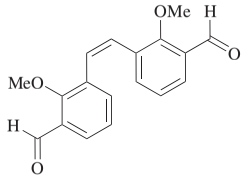
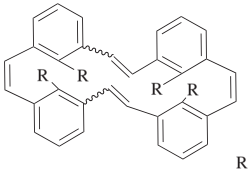
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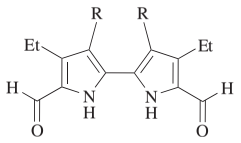
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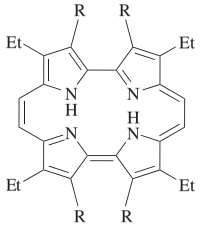
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	1. $TiCl_3(DME)_{1.5}$ or $TiCl_4$, Zn/Cu, DME 2. rt, 1 h 3. Reflux, 4–6 h	 (15–21) + (10–15)	794
	$TiCl_4$, Zn, DME	 (20–50)	795
	$TiCl_4$, Zn, THF	 (26) R = MeO	796

$C_{16–18}$

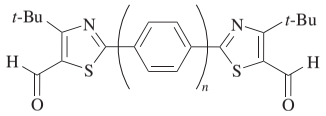


1. $TiCl_4$, Zn, CuCl, THF, reflux, time 1
2. Reflux, 15 min
3. Reflux, time 2

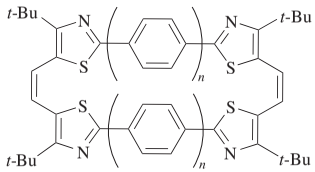


R	Time 1 (h)	Time 2 (min)		
Me	2	2	(16)	797, 798
Et	3	3	(15)	798

$C_{16–22}$



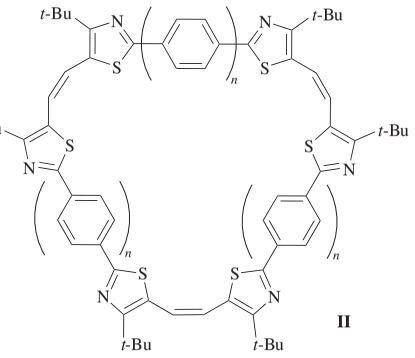
1. $TiCl_4$, Zn/Cu, py, THF, reflux, 2 h
2. Reflux, 60 h
3. Reflux, 5 h



n	**I**	**II**	
0	(6.4)	(9.8)	799
1	(9.8)	(21.8)	

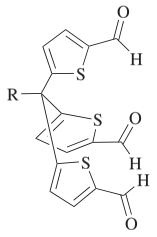
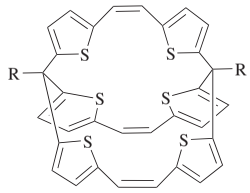
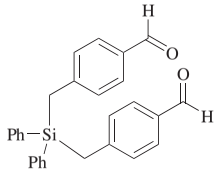
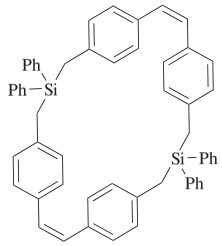
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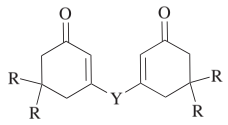


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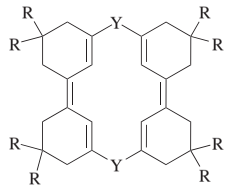
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{16–22}$ 	$TiCl_4$, Zn/CuI, DME, rt, overnight; then reflux, 24 h	 R: H (2–4) [800]; Me (8) [801]; *n*-C_6H_{13} (7) [801]	
C_{16} 	1. $TiCl_4$, Zn, DME, reflux, 1 h 2. Dropwise addition, rt 3. Reflux, 20 h	 (1.1)	356

$C_{18–26}$



$TiCl_4$, Zn, dioxane



448

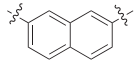
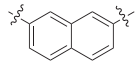
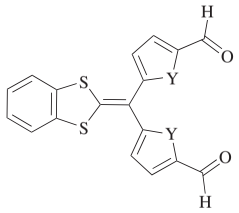
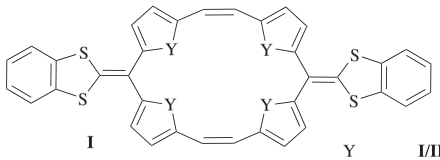
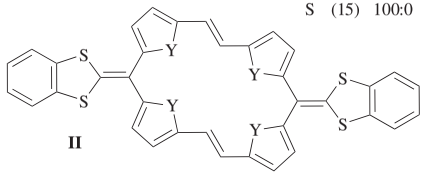
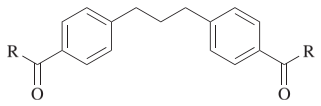
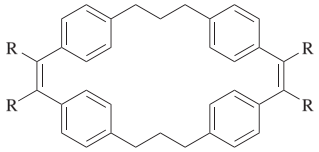
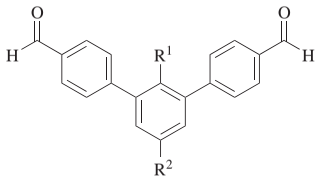
Y	R	
	H	(36)
	Me	(20)
	H	(20)
	Me	(4)

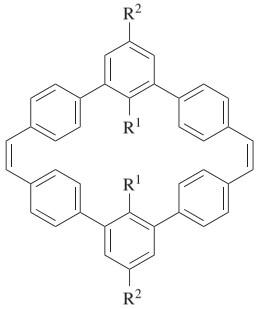
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	1. $TiCl_4$, Zn/Cu, THF, reflux, 2 h 2. Reflux, 48 h 3. Reflux, 1 h	 **I** Y (15) **I/II** O (15) 10:4 S (15) 100:0 +  **II**	802
$C_{19–21}$ 	1. $TiCl_4$, Zn, py, THF, reflux, 2 h 2. Reflux, 10–12 h	 R (32) Me (58) Et	234

C_{20-21}



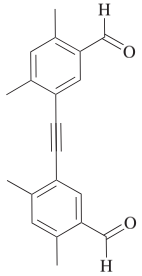
1. $TiCl_4$, Zn, py, THF, reflux, 1 h
2. Addition in one lot, reflux
3. Reflux, 6 h



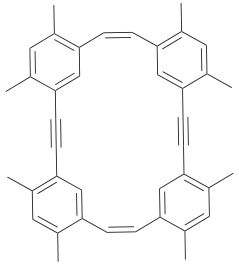
R^1	R^2	
H	H	(24)
Br	H	(18)
H	Br	(24)
MeO_2C	H	(25)

648, 647

C_{20}



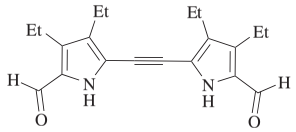
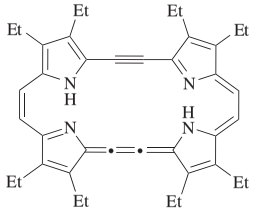
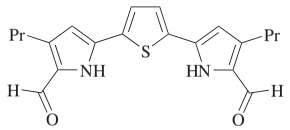
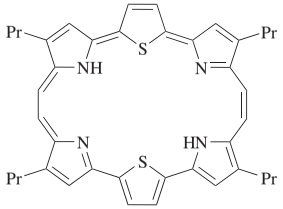
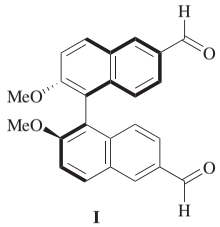
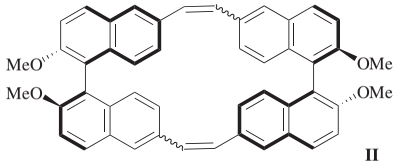
1. $TiCl_4$, Zn, CuI, DME, reflux, 3 h
2. rt, 7 h
3. rt, 15 h



(11)

232

TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	1. $TiCl_4$, Zn, CuCl, THF, reflux, 3 h 2. Addition in small portions, reflux 3. Reflux, 10 min	 (18)	803
	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Py, reflux, 1.5 h 3. Reflux, 16 h 4. Air oxidation, $CHCl_3$, 1 h	 (28)	804
C_{22}			
 **I**	1. $TiCl_4$, Zn, CuI, DME, reflux, 3.5 h 2. rt, 30 min 3. rt, 17 h; then reflux, 6 h	 **II** **I** **II** racemic racemic (16) (*R*) (*R*,*R*) (~40) (*S*) (*S*,*S*) (46)	805

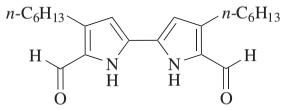
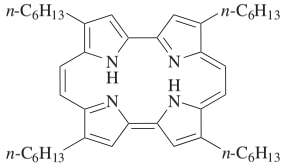
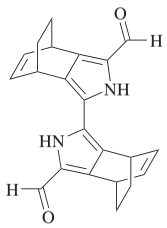
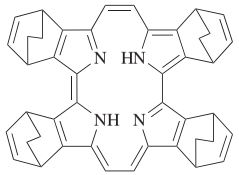
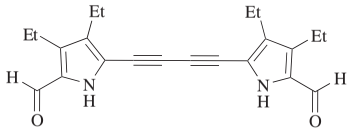
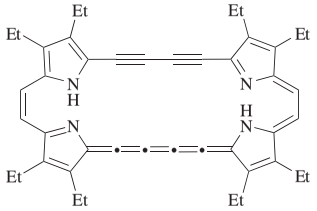
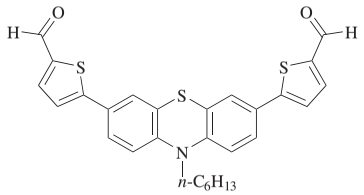
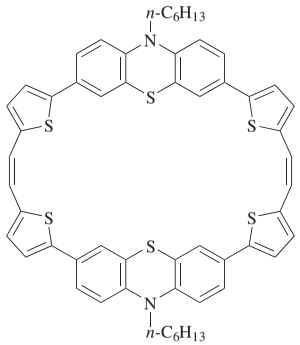
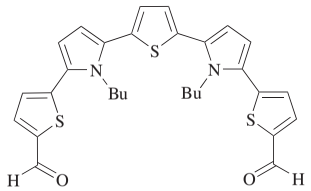
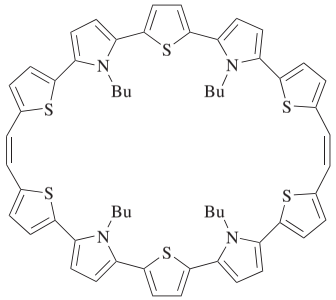
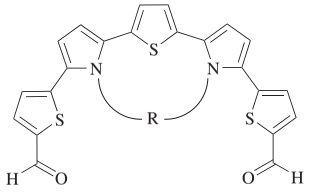
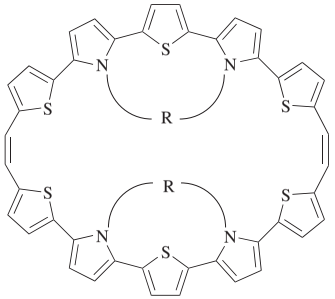
	1. $TiCl_4$, Zn, CuCl, THF, reflux, 2 h 2. Reflux, 2 h 3. Reflux, 1 h		(21)	152
	1. $TiCl_4$, Zn, CuCl, THF, reflux, 2 h 2. Reflux, 1 h 3. Reflux, 1 h		(24)	152
	1. $TiCl_4$, Zn, CuCl, THF, reflux, 3 h 2. Reflux 3. Reflux, 10 min		(9)	806

TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}			
	$TiCl_4$, Zn, dioxane, heat, 2–3 d	 (81)	789
	1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 1 h 2. Reflux 3. Reflux, 40 h	 (34)	662

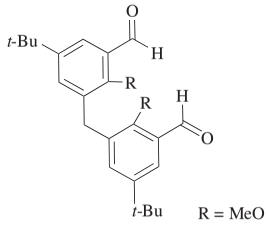
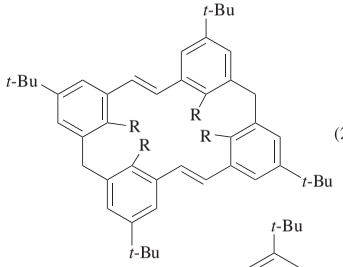
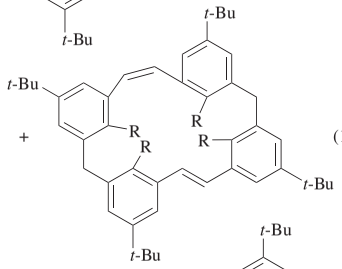
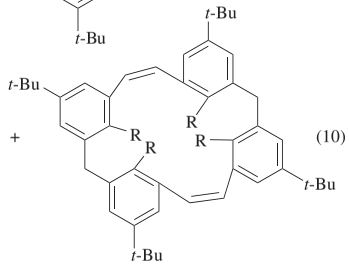


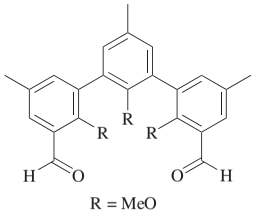
1. $TiCl_4$, Zn, THF/CH_2Cl_2, reflux, 1 h
2. Reflux
3. Reflux, 40 h



R	
$(CH_2)_8$	(14)
$(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3$	(37)

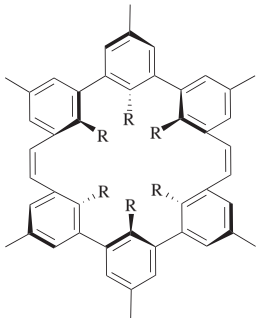
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23}  R = MeO	1. $TiCl_4$, Zn, THF, 55°, 2 h 2. Dropwise addition, 55° 3. 55°, 48 h	 (24) +  (1) +  (10)	807



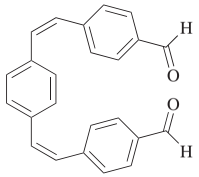
R = MeO

1. $TiCl_4$, Zn, KBr, dioxane, reflux, 2 h
2. Reflux, 48 h
3. Reflux, 48 h

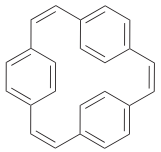


(14.4) 808

C_{24}

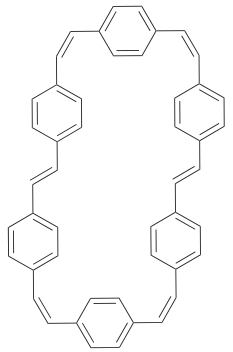


1. $TiCl_4$, Zn, solvent, reflux, 2 h
2. rt, 30 min
3. rt, 12 h; then reflux, 5 h



I

+

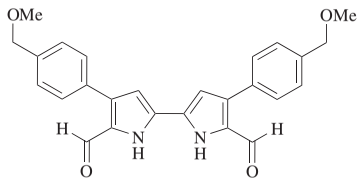
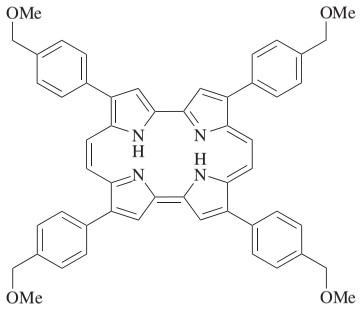
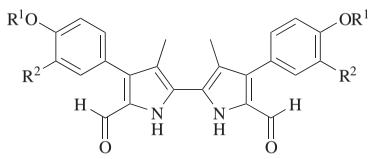
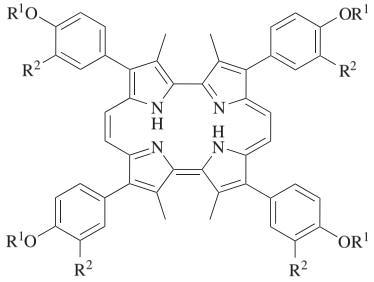


II

314

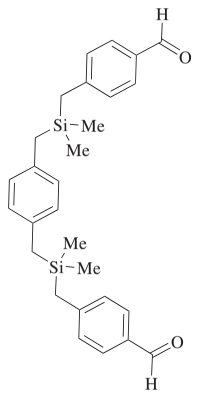
Solvent	**I**	**II**
DME	(34)	(12)[b]
DME/toluene (1:1)	(3)	(53)

TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

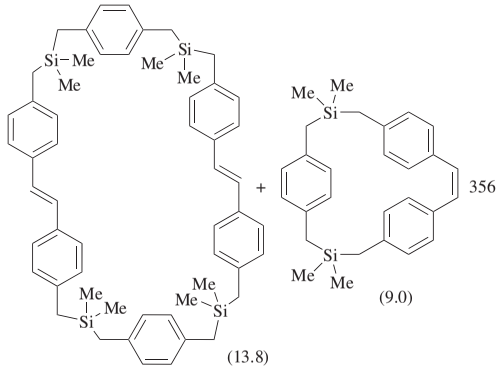
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24} 	$TiCl_4$, Zn, CuCl; then O_2	 (—)	809
C_{24-44} 	1. $TiCl_4$, Zn, CuCl, THF, reflux, 3 h 2. Reflux, 0.5–1 h 3. Reflux, 12 h	 (41) (33)	810

R^1	R^2	
n-$C_{10}H_{21}$	H	(41)
n-$C_{10}H_{21}$	*n*-$C_{10}H_{21}O$	(33)

C_{24}

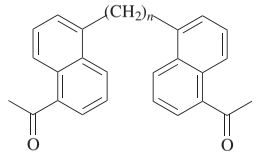


1. $TiCl_4$, Zn, THF, reflux, 1 h
2. Dropwise addition, rt
3. Reflux, 24 h

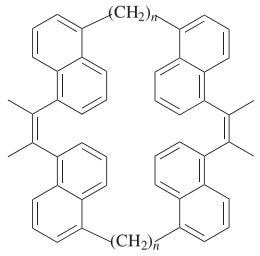


(13.8) + (9.0) 356

$C_{25–26}$



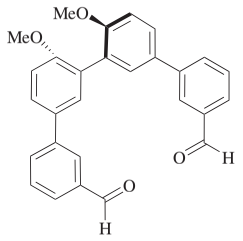
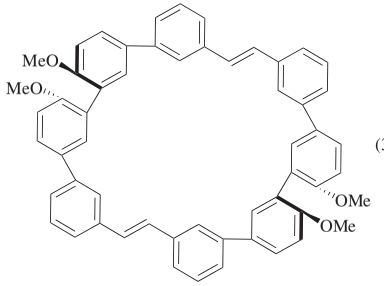
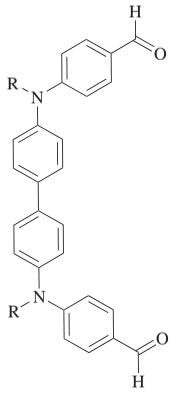
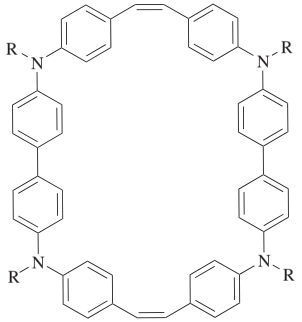
1. $TiCl_4$, Zn/Cu, DME, reflux, 2 h
2. Reflux, 72 h
3. Reflux, 12 h



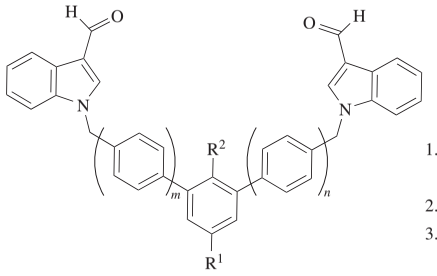
n	
1	(64)
2	(40)

150

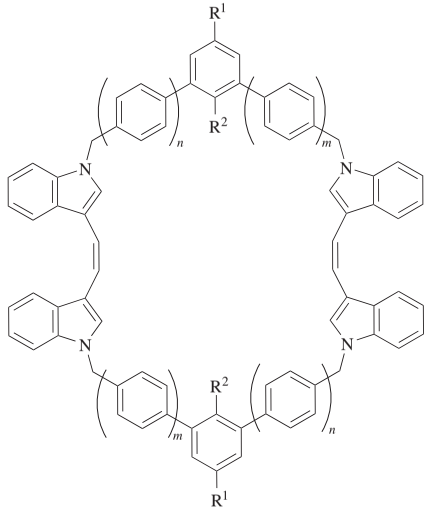
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}			
	1. $TiCl_4$, Zn, CuI, DME/toluene, reflux, 3 h 2. rt, 30 min 3. rt, overnight; then reflux, 8 h	 (37)	811
 R = 4-BuC_6H_4	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Dropwise addition, py, reflux 3. Reflux, 8 h	 (22.1)	786

$C_{26–38}$

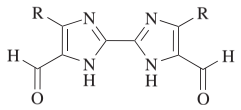
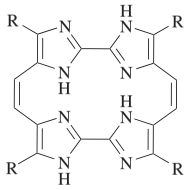
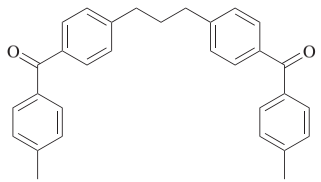
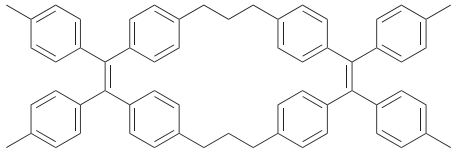
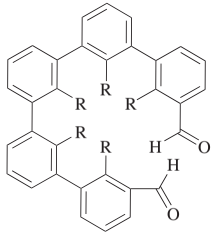
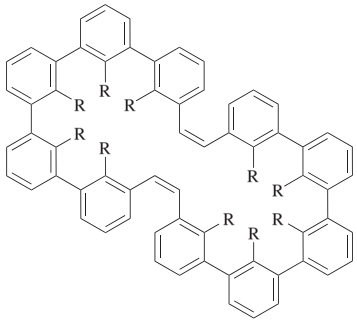


1. $TiCl_4$, Zn, py, THF, reflux, 1 h
2. Addition in one lot, reflux
3. Reflux, overnight

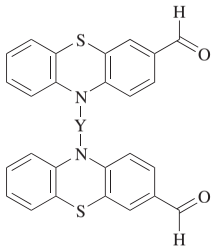


m	*n*	R^1	R^2		
0	0	H	H	(20)	648, 647
0	0	MeO	MeO	(23)	648, 647
1	0	H	H	(18)	648, 647
1	1	H	H	(8)	647
1	1	H	Br	(6)	647
1	1	H	I	(5)	647
1	1	Br	H	(8)	647

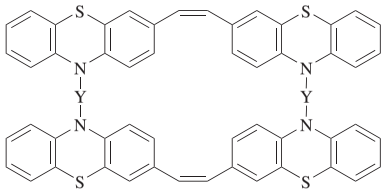
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}  R = 4-BuC_6H_4	1. $TiCl_4$, Zn/Cu, py, THF, reflux, 2 h 2. Dropwise addition, reflux 2. Reflux, 1 h	 (7)	812
C_{31} 	1. $TiCl_4$, Zn, dioxane, reflux, 2 h 2. Reflux, 80 h 3. Reflux, 10 h	 (6.6)	234
C_{32}  R = MeO	1. $TiCl_3$, Zn/Cu, DME, reflux, 1 h 2. Reflux, 6 d 3. Reflux, 2 d	 (5.2)	813

C_{32-44}

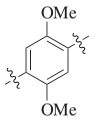


$TiCl_4$, Zn, py, THF,
reflux, overnight

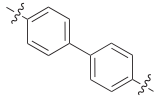


790

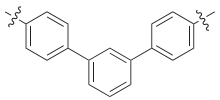
Y



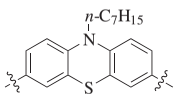
(28)



(25)

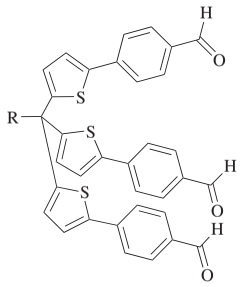
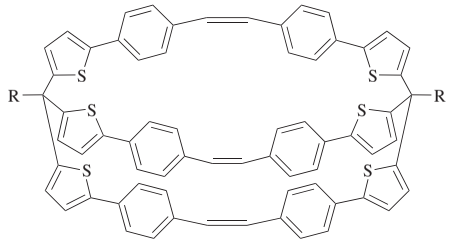
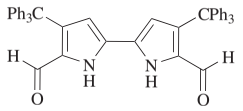
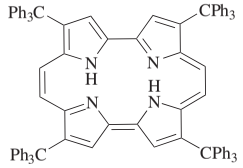


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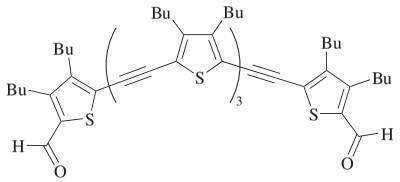


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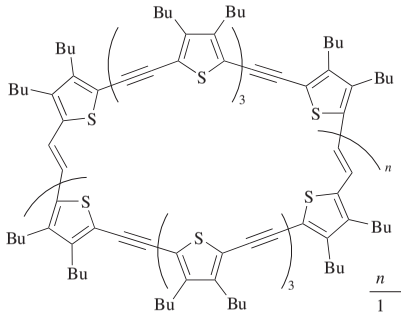
TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{35-40} 	$TiCl_4$, Zn/CuI, DME, reflux	 R: Me (17); *n*-C_6H_{13} (16)	814
C_{48} 	$TiCl_4$, Zn	 (3)	815

C_{70}



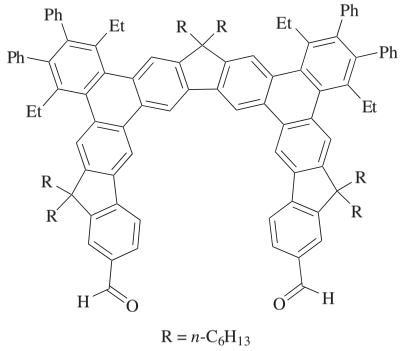
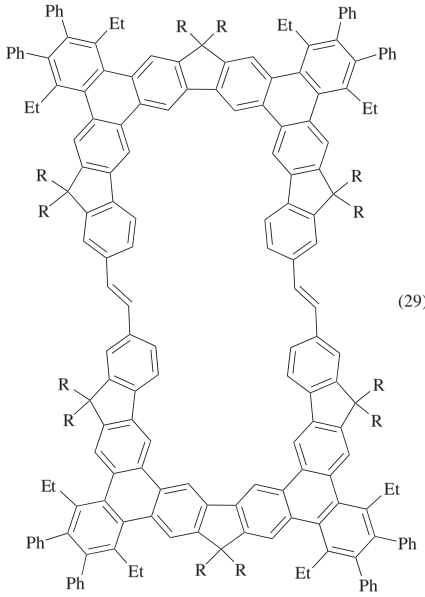
1. $TiCl_4$, Zn, THF, reflux, 3 h
2. Py, reflux, 2 h
3. Reflux, 18 h



816

n	
1	(32)
2	(9)
3	(6)
4	(4)
5	(2)

TABLE 4A. TANDEM HOMOCOUPLING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{121}  R = *n*-C_6H_{13}	1. $TiCl_4$, Zn, THF, reflux, 1 h 2. Dropwise addition, py, reflux 3. Reflux, 24 h	 (29)	817

[a] The initially formed coupling product was further oxidized to porphycene.

[b] The product is a mixture of stereoisomers.

TABLE 4B. TANDEM MIXED-COUPLING

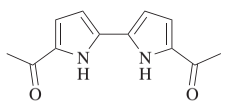
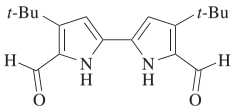
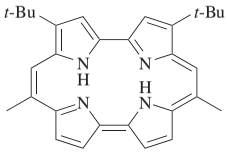
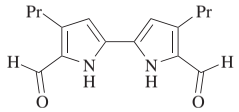
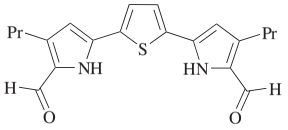
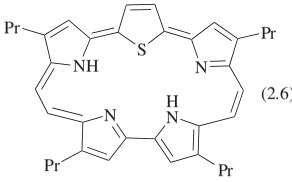
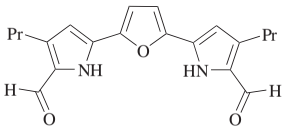
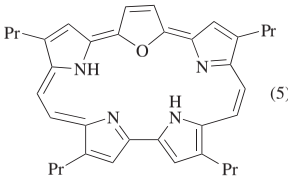
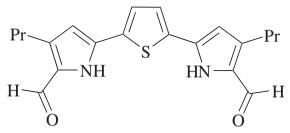
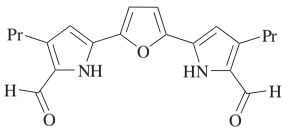
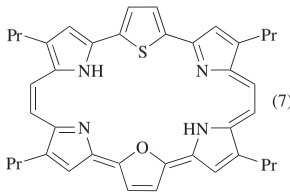
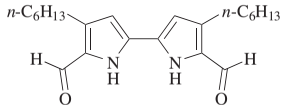
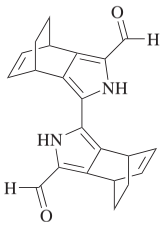
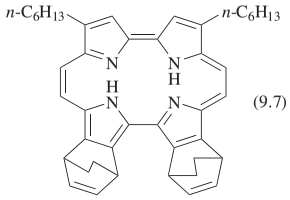
Dicarbonyl 1	Dicarbonyl 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
		$TiCl_4$, Zn	 (7)	815
C_{16}				
		1. $TiCl_4$, Zn, THF, reflux, 30 min 2. Py, reflux, 20 min 3. Reflux, 20 h	 (2.6)	818
		1. $TiCl_4$, Zn, reflux, 15 h 2. Py, reflux, 4 h 3. Reflux, 17 h	 (5)	819

TABLE 4B. TANDEM MIXED-COUPLING (*Continued*)

Dicarbonyl 1	Dicarbonyl 2	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 		1. $TiCl_4$, Zn, THF, reflux, 30 min 2. Py, reflux, 1.5 h 3. Reflux, 16 h	 (7)	818
C_{22} 		1. $TiCl_4$, Zn, CuCl, THF, reflux, 2 h 2. Reflux, 2 h 3. Reflux, 1 h	 (9.7)	152

REFERENCES

[1] Schreibmann, A. A. P. *Tetrahedron Lett.* **1970**, 4271.
[2] Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538.
[3] Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041.
[4] Tyrlik, S.; Wolochowicz, I. *Bull. Soc. Chim. Fr.* **1973**, 2147.
[5] McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708.
[6] McMurry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* **1989**, *54*, 3748.
[7] Fürstner, A.; Hupperts, A.; Ptock, A.; Janssen, E. *J. Org. Chem.* **1994**, *59*, 5215.
[8] Armbruster, J.; Grabowski, S.; Ruch, T.; Prinzbach, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2242.
[9] Auderset, P. C.; Gartenmann, T. C. C.; Gesing, E. R. F. *Kontakte (Darmstadt)* **1985**, *3*, 14.
[10] Betschart, C.; Seebach, D. *Chimia* **1989**, *43*, 39.
[11] Dang, Y.; Geise, H. J. *Janssen Chim. Acta* **1988**, *6*, 3.
[12] Dang, Y.; Geise, H. J. *Janssen Chim. Acta* **1989**, *7*, 3.
[13] Dushin, R. G. In *Comprehensive Organometallic Chemistry II*; Edward, W. A., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, 1995; Vol. 12 pp 1071–1095.
[14] Ephritikhine, M.; Villiers, C. In *Modern Carbonyl Olefination*; Takeda, T., Ed.; Wiley–VCH: Weinheim, 2004, pp 223–285.
[15] Fürstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2442.
[16] Fürstner, A. In *Transition Metals for Organic Synthesis (2nd Edition)*; Beller, M.; Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004, pp 449–468.
[17] Kahn, B. E.; Rieke, R. D. *Organometallics* **1988**, *7*, 463.
[18] König, B. *J. Prak. Chem./Chem.-Ztg.* **1995**, *337*, 250.
[19] Ladipo, F. T. *Curr. Org. Chem.* **2006**, *10*, 965.
[20] Lectka, T. *Active Metals* **1996**, 85.
[21] Lenoir, D. *Synthesis* **1989**, 883.
[22] McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405.
[23] McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.
[24] Takeda, T.; Tsubouchi, A. In *Science of Synthesis*; Rawal, V. H.; Kozmin, S. A., Eds.; Thime: Stuttgart, 2009; Vol. 46, pp 63–96.
[25] Welzel, P. *Nachr. Chem. Tech. Lab.* **1983**, *31*, 814.
[26] Ephritikhine, M. *Chem. Commun.* **1998**, 2549.
[27] McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255.
[28] Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *50*, 145.
[29] Ozerov, O. V.; Brock, C. P.; Carr, S. D.; Ladipo, F. T. *Organometallics* **2000**, *19*, 5016.
[30] Dams, R.; Malinowski, M.; Westdorp, I.; Geise, H. Y. *J. Org. Chem.* **1982**, *47*, 248.
[31] Pierce, K. G.; Barteau, M. A. *J. Org. Chem.* **1995**, *60*, 2405.
[32] Aleandri, L. E.; Becke, S.; Bogdanović, B.; Jones, D. J.; Rozière, J. *J. Organomet. Chem.* **1994**, *472*, 97.
[33] Bogdanović, B.; Bolte, A. *J. Organomet. Chem.* **1995**, *502*, 109.
[34] Eisch, J. J.; Shi, X.; Lasota, J. *Z. Naturforsch. B* **1995**, *50*, 342.
[35] Stahl, M.; Pidun, U.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2234.
[36] Covert, K. J.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J. *Inorg. Chem.* **1992**, *31*, 66.
[37] Villiers, C.; Ephritikhine, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2380.
[38] Villiers, C.; Ephritikhine, M. *Chem.-Eur. J.* **2001**, *7*, 3043.
[39] Villiers, C.; Vandais, A.; Ephritikhine, M. *J. Organomet. Chem.* **2001**, *617-618*, 744.
[40] Villiers, C.; Adam, R.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1144.
[41] Ephritikhine, M.; Maury, O.; Villiers, C.; Lance, M.; Nierlich, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3021.
[42] Maury, O.; Villiers, C.; Ephritikhine, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1129.
[43] Paquette, L. A.; Wells, G. J.; Wickham, G. *J. Org. Chem.* **1984**, *49*, 3618.
[44] Gupta, S.; Kar, G. K.; Ray, J. K. *Synth. Commun.* **2000**, *30*, 2393.
[45] Fujiwara, Y.; Ishikawa, R.; Akiyama, F.; Teranishi, S. *J. Org. Chem.* **1978**, *43*, 2477.

[46] Bhilare, S. V.; Darvatkar, N. B.; Deorukhkar, A. R.; Rasalkar, M. S.; Salunkhe, M. M. *Synth. Commun.* **2007**, *37*, 3111.
[47] Lenoir, D.; Burghard, H. *J. Chem. Res. (S)* **1980**, 396.
[48] Leimner, J.; Weyerstahl, P. *Chem. Ber.* **1982**, *115*, 3697.
[49] Senge, M. O.; Gerzevske, K. R.; Vicente, M. G. H.; Forsyth, T. P.; Smith, K. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 750.
[50] Kalisch, W. W.; Senge, M. O.; Ruhlandt-Senge, K. *Photochem. Photobiol.* **1998**, *67*, 312.
[51] Ace, K. W.; Armitage, M. A.; Bellingham, R. K.; Blackler, P. D.; Ennis, D. S.; Hussain, N.; Lathbury, D. C.; Morgan, D. O.; O'Connor, N.; Oakes, G. H.; Passey, S. C.; Powling, L. C. *Org. Process Res. Dev.* **2001**, *5*, 479.
[52] Chu, G.-H.; Peters, A.; Selcer, K. W.; Li, P.-K. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 141.
[53] Detsi, A.; Koufaki, M.; Calogeropoulou, T. *J. Org. Chem.* **2002**, *67*, 4608.
[54] Shani, J.; Gazit, A.; Livshitz, T.; Biran, S. *J. Med. Chem.* **1985**, *28*, 1504.
[55] Zolotareva, V. A.; Klimova, L. I.; Malanina, G. G.; Sokolova, A. S.; Grinenko, G. S. *Pharm. Chem. J.* **1990**, *24*, 241.
[56] Gauthier, S.; Sancéau, J.–Y.; Mailhot, J.; Caron, B.; Cloutier, J. *Tetrahedron* **2000**, *56*, 703.
[57] Moreau, A.; Praveen Rao, P. N.; Knaus, E. E. *Bioorg. Med. Chem.* **2006**, *14*, 5340.
[58] Uddin, M. J.; Rao, P. N. P.; Knaus, E. E. *Synlett* **2004**, 1513.
[59] Uddin, M. J.; Rao, P. N. P.; McDonald, R.; Knaus, E. E. *J. Med. Chem.* **2004**, *47*, 6108.
[60] Kahn, B. E.; Rieke, R. D. *Chem. Rev.* **1988**, *88*, 733.
[61] McMurry, J. E.; Kees, K. L. *J. Org. Chem.* **1977**, *42*, 2655.
[62] McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1976**, *41*, 896.
[63] McMurry, J. E.; Miller, D. D. *J. Am. Chem. Soc.* **1983**, *105*, 1660.
[64] Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7178.
[65] Dams, R.; Malinowski, M.; Geise, H. J. *Bull. Soc. Chim. Belg*. **1981**, *90*, 1141.
[66] Mundy, B. P.; Srinivasa, R.; Kim, Y.; Dolph, T.; Warnet, R. J. *J. Org. Chem.* **1982**, *47*, 1657.
[67] Rele, S.; Talukdar, S.; Banerji, A.; Chattopadhyay, S. *J. Org. Chem.* **2001**, *66*, 2990.
[68] Eisch, J. J.; Gitua, J. N.; Otieno, P. O.; Shi, X. *J. Organomet. Chem.* **2001**, *624*, 229.
[69] Fürstner, A.; Seidel, G. *Synthesis* **1995**, 63.
[70] Fürstner, A.; Seidel, G.; Gabor, B.; Kopiske, C.; Krüeger, C.; Mynott, R. *Tetrahedron* **1995**, *51*, 8875.
[71] Braga, D.; Ripamonti, A.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1978**, 927.
[72] Boldrini, G. P.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Organomet. Chem.* **1985**, *280*, 307.
[73] Fürstner, A.; Weidmann, H. *Synthesis* **1987**, 1071.
[74] Fürstner, A.; Csuk, R.; Rohrer, C.; Weidmann, H. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1729.
[75] Clive, D. L. J.; Murthy, K. S. K.; Wee, A. G. H.; Prasad, J. S.; da Silva, G. V. J.; Majewski, M.; Anderson, P. C.; Haugen, R. D.; Heerze, L. D. *J. Am. Chem. Soc.* **1988**, *110*, 6914.
[76] Burger, P.; Brintzinger, H. H. *J. Organomet. Chem.* **1991**, *407*, 207.
[77] Pitter, S.; Huttner, G.; Walter, O.; Zsolnai, L. *J. Organomet. Chem.* **1993**, *454*, 183.
[78] Fürstner, A.; Jumbam, D. N.; Weidmann, H. *Tetrahedron Lett.* **1991**, *32*, 6695.
[79] Fürstner, A.; Jumbam, D. N. *Tetrahedron* **1992**, *48*, 5991.
[80] Fürstner, A.; Jumbam, D. N. *J. Chem. Soc., Chem. Commun.* **1993**, 211.
[81] Fürstner, A.; Hupperts, A.; Ptock, A.; Janssen, E. *J. Org. Chem.* **1994**, *59*, 5215.
[82] Fürstner, A.; Jumbam, D. N.; Seidel, G. *Chem. Ber.* **1994**, *127*, 1125.
[83] Fürstner, A.; Hupperts, A. *J. Am. Chem. Soc.* **1995**, *117*, 4468.
[84] Clive, D. L. J.; Zhang, C. Z.; Murthy, K. S. K.; Hayward, W. D.; Daigneault, S. *J. Org. Chem.* **1991**, *56*, 6447.
[85] Fürstner, A.; Seidel, G.; Kopiske, C.; Krüeger, C.; Mynott, R. *Liebigs Ann.* **1996**, 655.
[86] Chen, T. L.; Chan, T. H.; Shaver, A. *J. Organomet. Chem.* **1984**, *268*, C1.
[87] Okamoto, S.; He, J.-Q.; Ohno, C.; Oh-iwa, Y.; Kawaguchi, Y. *Tetrahedron Lett.* **2010**, *51*, 387.
[88] Dutta, D. K.; Konwar, D. *Tetrahedron Lett.* **2000**, *41*, 6227.
[89] Sato, R.; Nagaoka, T.; Saito, M. *Tetrahedron Lett.* **1990**, *31*, 4165.

[90] Schmidt, A.; Beckert, R.; Weiß, D. *Tetrahedron Lett.* **1992**, *33*, 4299.
[91] Banerjee, A. K.; de Carrasco, M. C. S.; Frydrychhouge, C. S. V.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1803.
[92] Denifl, P.; Hradsky, A.; Bildstein, B.; Wurst, K. *J. Organomet. Chem.* **1996**, *523*, 79.
[93] Lee, S. J.; Kim, T. Y.; Choi, K. S.; Park, M. K.; Han, B. H. *Bull. Korean Chem. Soc.* **1997**, *18*, 224.
[94] Eisch, J. J.; Fregene, P. O. *Eur. J. Org. Chem.* **2008**, 4482.
[95] Sato, M.; Oshima, K. *Chem. Lett.* **1982**, 157.
[96] Kauffmann, T.; Kallweit, H. *Chem. Ber.* **1992**, *125*, 149.
[97] Szymoniak, J.; Luque, L.; Besançon, J.; Moïse, C. *Bull. Soc. Chim. Fr.* **1994**, *131*, 89.
[98] Howarth, J.; Finnegan, J. *Synth. Commun.* **1997**, *27*, 3663.
[99] Chisholm, M. H.; Klang, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2324.
[100] Chisholm, M. H. *Pure Appl. Chem.* **1991**, *63*, 665.
[101] Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 602.
[102] Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 607.
[103] Petit, M.; Mortreux, A.; Petit, F. *J. Chem. Soc., Chem. Commun.* **1984**, 341.
[104] Barman, D. C.; Thakur, A. J.; Prajapati, D.; Sandhu, J. S. *Synlett* **2001**, 515.
[105] Ogawa, A.; Takami, N.; Sekiguchi, M.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 8729.
[106] Xu, X.; Zhang, Y. *Tetrahedron* **2002**, *58*, 503.
[107] Xu, X.-L.; Zhang, Y.-M. *Chin. J. Chem.* **2002**, *20*, 1463.
[108] Ogawa, A.; Nanke, T.; Takami, N.; Sekiguchi, M.; Kambe, N.; Sonoda, N. *Appl. Organomet. Chem.* **1995**, *9*, 461.
[109] Rieke, R. D.; Rhyne, L. D. *J. Org. Chem.* **1979**, *44*, 3445.
[110] Ishida, A.; Mukaiyama, T. *Chem. Lett.* **1976**, 1127.
[111] Lenoir, D. *Synthesis* **1977**, 553.
[112] Härter, P.; Latzel, K.; Spiegler, M.; Herdtweck, E. *Polyhedron* **1998**, *17*, 1141.
[113] Rele, S.; Chattopadhyay, S.; Nayak, S. K. *Tetrahedron Lett.* **2001**, *42*, 9093.
[114] Rele, S. M.; Nayak, S. K.; Chattopadhyay, S. *Tetrahedron* **2008**, *64*, 7225.
[115] Talukdar, S.; Nayak, S. K.; Banerji, A. *J. Org. Chem.* **1998**, *63*, 4925.
[116] McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281.
[117] McMurry, J. E.; Silvestri, M. G.; Fleming, M. P.; Hoz, T.; Grayston, M. W. *J. Org. Chem.* **1978**, *43*, 3249.
[118] Walborsky, H. M.; Wüst, H. H. *J. Am. Chem. Soc.* **1982**, *104*, 5807.
[119] Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 817.
[120] Dams, R.; Malinowski, M.; Geise, H. J. *Recl. Trav. Chim. Pays–Bas* **1982**, *101*, 112.
[121] Ramana, M. M. V.; Singh, B. K. D.; Parihar, J. A. *J. Chem. Res.* **2004**, 760.
[122] Hoischen, D.; Colmenares, L. U.; Koukhareva, I.; Ho, M.; Liu, R. S. H. *J. Fluorine Chem.* **1999**, *97*, 165.
[123] Bauchat, P.; Le Bras, N.; Rigal, L.; Foucaud, A. *Tetrahedron* **1994**, *50*, 7815.
[124] Castedo, L.; Cid, M. M.; Domínguez, R.; Seijas, J. A.; Villaverde, M. C. *Heterocycles* **1990**, *31*, 1271.
[125] Kriste, A. G.; Tercel, M.; Anderson, R. F.; Ferry, D. M.; Wilson, W. R. *Radiat. Res.* **2002**, *158*, 753.
[126] Niemi, T.-A.; Coe, P. L.; Till, S. J. *J. Chem. Soc. Perkin Trans. 1* **2000**, 1519.
[127] Fujita, T.; Kuwahara, S.; Harada, N. *Eur. J. Org. Chem.* **2005**, 4533.
[128] Reddy, S. M.; Duraisamy, M.; Walborsky, H. M. *J. Org. Chem.* **1986**, *51*, 2361.
[129] Pons, J.; Santelli, M. *J. Org. Chem.* **1989**, *54*, 877.
[130] Kühn, R.; Otto, H.-H. *Arch. Pharm.* **1989**, *322*, 375.
[131] Fürstner, A.; Seidel, G.; Mons, H.-E.; Mynott, R. *Eur. J. Inorg. Chem.* **1998**, 1771.
[132] Nagafuji, A.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Kidorui* **1994**, *24*, 198.
[133] Jeong, H. J.; Yoon, U. Y.; Jang, S. H.; Yoo, U.-A.; Kim, S. N.; Truong, B. T.; Shin, S. C.; Yoon, Y.–J.; Singh, O. M.; Lee, S.-G. *Synlett* **2007**, 1407.
[134] Shi, D.-q.; Chen, J.-x.; Chai, W.-y.; Chen, W.-x.; Kao, T.-y. *Tetrahedron Lett.* **1993**, *34*, 2963.

[135] Watanabe, N.; Suganuma, H.; Kobayashi, H.; Mutoh, H.; Katao, Y.; Matsumoto, M. *Tetrahedron* **1999**, *55*, 4287.
[136] Sabelle, S.; Hydrio, J.; Leclerc, E.; Mioskowski, C.; Renard, P.–Y. *Tetrahedron Lett.* **2002**, *43*, 3645.
[137] Buchgraber, P.; Domostoj, M. M.; Scheiper, B.; Wirtz, C.; Mynott, R.; Rust, J.; Fürstner, A. *Tetrahedron* **2009**, *65*, 6519.
[138] Talukdar, S.; Nayak, S. K.; Banerji, A. *Synth. Commun.* **1998**, *28*, 2325.
[139] Baran, J.; Laszlo, P. *Tetrahedron Lett.* **1985**, *26*, 5135.
[140] Muszkat, K. A.; Jakob, A.; Castel, N.; Fischer, E.; Rauch, K.; Lüttke, W. *J. Photochem. Photobiol. A: Chem.* **1991**, *60*, 193.
[141] McMurry, J. E.; Krepski, L. R. *J. Org. Chem.* **1976**, *41*, 3929.
[142] Coe, P. L.; Scriven, C. E. *J. Chem. Soc., Perkin Trans. 1* **1986**, 475.
[143] Paquette, L. A.; Yan, T.-H.; Wells, G. J. *J. Org. Chem.* **1984**, *49*, 3610.
[144] Duan, X.-F.; Zeng, J.; Lü, J.-W.; Zhang, Z.-B. *J. Org. Chem.* **2006**, *71*, 9873.
[145] Duan, X.-F.; Zeng, J.; Zhang, Z.-B.; Zi, G.-F. *J. Org. Chem.* **2007**, *72*, 10283.
[146] Baumstark, A. L.; McCloskey, C. J.; Witt, K. E. *J. Org. Chem.* **1978**, *43*, 3609.
[147] Eguchi, T.; Kano, H.; Arakawa, K.; Kakinuma, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2545.
[148] Jendralla, H. *Tetrahedron Lett.* **1982**, *23*, 3657.
[149] Hu, Z.; Atwood, J. L.; Cava, M. P. *J. Org. Chem.* **1994**, *59*, 8071.
[150] Grützmacher, H.-F.; Nolte, G. *Chem. Ber.* **1994**, *127*, 1157.
[151] Dai, W.-M.; Mak, W. L. *Tetrahedron Lett.* **2000**, *41*, 10277.
[152] Kuzuhara, D.; Mack, J.; Yamada, H.; Okujima, T.; Ono, N.; Kobayashi, N. *Chem.—Eur. J.* **2009**, *15*, 10060.
[153] Rieke, R. D.; Bales, S. E.; Hudnall, P. M.; Burns, T. P.; Poindexter, G. S. *Org. Synth. Coll. Vol. 6*, **1988**, 845.
[154] Geluk, H. W. *Synthesis* **1970**, 652.
[155] De Selms R. C.; Fox, C. J.; Riordan, R. C. *Tetrahedron Lett.* **1970**, 781.
[156] Newman, M. S.; Sujeeth, P. K. *J. Org. Chem.* **1978**, *43*, 4367.
[157] Lansinger, J. M.; Ronald, R. C. *Synth. Commun.* **1979**, *9*, 341.
[158] Takeda, T.; Sasaki, R.; Yamauchi, S.; Fujiwara, T. *Tetrahedron* **1997**, *53*, 557.
[159] Matsubara, S.; Oshima, K. In *Modern Carbonyl Olefination*; Takeda, T., Ed.; Wiley–VCH: Weinheim, 2004, pp 200–222.
[160] Okazoe, T.; Takai, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1987**, *52*, 4410.
[161] Takai, K.; Fujimura, O.; Kataoka, Y.; Utimoto, K. *Tetrahedron Lett.* **1989**, *30*, 211.
[162] Takai, K.; Tezuka, M.; Kataoka, Y.; Utimoto, K. *Synlett* **1989**, 27.
[163] Takai, K.; Kakiuchi, T.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1994**, *59*, 2668.
[164] Takeda, T.; Sasaki, R.; Fujiwara, T. *J. Org. Chem.* **1998**, *63*, 7286.
[165] Shono, T.; Nagasawa, T.; Tsubouchi, A.; Takeda, T. *Tetrahedron Lett.* **2007**, *48*, 3521.
[166] Shono, T.; Ito, K.; Tsubouchi, A.; Takeda, T. *Org. Biomol. Chem.* **2005**, *3*, 2914.
[167] Takeda, T.; Tsubouchi, A. In *Modern Carbonyl Olefination*; Takeda, T., Ed.; Wiley–VCH: Weinheim, 2004, pp 151–159.
[168] Takeda, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 195.
[169] Takeda, T. *Chem. Rec.* **2007**, *7*, 24.
[170] Horikawa, Y.; Watanabe, M.; Fujiwara, T.; Takeda, T. *J. Am. Chem. Soc.* **1997**, *119*, 1127.
[171] Fujiwara, T.; Iwasaki, N.; Takeda, T. *Chem. Lett.* **1998**, 741.
[172] Takeda, T.; Watanabe, M.; Nozaki, N.; Fujiwara, T. *Chem. Lett.* **1998**, 115.
[173] Takeda, T.; Saito, J.; Tsubouchi, A. *Tetrahedron Lett.* **2003**, *44*, 5571.
[174] Takeda, T.; Kuroi, S.; Ozaki, M.; Tsubouchi, A. *Org. Lett.* **2004**, *6*, 3207.
[175] Takeda, T.; Ozaki, M.; Kuroi, S.; Tsubouchi, A. *J. Org. Chem.* **2005**, *70*, 4233.
[176] Takeda, T.; Sato, K.; Tsubouchi, A. *Synthesis* **2004**, 1457.
[177] Rahim, M. A.; Taguchi, H.; Watanabe, M.; Fujiwara, T.; Takeda, T. *Tetrahedron Lett.* **1998**, *39*, 2153.
[178] Rahim, M. A.; Sasaki, H.; Saito, J.; Fujiwara, T.; Takeda, T. *Chem. Commun.* **2001**, 625.
[179] Rahim, M. A.; Fujiwara, T.; Takeda, T. *Synlett* **1999**, 1029.

[180] Takeda, T.; Yatsumonji, Y.; Tsubouchi, A. *Tetrahedron Lett.* **2005**, *46*, 3157.
[181] Lenoir, D. *Chem. Ber.* **1978**, *111*, 411.
[182] Lenoir, D.; Malwitz, D.; Meyer, B. *Tetrahedron Lett.* **1984**, *25*, 2965.
[183] Timberlake, J. W.; Jun, Y. M. *J. Org. Chem.* **1979**, *44*, 4729.
[184] Böhrer, G.; Knorr, R. *Tetrahedron Lett.* **1984**, *25*, 3675.
[185] Frimer, A. A.; Roth, D. *J. Org. Chem.* **1979**, *44*, 3882.
[186] de Meijere, A.; Wenck, H.; Zöllner, S.; Merstetter, P.; Arnold, A.; Gerson, F.; Schreiner, P. R.; Boese, R.; Bläser, D.; Gleiter, R.; Kozhushkov, S. I. *Chem.-Eur. J.* **2001**, *7*, 5382.
[187] Oelgemöller, M.; Brem, B.; Frank, R.; Schneider, S.; Lenoir, D.; Hertkorn, N.; Origane, Y.; Lemmen, P.; Lex, J.; Inoue, Y. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1760.
[188] Laali, K. K.; Okazaki, T.; Bunge, S. D.; Lenoir, D. *J. Org. Chem.* **2008**, *73*, 4092.
[189] Seo, J. W.; Kim, H. J.; Lee, B. S.; Katzenellenbogen, J. A.; Chi, D. Y. *J. Org. Chem.* **2008**, *73*, 715.
[190] Marchand, A. P.; Reddy, G. M.; Deshpande, M. N.; Watson, W. H.; Nagl, A.; Lee, O. S.; Osawa, E. *J. Am. Chem. Soc.* **1990**, *112*, 3521.
[191] Marchand, A. P.; Sorokin, V. D.; Watson, W. H.; Carlson, T. F.; Krawiec, M. *Struct. Chem.* **1994**, *5*, 367.
[192] Marchand, A. P.; Zope, A.; Zaragoza, F.; Bott, S. G.; Ammon, H. L.; Du, Z. *Tetrahedron* **1994**, *50*, 1687.
[193] Watson, W. H.; Nagl, A.; Marchand, A. P.; Deshpande, M. N. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *45*, 1339.
[194] Gleiter, R.; Borzyk, O. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1001.
[195] Gleiter, R.; Fritzsche, G.; Borzyk, O.; Oeser, T.; Rominger, F.; Irngartinger, H. *J. Org. Chem.* **1998**, *63*, 2878.
[196] Burgstahler, A. W.; Jahansouz, H.; Véliz, E. A.; Takasugawa, F. *Chirality* **2002**, *14*, 180.
[197] Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1905.
[198] Czekelius, C.; Hafer, J.; Tonzetich, Z. J.; Schrock, R. R.; Christensen, R. L.; Müeller, P. *J. Am. Chem. Soc.* **2006**, *128*, 16664.
[199] Nguyen, T.–T.; Gouriou, Y.; Sallé, M.; Frère, P.; Jubault, M.; Gorgues, A.; Toupet, L.; Riou, A. *Bull. Soc. Chim. Fr.* **1996**, *133*, 301.
[200] Janssen, J.; Lüttke, W. *Chem. Ber.* **1982**, *115*, 1234.
[201] Valla, A.; Valla, B.; Le Guillou, R.; Cartier, D.; Dufossé, L.; Labia, R. *Helv. Chim. Acta* **2007**, *90*, 512.
[202] Broszeit, G.; Diepenbrock, F.; Gräf, O.; Hecht, D.; Heinze, J.; Martin, H.-D.; Mayer, B.; Schaper, K.; Smie, A.; Strehblow, H.-H. *Liebigs Ann./Recl.* **1997**, 2205.
[203] Valla, A. R.; Cartier, D. L.; Valla, B. G.; Le Guillou, R. Y.; Andriamialisoa, Z. R.; Labia, R.; Breithaupt, D. E.; Savy, S. M.; Binet, A.; Dufossé, L. H. *Helv. Chim. Acta* **2003**, *86*, 3314.
[204] Doering, W. von E.; Sarma, K. *J. Am. Chem. Soc.* **1992**, *114*, 6037.
[205] Wang, Y.-P.; Lui, X.-H.; Lin, B.-S.; Tang, W.-D.; Lin, T.-S.; Liaw, J.-H.; Wang, Y.; Liu, Y.-H. *J. Organomet. Chem.* **1999**, *575*, 310.
[206] Bildstein, B.; Denifl, P.; Wurst, K.; André, M.; Baumgarten, M.; Friedrich, J.; Ellmerer-Müller, E. *Organometallics* **1995**, *14*, 4334.
[207] Adams, C. M.; Holt, E. M. *Organometallics* **1990**, *9*, 980.
[208] Toullec, P.; Ricard, L.; Mathey, F. *Organometallics* **2002**, *21*, 2635.
[209] Cheng, J.; Sekher, P.; Singh, S. P.; Gano, J. E.; Morgan, A. R. *Synth. Commun.* **1997**, *27*, 673.
[210] Xie, H.; Lee, D. A.; Wallace, D. M.; Senge, M. O.; Smith, K. M. *J. Org. Chem.* **1996**, *61*, 8508.
[211] Cheng, J.; Gano, J. E.; Morgan, A. R. *Tetrahedron Lett.* **1996**, *37*, 2721.
[212] Windscheif, P.-M.; Vögtle, F. *Synthesis* **1994**, 87.
[213] Newkome, G. R.; Roper, J. M. *J. Org. Chem.* **1979**, *44*, 502.
[214] Senge, M. O.; Vicente, M. G. H.; Gerzevske, K. R.; Forsyth, T. P.; Smith, K. M. *Inorg. Chem.* **1994**, *33*, 5625.
[215] Graça, M.; Vicente, M. G. H.; Smith, K. M. *J. Org. Chem.* **1991**, *56*, 4407.
[215a] Graça, M.; Vicente, H.; Rezzano, I. N.; Smith, K. M. *Tetrahedron Lett.* **1990**, *31*, 1365.
[216] Collis, G. E.; Burrell, A. K.; Blandford, E. J.; Officer, D. L. *Tetrahedron* **2007**, *63*, 11141.

[217] Licandro, E.; Rigamonti, C.; Ticozzelli, M. T.; Monteforte, M.; Baldoli, C.; Giannini, C.; Maiorana, S. *Synthesis* **2006**, 3670.
[218] Elandaloussi, E. H.; Frère, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. *J. Am. Chem. Soc.* **1997**, *119*, 10774.
[219] Marshall, J. A.; Flynn, K. E. *J. Am. Chem. Soc.* **1984**, *106*, 723.
[220] McMurry, J. E.; Lectka, T. *J. Am. Chem. Soc.* **1993**, *115*, 10167.
[221] Nakazaki, M.; Yamamoto, K.; Maeda, M.; Sato, O.; Tsutsui, T. *J. Org. Chem.* **1982**, *47*, 1435.
[222] Dressel, J.; Chasey, K. L.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 5479.
[223] McMurry, J. E.; Swenson, R. *Tetrahedron Lett.* **1987**, *28*, 3209.
[224] Lee, W. Y.; Park, C. H.; Kim, Y. D. *J. Org. Chem.* **1992**, *57*, 4074.
[225] Vogel, E.; Püttmann, W.; Duchatsch, W.; Schieb, T.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 720.
[226] Yamamoto, K.; Kuroda, S.; Shibutani, M.; Yoneyama, Y.; Ojima, J.; Fujita, S.; Ejiri, E.; Yanagihara, K. *J. Chem. Soc., Perkin Trans. 1* **1988**, 395.
[227] Hopf, H.; Krüger, A. *Chem.—Eur. J.* **2001**, *7*, 4378.
[228] Eckhardt, M.; Brückner, R. *Liebigs Ann./Recl.* **1997**, 947.
[229] Ojima, J.; Yamamoto, K.; Kato, T.; Wada, K.; Yoneyama, Y.; Ejiri, E. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2209.
[230] McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 2932.
[231] McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Mitchell, J. *J. Am. Chem. Soc.* **1986**, *108*, 515.
[232] Esser, B.; Bandyopadhyay, A.; Rominger, F.; Gleiter, R. *Chem.—Eur. J.* **2009**, *15*, 3368.
[233] Dyker, G.; Körning, J.; Stirner, W. *Eur. J. Org. Chem.* **1998**, 149.
[234] Grützmacher, H.-F.; Neumann, E.; Ebmeyer, F.; Albrecht, K.; Schelenz, P. *Chem. Ber.* **1989**, *122*, 2291.
[235] Hopf, H.; Mlynek, C. *J. Org. Chem.* **1990**, *55*, 1361.
[236] Debroy, P.; Lindeman, S. V.; Rathore, R. *J. Org. Chem.* **2009**, *74*, 2080.
[237] Rajakumar, P.; Selvam, S. *Tetrahedron* **2007**, *63*, 8891.
[238] Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507.
[239] Shimizu, I.; Kamei, Y.; Tezuka, T.; Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 192.
[240] Arduini, A.; Fanni, S.; Pochini, A.; Sicuri, A. R.; Ungaro, R. *Tetrahedron* **1995**, *51*, 7951.
[241] Lhoták, P.; Shinkai, S. *Tetrahedron Lett.* **1996**, *37*, 645.
[242] Jaiyu, A.; Rojanathanes, R.; Sukwattanasinitt, M. *Tetrahedron Lett.* **2007**, *48*, 1817.
[243] Some, S.; Dutta, B.; Ray, J. K. *Tetrahedron Lett.* **2006**, *47*, 1221.
[244] Yamamoto, K.; Harada, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M.; Kai, Y.; Nakao, T.; Tanaka, M.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 3578.
[245] Tanaka, K.; Suzuki, H.; Osuga, H. *J. Org. Chem.* **1997**, *62*, 4465.
[246] Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *Chem.—Eur. J.* **2004**, *10*, 6531.
[247] Berlage, U.; Schmidt, J.; Peters, U.; Welzel, P. *Tetrahedron Lett.* **1987**, *28*, 3091.
[248] Disanayaka, B. W.; Weedon, A. C. *J. Org. Chem.* **1987**, *52*, 2905.
[249] Myers, A. G.; Condroski, K. R. *J. Am. Chem. Soc.* **1995**, *117*, 3057.
[250] Hu, T.; Corey, E. J. *Org. Lett.* **2002**, *4*, 2441.
[251] Clive, D. L. J.; Murthy, K. S. K.; Wee, A. G. H.; Prasad, J. S.; da Silva, G. V. J.; Majewski, M.; Anderson, P. C.; Evans, C. F.; Haugen, R. D.; Heerze, L. D.; Barrie, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 3018.
[252] Honda, T.; Namiki, H.; Nagase, H.; Mizutani, H. *Tetrahedron Lett.* **2003**, *44*, 3035.
[253] Rajendran, V.; Rong, S.-B.; Saxena, A.; Doctor, B. P.; Kozikowski, A. P. *Tetrahedron Lett.* **2001**, *42*, 5359.
[254] Koft, E. R.; Broadbent, T. A. *Org. Prep. Proced. Int.* **1988**, *20*, 199.
[255] Wu, Y.-J.; Burnell, D. J. *Tetrahedron Lett.* **1988**, *29*, 4369.
[256] Burnell, D. J.; Wu, Y.-J. *Can. J. Chem.* **1990**, *68*, 804.
[257] Mikami, K.; Takahashi, K.; Nakai, T.; Uchimaru, T. *J. Am. Chem. Soc.* **1994**, *116*, 10948.
[258] Ziegler, F. E.; Lim, H. *J. Org. Chem.* **1982**, *47*, 5229.

[259] Shimizu, I.; Ishikawa, T. *Tetrahedron Lett.* **1994**, *35*, 1905.
[260] Dauben, W. G.; Farkas, I.; Bridon, D. P.; Chuang, C.-P.; Henegar, K. E. *J. Am. Chem. Soc.* **1991**, *113*, 5883.
[261] Nicolaou, K. C.; Yang, Z.; Liu, J.–J.; Nantermet, P. G.; Claiborne, C. F.; Renaud, J.; Guy, R. K.; Shibayama, K. *J. Am. Chem. Soc.* **1995**, *117*, 645.
[262] Kende, A. S.; Johnson, S.; Sanfilippo, P.; Hodges, J. C.; Jungheim, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 3513.
[263] Dauben, W. G.; Warshawsky, A. M. *J. Org. Chem.* **1990**, *55*, 3075.
[264] Snider, B. B.; Yang, K. *J. Org. Chem.* **1992**, *57*, 3615.
[265] McMurry, J. E.; Bosch, G. K. *Tetrahedron Lett.* **1985**, *26*, 2167.
[266] McMurry, J. E.; Bosch, G. K. *J. Org. Chem.* **1987**, *52*, 4885.
[267] Cane, D. E.; Tsantrizos, Y. S. *J. Am. Chem. Soc.* **1996**, *118*, 10037.
[268] McMurry, J. E.; KočovskÁ, P. *Tetrahedron Lett.* **1985**, *26*, 2171.
[269] Dauben, W. G.; Lorenz, K. L.; Dean, D. W.; Shapiro, G.; Farkas, I. *Tetrahedron Lett.* **1998**, *39*, 7079.
[270] McMurry, J. E.; Matz, J. R. *Tetrahedron Lett.* **1982**, *23*, 2723.
[271] Begley, M. J.; Jackson, C. B.; Pattenden, G. *Tetrahedron* **1990**, *46*, 4907.
[272] Jackson, C. B.; Pattenden, G. *Tetrahedron Lett.* **1985**, *26*, 3393.
[273] Li, W.; Li, Y.; Li, Y.-L. *Sci. China Ser. B* **1993**, *36*, 1161.
[274] Mao, J.–M.; Li, Y.; Hou, Z.–J.; Li, Y.-L.; Liang, X.-T. *Sci. China Ser. B* **1992**, *35*, 257.
[275] Li, W.; Li, Y.; Li, Y. *Synth. Commun.* **1992**, *22*, 817.
[276] Li, Y.; Li, W.; Li, Y. L. *Synth. Commun.* **1994**, *24*, 721.
[277] Liu, Z.; Li, W. Z.; Li, Y. *Tetrahedron: Asymmetry* **2001**, *12*, 95.
[278] Yue, X.; Li, Y. *Synthesis* **1996**, 736.
[279] Li, Y.; Liu, Z.; Lan, J.; Li, J.; Peng, L.; Li, W. Z.; Li, Y.; Chan, A. S. C. *Tetrahedron Lett.* **2000**, *41*, 7465.
[280] Li, Y.; Li, W.; Li, Y. *Tetrahedron Lett.* **1992**, *33*, 1225.
[281] Liu, Z.; Zhang, T.; Li, Y. *Tetrahedron Lett.* **2001**, *42*, 275.
[282] Xing, Y.; Cen, W.; Lan, J.; Li, Y.; Li, Y. *J. Chin. Chem. Soc. (Taipei, Taiwan)* **1999**, *46*, 595.
[283] Zhang, T.; Liu, Z.; Li, Y. *Synthesis* **2001**, 393.
[284] Li, W.-D.; Li, Y.; Li, Y. *Tetrahedron Lett.* **1999**, *40*, 965.
[285] Li, W.; Mao, J.; Li, Y.; Li, Y. *Org. Prep. Proced. Int.* **1994**, *26*, 445.
[286] Dauben, W. G.; Wang, T.-Z.; Stephens, R. W. *Tetrahedron Lett.* **1990**, *31*, 2393.
[287] Li, J.; Yue, X.; Li, Y.; Hou, L.; Li, W.; Li, Y. *Bull. Soc. Chim. Belg.* **1996**, *105*, 297.
[288] Lan, J.; Liu, Z.; Li, Y.; Cen, W.; Xing, Y. *J. Chin. Chem. Soc. (Taipei, Taiwan)* **1999**, *46*, 941.
[289] Liu, Z.; Peng, L.; Li, W. Z.; Li, Y. *Synlett* **2003**, 1977.
[290] McMurry, J.; Matz, J. R.; Kees, K. L.; Bock, P. A. *Tetrahedron Lett.* **1982**, *23*, 1777.
[291] McMurry, J. E.; Matz, J. R.; Kees, K. L. *Tetrahedron* **1987**, *43*, 5489.
[292] Mermet-Mouttet, M. P.; Gabriel, K.; Heissler, D. *Tetrahedron Lett.* **1999**, *40*, 843.
[293] Brown, R. F. C.; Robinson, A. J. *Aust. J. Chem.* **1995**, *48*, 515.
[294] Maercker, A. *Org. React.* **1965**, *14*, 270.
[295] Wadsworth, Jr., W. S. *Org. React.* **1977**, *25*, 73.
[296] Murphy, P. J.; Lee, S. E. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3049.
[297] Bégúe, J. P.; Bonnet Delpon, D.; Wu, S.–W.; M'bida, A.; Shintani, T.; Nakai, T. *Tetrahedron Lett.* **1994**, *35*, 2907.
[298] Kraus, G. A.; Shi, J. *J. Org. Chem.* **1991**, *56*, 4147.
[299] Ager, D. J. *Org. React.* **1990**, *38*, 1.
[300] Kano, N.; Kawashima, T. In *Modern Carbonyl Olefination*; Takeda, T., Ed.; Wiley–VCH: Weinheim, 2004, pp 18–103.
[301] Kocienski, P. J. *Chem. Ind. (London)* **1981**, 548.
[302] Kocienski, P. *Phosphorus, Sulfur Relat. Elem.* **1985**, *24*, 97.
[303] Blakemore, P. R. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2563.
[304] Dumeunier, R.; Marko, I. E. In *Modern Carbonyl Olefination*; Takeda, T., Ed.; Wiley–VCH: Weinheim, 2004, pp 104–150.

[305] Aïssa, C. *Eur. J. Org. Chem.* **2009**, 1831.
[306] Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399.
[307] Pine, S. H. *Org. React.* **1993**, *43*, 1.
[308] Petasis, N. A. In *Transition Metals for Organic Synthesis (2nd Edition)*; Beller, M.; Bolm, C., Eds.; Wiley–VCH: Weinheim, 2004, pp 427–447.
[309] Petasis, N. A.; Lu, S.–P.; Bzowej, E. I.; Fu, D.–K.; Staszewski, J. P.; Akritopoulou–Zanze, I.; Patane, M. A.; Hu, Y. H. *Pure Appl. Chem.* **1996**, *68*, 667.
[310] Takai, K. *Org. React.* **2004**, *64*, 253.
[311] Chen, J.; Li, J.; Yu, M.-h.; Chen, W.-x.; Fu, H.–l. *Org. Prep. Proced. Int.* **1997**, *29*, 569.
[312] Nayak, S. K.; Banerji, A. *J. Org. Chem.* **1991**, *56*, 1940.
[313] Bolton, R.; Luff, S.; Sutcliffe, L. H. *J. Labelled Compd. Radiopharm.* **1995**, *36*, 1205.
[314] Kawase, T.; Ueda, N.; Tanaka, K.; Seirai, Y.; Oda, M. *Tetrahedron Lett.* **2001**, *42*, 5509.
[315] Chen, H.–B.; Yin, J.; Wang, Y.; Pei, J. *Org. Lett.* **2008**, *10*, 3113.
[316] Murata, M.; Maeda, S.; Morinaka, Y.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2008**, *130*, 15800.
[317] Stuhr-Hansen, N. *Tetrahedron Lett.* **2005**, *46*, 5491.
[318] Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224.
[319] Meier, H.; Rose, B.; Schollmeyer, D. *Liebigs Ann./Recl.* **1997**, 1173.
[320] Hughes, R. P.; Kowalski, A. S.; Lomprey, J. R.; Neithamer, D. R. *J. Org. Chem.* **1996**, *61*, 401.
[321] Begley, M. J.; Pattenden, G.; Robertson, G. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1085.
[322] Li, W.; Li, Y.; Li, Y. L. *Synthesis* **1994**, 267.
[323] Elandaloussi, E. H.; Frère, P.; Benahmed-Gasmi, A.; Riou, A.; Gorgues, A.; Roncali, J. *J. Mater. Chem.* **1996**, *6*, 1859.
[324] Nakayama, J.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1986**, *24*, 2639.
[325] Starčević, K.; Boykin, D. W.; Karminski-Zamola, G. *Heteroat. Chem.* **2003**, *14*, 218.
[326] Nakayama, J.; Fujimori, T. *Heterocycles* **1991**, *32*, 991.
[327] Chen, R.; Yang, X.; Tian, H.; Wang, X.; Hagfeldt, A.; Sun, L. *Chem. Mater.* **2007**, *19*, 4007.
[328] Yamamoto, T.; Miyazaki, E.; Takimiya, K. *Heterocycles* **2008**, *76*, 583.
[329] Akoudad, S.; Frère, P.; Mercier, N.; Roncali, J. *J. Org. Chem.* **1999**, *64*, 4267.
[330] Harwood, L. M.; Jones, G.; Pickard, J.; Thomas, R. M.; Watkin, D. *Tetrahedron Lett.* **1988**, *29*, 5825.
[331] Carroll, A. R.; Taylor, W. C. *Aust. J. Chem.* **1990**, *43*, 1439.
[332] Banerji, A.; Nayak, S. K. *J. Chem. Soc., Chem. Commun.* **1991**, 1432.
[333] Talukdar, S.; Nayak, S. K.; Banerji, A. *Fullerene Sci. Technol.* **1995**, *3*, 327.
[334] Zhang, W.; Go, M. L. *Eur. J. Med. Chem.* **2007**, *42*, 841.
[335] Warren, S.; Wyatt, P.; McPartlin, M.; Woodroffe, T. *Tetrahedron Lett.* **1996**, *37*, 5609.
[336] Warren, S.; Wyatt, P. *Tetrahedron: Asymmetry* **1996**, *7*, 989.
[337] Létard, J.-F.; Lapouyade, R.; Rettig, W. *Chem. Phys. Lett.* **1994**, *222*, 209.
[338] Sigalov, M.; Ben-Asuly, A.; Shapiro, L.; Ellern, A.; Khodorkovsky, V. *Tetrahedron Lett.* **2000**, *41*, 8573.
[339] Tanner, D.; Johansson, F.; Harden, A.; Andersson, P. G. *Tetrahedron* **1998**, *54*, 15731.
[340] Wang, X.; Zhou, G.; Wang, D.; Wang, C.; Fang, Q.; Jiang, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1977.
[341] Afonso, C. A. M.; Motherwell, W. B.; O'Shea, D. M.; Roberts, L. R. *Tetrahedron Lett.* **1992**, *33*, 3899.
[342] Rauniyar, V.; Hall, D. G. *J. Org. Chem.* **2009**, *74*, 4236.
[343] Bhatt, S.; Nayak, S. K. *Tetrahedron Lett.* **2009**, *50*, 5823.
[344] Hirsenkorn, R. *Tetrahedron Lett.* **1990**, *31*, 7591.
[345] Cheng, J.-C.; Fang, J.-G.; Chen, W.-F.; Zhou, B.; Yang, L.; Liu, Z.–L. *Bioorg. Chem.* **2006**, *34*, 142.
[346] Shadakshari, U.; Rele, S.; Nayak, S. K.; Chattopadhyay, S. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **2004**, *43*, 1934.
[347] Guha, P.; Dey, A.; Sarkar, B.; Dhyani, M. V.; Chattopadhyay, S.; Bandyopadhyay, S. K. *J. Pharmacol. Exp. Ther.* **2009**, *328*, 829.

[348] Wyatt, P.; Warren, S.; McPartlin, M.; Woodroffe, T. *J. Chem. Soc., Perkin Trans. 1* **2001**, 279.
[349] Castedo, L.; Saá, J. M.; Suau, R.; Tojo, G. *J. Org. Chem.* **1981**, *46*, 4292.
[350] Ali, M. A.; Kondo, K.; Tsuda, Y. *Chem. Pharm. Bull.* **1992**, *40*, 1130.
[351] Schertl, S.; Hartmann, R. W.; Batzl-Hartmann, C.; Schlemmer, R.; Spruss, T.; Bernhardt, G.; Gust, R.; Schönenberger, H. *Arch. Pharm. (Weinheim)* **2001**, *334*, 125.
[352] Subramanian, M.; Shadakshari, U.; Chattopadhyay, S. *Bioorg. Med. Chem.* **2004**, *12*, 1231.
[353] Donnoli, M. I.; Scafato, P.; Superchi, S.; Rosini, C. *Chirality* **2001**, *13*, 258.
[354] Lindsten, G.; Wennerström, O.; Thulin, B. *Acta Chem. Scand. Ser. B* **1986**, *40*, 545.
[355] Snider, B. B.; Jackson, A. C. *J. Org. Chem.* **1983**, *48*, 1471.
[356] Maeda, H.; Nishimura, K.; Mizuno, K.; Yamaji, M.; Oshima, J.; Tobita, S. *J. Org. Chem.* **2005**, *70*, 9693.
[357] Boeré, R. T.; Robbins, S. J. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2008**, *E64*, o363.
[358] Witiak, D. T.; Kamat, P. L.; Allison, D. L.; Liebowitz, S. M.; Glaser, R.; Holliday, J. E.; Moeschberger, M. L.; Schaller, J. P. *J. Med. Chem.* **1983**, *26*, 1679.
[359] Peeters, E.; van Hal, P. A.; Knol, J.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *104*, 10174.
[360] Zimmerman, H. E.; Kamath, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 900.
[361] Gapski, G.; Kini, A.; Liu, R. S. H. *Chem. Lett.* **1978**, 803.
[362] Fritsch, R.; Hartmann, E.; Andert, D.; Mannschreck, A. *Chem. Ber.* **1992**, *125*, 849.
[363] Mannschreck, A.; Hartmann, E.; Buchner, H.; Andert, D. *Tetrahedron Lett.* **1987**, *28*, 3479.
[364] Saltiel, J.; Wang, S. *Photochem. Photobiol. Sci.* **2006**, *5*, 883.
[365] Ray, J. K.; Gupta, S.; Raj, S. S. S.; Fun, H.-K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *C55*, 1847.
[366] Wallace, R. H.; Lu, Y.; Liu, J.; Atwood, J. L. *Synlett* **1992**, 992.
[367] Mallory, F. B.; Butler, K. E.; Bérubé, A.; Luzik, Jr., E. D.; Mallory, C. W.; Brondyke, E. J.; Hiremath, R.; Ngo, P.; Carroll, P. J. *Tetrahedron* **2001**, *57*, 3715.
[368] Bringmann, G.; Pabst, T.; Henschel, P.; Michel, M. *Tetrahedron* **2001**, *57*, 1269.
[369] Merz, A.; Gromann, L.; Karl, A.; Parkanyi, L.; Schneider, O. *Eur. J. Org. Chem.* **1998**, 403.
[370] Maiorana, S.; Papagni, A.; Licandro, E.; Annunziata, R.; Paravidino, P.; Perdicchia, D.; Giannini, C.; Bencini, M.; Clays, K.; Persoons, A. *Tetrahedron* **2003**, *59*, 6481.
[371] Lee, H.-J.; Noh, D.-Y. *Synth. Met.* **1999**, *102*, 1696.
[372] Neidlein, R.; Winkler, R. *Collect. Czech. Chem. Commun.* **1991**, *56*, 2258.
[373] Agustsson, S. O.; Hu, C.; Englert, U.; Marx, T.; Wesemann, L.; Ganter, C. *Organometallics* **2002**, *21*, 2993.
[374] Ishii, T.; Sawada, T.; Mataka, S.; Tashiro, M.; Thiemann, T. *Chem. Ber.* **1996**, *129*, 289.
[375] Simokaitiene, J.; Grigalevicius, S.; Grazulevicius, J. V.; Rutkaite, R.; Kazlauskas, K.; Jursenas, S.; Jankauskas, V.; Sidaravicius, J. *J. Optoelectron. Adv. Mater.* **2006**, *8*, 876.
[376] Chen, C.-H.; Lin, J. T.; Yeh, M.-C. P. *Tetrahedron* **2006**, *62*, 8564.
[377] Song, Y.; Di, C.-a.; Wei, Z.; Zhao, T.; Xu, W.; Liu, Y.; Zhang, D.; Zhu, D. *Chem.-Eur. J.* **2008**, *14*, 4731.
[378] Elandaloussi, E. H.; Frère, P.; Roncali, J. *Tetrahedron Lett.* **1996**, *37*, 6121.
[379] Mandai, T.; Yamaguchi, H.; Nishikawa, K.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1981**, *22*, 763.
[380] Stuhr-Hansen, N.; Christensen, J. B.; Harrit, N.; Bjørnholm, T. *J. Org. Chem.* **2003**, *68*, 1275.
[381] Cravey, M. J.; Doss, D. J. *J. Org. Chem.* **1988**, *53*, 5963.
[382] Hu, Y.; Wex, B.; Perkovic, M. W.; Neckers, D. C. *Tetrahedron* **2008**, *64*, 2251.
[383] Larsen, J.; Bechgaard, K. *Acta Chem. Scand.* **1996**, *50*, 71.
[384] Märkl, G.; Aschenbrenner, N.; Baur, A.; Rastorfer, C.; Kreitmeier, P. *Helv. Chim. Acta* **2003**, *86*, 2589.
[385] Jestin, I.; Frère, P.; Blanchard, P.; Roncali, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 942.
[386] Jestin, I.; Frère, P.; Mercier, N.; Levillain, E.; Stievenard, D.; Roncali, J. *J. Am. Chem. Soc.* **1998**, *120*, 8150.

[387] Oswald, F.; Islam, D.–M. S.; Araki, Y.; Troiani, V.; de la Cruz, P.; Moreno, A.; Ito, O.; Langa, F. *Chem.—Eur. J.* **2007**, *13*, 3924.
[388] Ono, N.; Okumura, H.; Murashima, T. *Heteroat. Chem.* **2001**, *12*, 414.
[389] Thomas, K. R. J.; Lin, J. T.; Wen, Y. S. *Organometallics* **2000**, *19*, 1008.
[390] Jung, M. E.; Liu, C.-Y. *J. Org. Chem.* **1986**, *51*, 5446.
[391] Tsuge, A.; Nishimoto, T.; Uchida, T.; Yasutake, M.; Moriguchi, T.; Sakata, K. *J. Org. Chem.* **1999**, *64*, 7246.
[392] Siutkowski, M.; Mercier, F.; Ricard, L.; Mathey, F. *Organometallics* **2006**, *25*, 2585.
[393] Blanchard, P.; Verlhac, P.; Michaux, L.; Frére, P.; Roncali, J. *Chem.—Eur. J.* **2006**, *12*, 1244.
[394] Paolesse, R.; Pandey, R. K.; Forsyth, T. P.; Jaquinod, L.; Gerzevske, K. R.; Nurco, D. J.; Senge, M. O.; Licoccia, S.; Boschi, T.; Smith, K. M. *J. Am. Chem. Soc.* **1996**, *118*, 3869.
[395] Pandey, R. K.; Forsyth, T. P.; Gerzevske, K. R.; Lin, J. J.; Smith, K. M. *Tetrahedron Lett.* **1992**, *33*, 5315.
[396] Goswami, L. N.; Ethirajan, M.; Dobhal, M. P.; Zhang, M.; Missert, J. R.; Shibata, M.; Kadish, K. M.; Pandey, R. K. *J. Org. Chem.* **2009**, *74*, 568.
[397] Jaquinod, L.; Nurco, D. J.; Medforth, C. J.; Pandey, R. K.; Forsyth, T. P.; Olmstead, M. M.; Smith, K. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1013.
[398] Senge, M. O.; Kalisch, W. W.; Ruhlandt-Senge, K. *Chem. Commun.* **1996**, 2149.
[399] Cosmo, R.; Kautz, C.; Meerholz, K.; Heinze, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 604.
[400] Wang, J.-L.; Duan, X.-F.; Jiang, B.; Gan, L.-B.; Pei, J.; He, C.; Li, Y.-F. *J. Org. Chem.* **2006**, *71*, 4400.
[401] Gano, J. E.; Lenoir, D.; Park, B.-S.; Roesner, R. A. *J. Org. Chem.* **1987**, *52*, 5636.
[402] Bellucci, G.; Bianchini, R.; Chiappe, C.; Lenoir, D.; Attar, A. *J. Am. Chem. Soc.* **1995**, *117*, 6243.
[403] Doering, W. von E.; Kitagawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 4288.
[404] Doering, W. von E.; Roth, W. R.; Bauer, F.; Breuckmann, R.; Ebbrecht, T.; Herbold, M.; Schmidt, R.; Lennartz, H.-W.; Lenoir, D.; Boese, R. *Chem. Ber.* **1989**, *122*, 1263.
[405] Klein, O.; Hopf, H.; Grunenberg, J. *Eur. J. Org. Chem.* **2009**, 2141.
[406] Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1781.
[407] Sander, M.; Dehmlow, E. V. *Eur. J. Org. Chem.* **2001**, 399.
[408] Zhu, B. L.; Miljanić, O. Š.; Vollhardt, K. P. C.; West, M. J. *Synthesis* **2005**, 3373.
[409] Wang, Y.; Doering, W. von E.; Staples, R. J. *J. Chem. Crystallogr.* **1999**, *29*, 977.
[410] Nelsen, S. F.; Reinhardt, L. A. *J. Phys. Org. Chem.* **2001**, *14*, 847.
[411] Blanchard, P.; Brisset, H.; Illien, B.; Riou, A.; Roncali, J. *J. Org. Chem.* **1997**, *62*, 2401.
[412] Kakiuchi, K.; Okada, H.; Kanehisa, N.; Kai, Y.; Kurosawa, H. *J. Org. Chem.* **1996**, *61*, 2972.
[413] Ayats, C.; Camps, P.; Fernández, J. A.; Vázquez, S. *Chem.—Eur. J.* **2007**, *13*, 1522.
[414] Andersson, P. G. *Tetrahedron Lett.* **1994**, *35*, 2609.
[415] Anke, L.; Reinhard, D.; Weyerstahl, P. *Liebigs Ann. Chem.* **1981**, 591.
[416] Kadam, S. M.; Nayak, S. K.; Banerji, A. *Synth. Commun.* **1995**, *25*, 135.
[417] Richardson, W. H. *Synth. Commun.* **1981**, *11*, 895.
[418] Daik, R.; Feast, W. J.; Batsanov, A. S.; Howard, J. A. K. *New J. Chem.* **1998**, *22*, 1047.
[419] Nayak, S. K.; Banerji, A. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **1991**, *30*, 286.
[420] Bottino, F. A.; Finocchiaro, P.; Libertini, E.; Reale, A.; Recca, A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 77.
[421] Schneider, S.; Brem, B.; Jäger, W.; Rehaber, H.; Lenoir, D.; Frank, R. *Chem. Phys. Lett.* **1999**, *308*, 211.
[422] Besançon, J.; Szymoniak, J.; Moïse, C. *J. Organomet. Chem.* **1992**, *426*, 325.
[423] Amposta, R.; Camps, P.; Figueredo, M.; Jaime, C.; Virgili, A. *An. Quim., Ser. C* **1981**, *77*, 267.
[424] Kochanny, M. J.; Härd, T.; Katzenellenbogen, J. A. *Magn. Reson. Chem.* **1993**, *31*, 977.
[425] Rhee, C. K.; Chae, K.; Levy, L. A.; Korach, K. S. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 133.
[426] Chen, W.-X.; Feng, J.-C.; Zhou, Z.-L.; Zhang, J.-H. *Synthesis* **1989**, 182.
[427] De Clercq, P. J.; Van Peteghem, C. H.; Jonckheere, J. A.; Deleenheer, A. P. *J. Labelled Compd. Radiopharm.* **1984**, *21*, 649.
[428] McLachlan, J. A.; Baucom, K.; Korach, K. S.; Levy, L.; Metzler, M. *Steroids* **1979**, *33*, 543.

[429] Khoury, R. G.; Jaquinod, L.; Smith, K. M. *Chem. Commun.* **1997**, 1057.
[430] Lenoir, D.; Lemmen, P. *Chem. Ber.* **1980**, *113*, 3112.
[431] Saltiel, J.; Mace, J. E.; Watkins, L. P.; Gormin, D. A.; Clark, R. J.; Dmitrenko, O. *J. Am. Chem. Soc.* **2003**, *125*, 16158.
[432] Lemmen, P.; Lenoir, D. *Chem. Ber.* **1984**, *117*, 2300.
[433] Tolstikov, G. A.; Lerman, B. M.; Belogaeva, T. A. *Synth. Commun.* **1991**, *21*, 877.
[434] Doering, W. von E.; Birladeanu, L.; Cheng, X.-H.; Kitagawa, T.; Sarma, K. *J. Am. Chem. Soc.* **1991**, *113*, 4558.
[435] Wenck, H.; de Meijere, A.; Gerson, F.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 335.
[436] Hwang, K.–J.; Carlson, K. E.; Anstead, G. M.; Katzenellenbogen, J. A. *Biochemistry* **1992**, *31*, 11536.
[437] Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1977**, *42*, 580.
[438] Nickon, A.; Zurer, P. St. Jr.; Hrnjez, B.; Tino, J. *Tetrahedron* **1983**, *39*, 2679.
[439] Doering, W. von E.; Shi, Y.-q.; Zhao, D.-c. *J. Am. Chem. Soc.* **1992**, *114*, 10763.
[440] Doering, W. von E.; Birladeanu, L.; Sarma, K.; Shao, L.-S. *J. Am. Chem. Soc.* **1996**, *118*, 6660.
[441] Yamamoto, K.; Ojima, J.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1281.
[442] Yamamoto, K.; Ojima, J.; Morita, N.; Asao, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1851.
[443] Olah, G. A.; Prakash, G. K. S.; Liang, G. *Synthesis* **1976**, 318.
[444] Sofikiti, N.; Tofi, M.; Montagnon, T.; Vassilikogiannakis, G.; Stratakis, M. *Org. Lett.* **2005**, *7*, 2357.
[445] Ikeda, H.; Sakai, A.; Namai, H.; Kawabe, A.; Mizuno, K. *Tetrahedron Lett.* **2007**, *48*, 8338.
[446] Shimasaki, T.; Kato, S.; Shinmyozu, T. *J. Org. Chem.* **2007**, *72*, 6251.
[447] Blanchard, P.; Riou, A.; Roncali, J. *J. Org. Chem.* **1998**, *63*, 7107.
[448] Vögtle, F.; Thilgen, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1162.
[449] Cory, R. M.; Walker, J. R.; Zabel, P. D. *Synth. Commun.* **1994**, *24*, 799.
[450] Blanchard, P.; Brisset, H.; Riou, A.; Hierle, R.; Roncali, J. *J. Org. Chem.* **1998**, *63*, 8310.
[451] Blanchard, P.; Brisset, H.; Riou, A.; Hierle, R.; Roncali, J. *New J. Chem.* **1998**, *22*, 547.
[452] Laatsch, H.; Talvitie, A.; Kral, A.; Ernst, B.-P.; Moltemeyer, M. *J. Prakt. Chem.-Chem. Ztg.* **1996**, *338*, 140.
[453] Anderson, J. E.; Bettels, B. R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1121.
[454] Pollard, M. M.; Meetsma, A.; Feringa, B. L. *Org. Biomol. Chem.* **2008**, *6*, 507.
[455] Andersen, N. G.; Parvez, M.; Keay, B. A. *Org. Lett.* **2000**, *2*, 2817.
[456] Chen, Y. J.; Pan, D.-S.; Chiu, C.-F.; Su, J.-X.; Lin, S. J.; Kwan, K. S. *Inorg. Chem.* **2000**, *39*, 953.
[457] Chiu, C.-F.; Song, M.; Chen, B.-H.; Kwan, K. S. *Inorg. Chim. Acta* **1997**, *266*, 73.
[458] Gano, J. E.; Osborn, III, D. J.; Kodali, N.; Sekher, P.; Liu, M.; Luzik, E. D. *J. Org. Chem.* **2003**, *68*, 3710.
[459] Columbus, I.; Biali, S. E. *J. Org. Chem.* **1994**, *59*, 3402.
[460] Columbus, I.; Biali, S. E. *Chirality* **1998**, *10*, 159.
[461] Tong, H.; Hong, Y. N.; Dong, Y.; Häußler, M.; Li, Z.; Lam, J. W. Y.; Dong, Y. P.; Sung, H. H. Y.; Williams, I. D.; Tang, B. Z. *J. Phys. Chem. B* **2007**, *111*, 11817.
[462] Chung, M.-K.; Fancy, P.; Stryker, J. M. *Can. J. Chem.* **2006**, *84*, 1250.
[463] Kuntz, J.-F.; Schneider, R.; Walcarius, A.; Fort, Y. *Tetrahedron Lett.* **2005**, *46*, 8793.
[464] Hong, Y.; Häußler, M.; Lam, J. W. Y.; Li, Z.; Sin, K. K.; Dong, Y; Tong, H.; Liu, J.; Qin, A.; Renneberg, R.; Tang, B. Z. *Chem.—Eur. J.* **2008**, *14*, 6428.
[465] Schreivogel, A.; Maurer, J.; Winter, R.; Baro, A.; Laschat, S. *Eur. J. Org. Chem.* **2006**, 3395.
[466] Schultz, A.; Diele, S.; Laschat, S.; Nimtz, M. *Adv. Funct. Mater.* **2001**, *11*, 441.
[467] Hussain, Z.; Hopf, H.; Oeser, T. *Lett. Org. Chem.* **2005**, *2*, 518.
[468] Schultz, A.; Laschat, S.; Diele, S.; Nimtz, M. *Eur. J. Org. Chem.* **2003**, 2829.
[469] Chung, M.-K.; Qi, G.; Stryker, J. M. *Org. Lett.* **2006**, *8*, 1491.
[470] Navale, T. S.; Zhai, L.; Lindeman, S. V.; Rathore, R. *Chem. Commun.* **2009**, 2857.
[471] Fürstner, A.; Hupperts, A.; Seidel, G. *Org. Synth.* **1999,** *76* 142.
[472] Belen'kii, L. I.; Gromova, G. P.; Kolotaev, A. V.; Nabatov, B. V.; Krayushkin, M. M. *Russ. Chem. Bull.* **2005**, *54*, 1208.

[473] Halvorsen, H.; Skramstad, J.; Hope, H. *Synth. Commun.* **2007**, *37*, 1179.
[474] Larsen, J.; Bechgaard, K. *Acta Chem. Scand.* **1996**, *50*, 77.
[475] Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6931.
[476] ter Wiel, M. K. J.; Koumura, N.; van Delden, R. A.; Meetsma, A.; Harada, N.; Feringa, B. L. *Chirality* **2000**, *12*, 734.
[477] ter Wiel, M. K. J.; van Delden, R. A.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2003**, *125*, 15076.
[478] ter Wiel, M. K. J.; Feringa, B. L. *Synthesis* **2005**, 1789.
[479] Harada, N.; Saito, A.; Koumura, N.; Uda, H.; deLange, B.; Jager, W. F.; Wynberg, H.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7241.
[480] Schwager, H.; Wilke, G. *Chem. Ber.* **1987**, *120*, 79.
[481] Dang, Y.; Geise, H.; Dommisse, R.; Esmans, E. *Inorg. Chim. Acta* **1990**, *175*, 115.
[482] Lorcy, D.; Rault-Berthelot, J.; Poriel, C. *Electrochem. Commun.* **2000**, *2*, 382.
[483] Willem, R.; Pepermans, H.; Hallenga, K.; Gielen, M.; Dams, R.; Geise, H. J. *J. Org. Chem.* **1983**, *48*, 1890.
[484] Grützmacher, H.-F.; Husemann, W. *Tetrahedron Lett.* **1985**, *26*, 2431.
[485] Shultz, D. A.; Fox, M. A. *Tetrahedron Lett.* **1988**, *29*, 4377.
[486] Keyes, R. F.; Cushman, M. *Med. Chem. Res.* **1996**, *6*, 372.
[487] Koumura, N.; Osawa, S.; Harada, N. *Enantiomer* **2000**, *5*, 129.
[488] Agranat, I.; Cohen, S.; Isaksson, R.; Sandström, J.; Suissa, M. R. *J. Org. Chem.* **1990**, *55*, 4943.
[489] ter Wiel, M. K. J.; van Delden, R. A.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 14208.
[490] van Delden, R. A.; ter Wiel, M. K. J.; Feringa, B. L. *Chem. Commun.* **2004**, 200.
[491] Tapuhi, Y.; Suissa, M. R.; Cohen, S.; Biedermann, P. U.; Levy, A.; Agranat, I. *J. Chem. Soc. Perkin Trans. 2* **2000**, 93.
[492] Hopf, H.; Kreutzer, M.; Jones, P. G. *Chem. Ber.* **1991**, *124*, 1471.
[493] Jousselme, B.; Blanchard, P.; Frère, P.; Roncali, J. *Tetrahedron Lett.* **2000**, *41*, 5057.
[494] Nützel, R.; Haslinger, E. *Fett. Wiss. Technol.* **1995**, *97*, 137.
[495] Matile, S.; Berova, N.; Nakanishi, K.; Fleischhauer, J.; Woody, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 5198.
[496] Kim, S.–K.; Park, Y.–I.; Park, J.–W. *Mol. Cryst. Liq. Cryst.* **2006**, *458*, 209.
[497] Märkl, G.; Hafner, M.; Kreitmeier, P.; Stadler, C.; Daub, J.; Nöth, H.; Schmidt, M.; Gescheidt, G. *Helv. Chim. Acta* **1997**, *80*, 2456.
[498] Heirtzler, F. R.; Hopf, H.; Jones, P. G.; Bubenitschek, P. *Tetrahedron Lett.* **1995**, *36*, 1239.
[499] Gano, J. E.; Kirschbaum, K.; Luzik, Jr., E. D.; Sekher, P. *Tetrahedron Lett.* **1998**, *39*, 6641.
[500] Kim, S.-K.; Park, Y.-I.; Park, J.-W.; Kim, K.-S.; Choi, C.-K.; Lee, S.-D. *Mol. Cryst. Liq. Cryst.* **2007**, *462*, 209.
[501] Grieser, U.; Hafner, K. *Tetrahedron Lett.* **1994**, *35*, 7759.
[502] Caroli, G.; Kwit, M. G.; Feringa, B. L. *Tetrahedron* **2008**, *64*, 5956.
[503] Khotina, I. A.; Izumrudov, V. A.; Tchebotareva, N. V.; Rusanov, A. L. *Macromol. Chem. Phys.* **2001**, *202*, 2360.
[504] Kim, S.-K.; Park, J.-W.; Oh, S.-Y. *Mol. Cryst. Liq. Cryst.* **2007**, *471*, 89.
[505] Shimasaki, T.; Kato, S.; Ideta, K.; Goto, K.; Shinmyozu, T. *J. Org. Chem.* **2007**, *72*, 1073.
[506] Cao, X.-Y.; Zhang, W.; Zi, H.; Pei, J. *Org. Lett.* **2004**, *6*, 4845.
[507] Agbaria, K.; Biali, S. E. *J. Org. Chem.* **2001**, *66*, 5482.
[508] Reference deleted.
[509] Li, J.; Liu, Z.; Lan, J.; Li, Y. *J. Chin. Chem. Soc. (Taipei, Taiwan)* **1999**, *46*, 259.
[510] Li, J.; Liu, Z.; Lan, J.; Li, Y. *Chem. Lett.* **1997**, 229.
[511] Seijas, J. A.; de Lera, A. R.; Villaverde, M. C.; Castedo, L. *J. Chem. Soc., Chem. Commun.* **1985**, 839.
[512] De Boeck, B.; Harrington-Frost, N. M.; Pattenden, G. *Org. Biomol. Chem.* **2005**, *3*, 340.
[513] De Boeck, B.; Pattenden, G. *Tetrahedron Lett.* **1998**, *39*, 6975.
[514] McMurry, J. E.; Dushin, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6942.

[515] Bonazzola, L.; Michaut, J.–P.; Roncin, J.; Misawa, H.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 347.
[516] Feringa, B.; Wynberg, H. *Recl. Trav. Chim. Pay–Bas* **1978**, *97*, 249.
[517] Yu, D. D.; Forman, B. M. *J. Org. Chem.* **2003**, *68*, 9489.
[518] Seo, J. W.; Comninos, J. S.; Chi, D. Y.; Kim, D. W.; Carlson, K. E.; Katzenellenbogen, J. A. *J. Med. Chem.* **2006**, *49*, 2496.
[519] Ruasse, M.-F.; Motallebi, S.; Galland, B.; Lomas, J. S. *J. Org. Chem.* **1990**, *55*, 2298.
[520] Loza, M. I.; Sanz, F.; Cadavid, M. I.; Honrubia, M.; Orallo, F.; Fontenla, J. A.; Calleja, J. M.; Dot, T.; Manaut, F.; Cid, M. M.; Dominguez, R.; Seijas, J. A.; Villaverde, M. C. *J. Pharm. Sci.* **1993**, *82*, 1090.
[521] Cid, M. M.; Seijas, J. A.; Villaverde, M. C.; Castedo, L. *Tetrahedron* **1988**, *44*, 6197.
[522] Xu, G.; Kannan, A.; Hartman, T. L.; Wargo, H.; Watson, K.; Turpin, J. A.; Buckheit, Jr., R. W.; Johnson, A. A.; Pommier, Y.; Cushman, M. *Bioorg. Med. Chem.* **2002**, *10*, 2807.
[523] Honrubia, M. A.; Rodriguez, J.; Dominguez, R.; Lozoya, E.; Manaut, F.; Seijas, J. A.; Villaverde, M. C.; Calleja, J. M.; Cadavid, M. I.; Maayani, S.; Sanz, F.; Loza, M. I. *Chem. Pharm. Bull.* **1997**, *45*, 842.
[524] Zhang, X.; Rice, K. C.; Calderon, S. N.; Kayakiri, H.; Smith, L.; Coop, A.; Jacobson, A. E.; Rothman, R. B.; Davis, P.; Dersch, C. M.; Porreca, F. *J. Med. Chem.* **1999**, *42*, 5455.
[525] Gao, M.; Wang, M.; Mock, B. H.; Miller, K. D.; Sledge, G. W.; Hutchins, G. D.; Zheng, Q.-H. *Appl. Radiat. Isot.* **2008**, *66*, 523.
[526] Gärtner, P.; Hofbauer, K.; Reichel, C.; Geisendorfer, T.; Gmeiner, G. *J. Mass Spectrom.* **2008**, *43*, 958.
[527] Pettersson, I.; Berg, U. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1365.
[528] Pettersson, I.; Berg, U. *J. Chem. Res. (S)* **1984**, 208.
[529] Muthyala, R. S.; Sheng, S.; Carlson, K. E.; Katzenellenbogen, B. S.; Katzenellenbogen, J. A. *J. Med. Chem.* **2003**, *46*, 1589.
[530] Uddin, M. J.; Rao, P. N. P.; Knaus, E. E. *Bioorg. Med. Chem.* **2005**, *13*, 417.
[531] Meegan, M. J.; Hughes, R. B.; Lloyd, D. G.; Williams, D. C.; Zisterer, D. M. *Anti-Cancer Drug Des.* **2001**, *16*, 57.
[532] Muthyala, R. S.; Carlson, K. E.; Katzenellenbogen, J. A. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 4485.
[533] Uddin, M. J.; Rao, P. N. P.; Knaus, E. E. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 1953.
[534] Uddin, M. J.; Rao, P. N. P.; Knaus, E. E. *Bioorg. Med. Chem.* **2004**, *12*, 5929.
[535] Tanpure, R. P.; Harkrider, A. R.; Strecker, T. E.; Hamel, E.; Trawick, M. L.; Pinney, K. G. *Bioorg. Med. Chem.* **2009**, *17*, 6993.
[536] Zheng, L.; Wei, Q.; Zhou, B.; Yang, L.; Liu, Z.-L. *Anti-Cancer Drugs* **2007**, *18*, 1039.
[537] Richardson, W. H.; Thomson, S. A. *J. Org. Chem.* **1985**, *50*, 1803.
[538] Top, S.; Kaloun, E. B.; Vessières, A.; Laïos, I.; Leclercq, G.; Jaouen, G. *J. Organomet. Chem.* **2002**, *643–644*, 350.
[539] Top, S.; Kaloun, E. B.; Jaouen, G. *J. Am. Chem. Soc.* **2000**, *122*, 736.
[540] Top, S.; Kaloun, E. B.; Toppi, S.; Herrbach, A.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **2001**, *20*, 4554.
[541] Hillard, E. A.; Vessières, A.; Top, S.; Pigeon, P.; Kowalski, K.; Huché, M.; Jaouen, G. *J. Organomet. Chem.* **2007**, *692*, 1315.
[542] Top, S.; Vessières, A.; Pigeon, P.; Rager, M.–N.; Huché, M.; Salomon, E.; Cabestaing, C.; Vaissermann, J.; Jaouen, G. *ChemBioChem* **2004**, *5*, 1104.
[543] Jaouen, G.; Top, S.; Vessiéres, A.; Pigeon, P.; Leclercq, G.; Laios, I. *Chem. Commun.* **2001**, 383.
[544] Pons, J.; Santelli, M. *Tetrahedron* **1990**, *46*, 513.
[545] Schwarz, W.; Hartmann, R. W.; Schönenberger, H. *Arch. Pharm.* **1991**, *324*, 223.
[546] Pigeon, P.; Top, S.; Zekri, O.; Hillard, E. A.; Vessières, A.; Plamont, M.-A.; Buriez, O.; Labbé, E.; Huché, M.; Boutamine, S.; Amatore, C.; Jaouen, G. *J. Organomet. Chem.* **2009**, *694*, 895.
[547] Shi, Y.; Koh, J. T. *ChemBioChem* **2004**, *5*, 788.
[548] Vessiéres, A.; Top, S.; Pigeon, P.; Hillard, E.; Boubeker, L.; Spera, D.; Jaouen, G. *J. Med. Chem.* **2005**, *48*, 3937.

[549] Rubin, V. N.; Ruenitz, P. C.; Boudinot, F. D.; Boyd, J. L. *Bioorg. Med. Chem.* **2001**, *9*, 1579.
[550] McGlinchey, M. J.; Nikitin, K.; Ortin, Y.; Müller-Bunz, H.; Plamont, M.-A.; Jaouen, G.; Vessières, A. *J. Organomet. Chem.* **2010**, *695*, 595.
[551] Ruenitz, P. C.; Bourne, C. S.; Sullivan, K. J.; Moore, S. A. *J. Med. Chem.* **1996**, *39*, 4853.
[552] Kraft, K. S.; Ruenitz, P. C.; Bartlett, M. G. *J. Med. Chem.* **1999**, *42*, 3126.
[553] Chao, E. Y. H.; Collins, J. L.; Gaillard, S.; Miller, A. B.; Wang, L.; Orband-Miller, L. A.; Nolte, R. T.; McDonnell, D. P.; Willson, T. M.; Zuercher, W. J. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 821.
[554] Meegan, M. J.; Hughes, R. B.; Lloyd, D. G.; Williams, D. C.; Zisterer, D. M. *J. Med. Chem.* **2001**, *44*, 1072.
[555] Lloyd, D. G.; Smith, H. M.; O'Sullivan, T.; Knox, A. S.; Zisterer, D. M.; Meegan, M. J. *Medicinal Chemistry* **2006**, *2*, 147.
[556] Jan, S.-T.; Rogan, E. G.; Cavalieri, E. L. *Chem. Res. Toxicol.* **1998**, *11*, 408.
[557] Nguyen, A.; Top, S.; Vessiéres, A.; Pigeon, P.; Huché, M.; Hillard, E. A.; Jaouen, G. *J. Organomet. Chem.* **2007**, *692*, 1219.
[558] Nguyen, A.; Top, S.; Pigeon, P.; Vessières, A.; Hillard, E. A.; Plamont, M.-A.; Huché, M.; Rigamonti, C.; Jaouen, G. *Chem.—Eur. J.* **2009**, *15*, 684.
[559] Dobrydneva, Y.; Weatherman, R. V.; Trebley, J. P.; Morrell, M. M.; Fitzgerald, M. C.; Fichandler, C. E.; Chatterjie, N.; Blackmore, P. F. *J. Cardiovasc. Pharmacol.* **2007**, *50*, 380.
[560] Gauthier, S.; Mailhot, J.; Labrie, F. *J. Org. Chem.* **1996**, *61*, 3890.
[561] Letard, J.-F.; Lapouyade, R.; Rettig, W. *Mol. Cryst. Liq. Cryst.* **1993**, *234*, 581.
[562] Asveld, E. W. H.; Kellogg, R. M. *J. Org. Chem.* **1982**, *47*, 1250.
[563] Kim, S.-H.; Katzenellenbogen, J. A. *Bioorg. Med. Chem.* **2000**, *8*, 785.
[564] Imanishi, T.; Ueda, Y.; Minagawa, M.; Hoshino, N.; Miyashita, K. *Tetrahedron Lett.* **1997**, *38*, 3967.
[565] Imanishi, T.; Ueda, Y.; Tainaka, R.; Miyashita, K.; Hoshino, N. *Tetrahedron Lett.* **1997**, *38*, 841.
[566] Miyashita, K.; Minagawa, M.; Ueda, Y.; Tada, Y.; Hoshino, N.; Imanishi, T. *Tetrahedron* **2001**, *57*, 3361.
[567] Chan, K. H.; Leong, W. K.; Jaouen, G.; Leclerq, L.; Top, S.; Vessières, A. *J. Organomet. Chem.* **2006**, *691*, 9.
[568] Duan, X.-F.; Zeng, J.; Lü, J.-W.; Zhang, Z.-B. *Synthesis* **2007**, 713.
[569] Top, S.; Kaloun, E. B.; Vessières, A.; Leclercq, G.; Laïos, I.; Ourevitch, M.; Deuschel, C.; McGlinchey, M. J.; Jaouen, G. *ChemBioChem* **2003**, *4*, 754.
[570] Ortin, Y.; Grealis, J.; Scully, C.; Müller-Bunz, H.; Manning, A. R.; McGlinchey, M. J. *J. Organomet. Chem.* **2004**, *689*, 4683.
[571] Gupta, A.; Dwivedy, A.; Keshri, G.; Sharma, R.; Balapure, A. K.; Singh, M. M.; Ray, S. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 6006.
[572] Zekri, O.; Hillard, E. A.; Top, S.; Vessières, A.; Pigeon, P.; Plamont, M.-A.; Huché, M.; Boutamine, S.; McGlinchey, M. J.; Müller-Bunz, H.; Jaouen, G. *Dalton Trans.* **2009**, 4318.
[573] Top, S.; Dauer, B.; Vaissermann, J.; Jaouen, G. *J. Organomet. Chem.* **1997**, *541*, 355.
[574] Jaouen, G.; Top, S.; Vessières, A.; Leclercq, G.; Quivy, J.; Jin, L.; Croisy, A. *C. R. Acad. Sci., Ser. IIc: Chim.* **2000**, *3*, 89.
[575] Heilmann, J. B.; Hillard, E. A.; Plamont, M.-A.; Pigeon, P.; Bolte, M.; Jaouen, G.; Vessiéres, A. *J. Organomet. Chem.* **2008**, *693*, 1716.
[576] Pigeon, P.; Top, S.; Vessières, A.; Huché, M.; Hillard E., A.; Salomon, E.; Jaouen, G. *J. Med. Chem.* **2005**, *48*, 2814.
[577] Top, S.; Vessières, A.; Leclercq, G.; Quivy, J.; Tang, J.; Vaissermann, J.; Huché, M.; Jaouen, G. *Chem.—Eur. J.* **2003**, *9*, 5223.
[578] Top, S.; Vessières, A.; Cabestaing, C.; Laïos, I.; Leclercq, G.; Provot, C.; Jaouen, G. *J. Organomet. Chem.* **2001**, *637–639*, 500.
[579] Hillard, E. A.; Pigeon, P.; Vessières, A.; Amatore, C.; Jaouen, G. *Dalton Trans.* **2007**, 5073.
[580] Kowalski, K.; Vessières, A.; Top, S.; Jaouen, G.; Zakrzewski, J. *Tetrahedron Lett.* **2003**, *44*, 2749.
[581] Cushman, M.; Golebiewski, W. M.; Pommier, Y.; Mazumder, A.; Reymen, D.; De Clercq, E.; Graham, L.; Rice, W. G. *J. Med. Chem.* **1995**, *38*, 443.

[582] Kim, S.-K.; Park, Y.-I.; Kang, I.-N.; Park, J.-W. *J. Mater. Chem.* **2007**, *17*, 4670.
[583] Casimiro-Garcia, A.; De Clercq, E.; Pannecouque, C.; Witvrouw, M.; Loftus, T. L.; Turpin, J. A.; Buckheit, Jr., R. W.; Fanwick, P. E.; Cushman, M. *Bioorg. Med. Chem.* **2001**, *9*, 2827.
[584] Xiao, X.; Antony, S.; Kohlhagen, G.; Pommier, Y.; Cushman, M. *Bioorg. Med. Chem.* **2004**, *12*, 5147.
[585] Xu, G. Z.; Micklatcher, M.; Silvestri, M. A.; Hartman, T. L.; Burrier, J.; Osterling, M. C.; Wargo, H.; Turpin, J. A.; Buckheit, Jr., R. W.; Cushman, M. *J. Med. Chem.* **2001**, *44*, 4092.
[586] Xiao, X.; Antony, S.; Kohlhagen, G.; Pommier, Y.; Cushman, M. *J. Org. Chem.* **2004**, *69*, 7495.
[587] Yan, T.-H.; Paquette, L. A. *Tetrahedron Lett.* **1982**, *23*, 3227.
[588] Karjalainen, A.; Kalapudas, A.; Södervall, M.; Pelkonen, O.; Lammintausta, R. *Eur. J. Pharm. Sci.* **2000**, *11*, 109.
[589] Fox, B. M.; Xiao, X.; Antony, S.; Kohlhagen, G.; Pommier, Y.; Staker, B. L.; Stewart, L.; Cushman, M. *J. Med. Chem.* **2003**, *46*, 3275.
[590] Ishiduka, T.; Tsukayama, M.; Kawamura, Y. *Int. J. Mod. Phys. B* **2006**, *20*, 4595.
[591] Casimiro-Garcia, A.; Micklatcher, M.; Turpin, J. A.; Stup, T. L.; Watson, K.; Buckheit, R. W.; Cushman, M. *J. Med. Chem.* **1999**, *42*, 4861.
[592] Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 8296.
[593] Ruenitz, P. C.; Arrendale, R. F.; Schmidt, W. F.; Thompson, C. B.; Nanavati, N. T. *J. Med. Chem.* **1989**, *32*, 192.
[594] Liu, J.; Murray, E. M.; Young, Jr., V. G., Jr. *Chem. Commun.* **2003**, 1904.
[595] Liu, J.; Suits, E. L.; Boarman, K. J. *Tetrahedron Lett.* **2003**, *44*, 8103.
[596] Schmidt, J. M.; Tremblay, G. B.; Plastina, M. A.; Ma, F.; Bhal, S.; Feher, M.; Dunn-Dufault, R.; Redden, P. R. *Bioorg. Med. Chem.* **2005**, *13*, 1819.
[597] Kannan, A.; De Clercq, E.; Pannecouque, C.; Witvrouw, M.; Hartman, T. L.; Turpin, J. A.; Buckheit, R. W.; Cushman, M. *Tetrahedron* **2001**, *57*, 9385.
[598] Golebiewski, W. M.; Keyes, R. F.; Cushman, M. *Bioorg. Med. Chem.* **1996**, *4*, 1637.
[599] Ruell, J. A.; De Clercq, E.; Pannecouque, C.; Witvrouw, M.; Stup, T. L.; Turpin, J. A.; Buckheit, R. W.; Cushman, M. *J. Org. Chem.* **1999**, *64*, 5858.
[600] Matsumoto, M.; Hiroshima, T.; Chiba, S.; Isobe, R.; Watanabe, N.; Kobayashi, H. *Luminescence* **1999**, *14*, 345.
[601] Watanabe, N.; Kobayashi, H.; Azami, M.; Matsumoto, M. *Tetrahedron* **1999**, *55*, 6831.
[602] Schubert, F.; Knaf, A.; Möller, U.; Cech, D. *Nucleic Acids Res.* **1995**, *23*, 4657.
[603] Bastos, E. L.; Monteiro Leite Ciscato, L. F.; Weiss, D.; Beckert, R.; Baader, W. J. *Synthesis* **2006**, 1781.
[604] Matsumoto, M.; Kawahara, M.; Watanabe, N. *Luminescence* **1999**, *14*, 341.
[605] Gleiter, R.; Krennrich, G.; Bischof, P.; Tsuji, T.; Nishida, S. *Helv. Chim. Acta* **1986**, *69*, 962.
[606] Winkler, J. D.; Sridar, V.; Siegel, M. G. *Tetrahedron Lett.* **1989**, *30*, 4943.
[607] Lima, E. L. D.; Correia, C. R. D. *J Braz. Chem. Soc.* **1997**, *8*, 275.
[608] Brudermüller, M.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 298.
[609] Krause, A.; Musso, H.; Boland, W.; Ahlrichs, R.; Gleiter, R.; Boese, R.; Bär, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1379.
[610] Masson, G.; Lough, A. J.; Manners, I. *Macromolecules* **2008**, *41*, 539.
[611] Shirani, H.; Janosik, T. *J. Org. Chem.* **2007**, *72*, 8984.
[612] Shirani, H.; Bergman, J.; Janosik, T. *Tetrahedron* **2009**, *65*, 8350.
[613] Shirani, H.; Janosik, T. *Organometallics* **2008**, *27*, 3960.
[614] Gies, A.-E.; Pfeffer, M. *J. Org. Chem.* **1999**, *64*, 3650.
[615] Märkl, G.; Sauer, H.; Kreitmeier, P.; Burgemeister, T.; Kastner, F. *Tetrahedron* **1999**, *55*, 13407.
[616] Märkl, G.; Ehrl, R.; Sauer, H.; Kreitmeier, P.; Burgemeister, T. *Helv. Chim. Acta* **1999**, *82*, 59.
[617] Fürstner, A.; Thiel, O. R.; Kindler, N.; Bartkowska, B. *J. Org. Chem.* **2000**, *65*, 7990.
[618] Mayekar, N. V.; Chattopadhyay, S.; Nayak, S. K. *Lett. Org. Chem.* **2004**, *1*, 203.
[619] Mayekar, N. V.; Chattopadhyay, S.; Nayak, S. K. *Synthesis* **2003**, 2041.
[620] Darabi, H. R.; Jadidi, K.; Mohebbi, A. R.; Faraji, L.; Aghapoor, K.; Shahbazian, S.; Azimzadeh, M.; Nasseri, S. M. *Supramol. Chem.* **2008**, *20*, 327.
[621] Yamato, T.; Fujita, K.; Futatsuki, K.; Tsuzuki, H. *Can. J. Chem.* **2000**, *78*, 1089.

[622] Saisyo, T.; Shiino, M.; Hironaka, T.; Yamato, T. *J. Chem. Res.* **2007**, 141.
[623] Saisyo, T.; Shiino, M.; Shimizu, T.; Paudel, A.; Yamato, T. *J. Chem. Res.* **2008**, 479.
[624] Darabi, H. R.; Mirza-Aghayan, M.; Ali-Saraie, L.; Bolourtchian, M.; Neumüller, B.; Ghassemzadeh, M. *Supramol. Chem.* **2003**, *15*, 55.
[625] Mamane, V.; Fort, Y. *J. Org. Chem.* **2005**, *70*, 8220.
[626] Tirado-Rives, J.; Oliver, M. A.; Fronczek, F. R.; Gandour, R. D. *J. Org. Chem.* **1984**, *49*, 1627.
[627] Wang, Z.; Zhu, S.; Shi, J.; Wang, H. *Beilstein J. Org. Chem.* **2009**, *5*, No. 55.
[628] Tirado-Rives, J.; Gandour, R. D.; Fronczek, F. R. *Tetrahedron Lett.* **1982**, *23*, 1639.
[629] Grützmacher, H.-F.; Neumann, E. *Chem. Ber.* **1993**, *126*, 1495.
[630] Kuroda, S.; Yazaki, J.-i.; Maeda, S.; Yamazaki, K.; Yamada, M.; Shimao, I.; Yasunami, M. *Tetrahedron Lett.* **1992**, *33*, 2825.
[631] Macomber, R. S.; Rardon, D. E.; Emge, T. J. *J. Org. Chem.* **1992**, *57*, 433.
[632] Mateo, C.; Pérez-Melero, C.; Peláez, R.; Medarde, M. *J. Org. Chem.* **2005**, *70*, 6544.
[633] Merz, A.; Karl, A.; Futterer, T.; Stacherdinger, N.; Schneider, O.; Lex, J.; Luboch, E.; Biernat, J. F. *Liebigs Ann. Chem.* **1994**, 1199.
[634] Marshall, J. A.; Chung, K.-H. *J. Org. Chem.* **1979**, *44*, 1566.
[635] Mirza-Aghayan, M.; Darabi, H. R.; Ali-Saraie, L.; Ghassemzadeh, M.; Bolourtchian, M.; Jalali-Heravi, M.; Neumüller, B. *Z Anorg. Allg. Chem.* **2002**, *628*, 681.
[636] Ravishankar, T.; Chinnakali, K.; Rajakumar, P.; Murali, V.; Usman, A.; Fun, H.-K. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *59*, O290.
[637] Ben, I.; Castedo, L.; Saá, J. M.; Seijas, J. A.; Suau, R.; Tojo, G. *J. Org. Chem.* **1985**, *50*, 2236.
[638] Rajakumar, P.; Murali, V. *Tetrahedron* **2004**, *60*, 2351.
[639] Dubois, F.; Gingras, M. *Tetrahedron Lett.* **1998**, *39*, 5039.
[640] Srinivasan, M.; Sankararaman, S.; Dix, I.; Jones, P. G. *Org. Lett.* **2000**, *2*, 3849.
[641] Castedo, L.; Saá, J. M.; Suau, R.; Tojo, G. *Tetrahedron Lett.* **1983**, *24*, 5419.
[642] Yamato, T.; Fujita, K.; Okuyama, K.; Tsuzuki, H. *New J. Chem.* **2000**, *24*, 221.
[643] Tanner, D.; Wennerström, O.; Norinder, U.; Müllen, K.; Trinks, R. *Tetrahedron* **1986**, *42*, 4499.
[644] Meier, H.; Fetten, M. *Tetrahedron Lett.* **2000**, *41*, 1535.
[645] Tanaka, K.; Suzuki, H.; Osuga, H. *Tetrahedron Lett.* **1997**, *38*, 457.
[646] Shimizu, I.; Umezawa, H.; Kanno, T.; Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2023.
[647] Rajakumar, P.; Gayatri Swaroop, M.; Jayavelu, S.; Murugesan, K. *Tetrahedron* **2006**, *62*, 12041.
[648] Rajakumar, P.; Gayatri Swaroop, M. *Tetrahedron Lett.* **2004**, *45*, 6165.
[649] Müllen, K.; Unterberg, H.; Huber, W.; Wennerström, O.; Norinder, U.; Tanner, D.; Thulin, B. *J. Am. Chem. Soc.* **1984**, *106*, 7514.
[650] Yamato, T.; Hironaka, T.; Saisyo, T.; Manabe, T.; Okuyama, K. *J. Chem. Res. (S)* **2003**, 63.
[651] Kasahara, A.; Izumi, T.; Shimizu, I.; Satou, M.; Katou, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2434.
[652] Saisyo, T.; Shiino, M.; Hu, J.−Y.; Yamato, T. *J. Chem. Res.* **2007**, 621.
[653] Speicher, A.; Kolz, J.; Sambanje, R. P. *Synthesis* **2002**, 2503.
[654] Yamamoto, K. *Pure Appl. Chem.* **1993**, *65*, 157.
[655] Kasahara, A.; Izumi, T.; Shimizu, I.; Oikawa, T.; Umezawa, H.; Hoshino, I. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1143.
[656] Kasahara, A.; Izumi, T.; Shimizu, I. *Chem. Lett.* **1979**, 1119.
[657] Esser, B.; Rominger, F.; Gleiter, R. *J. Am. Chem. Soc.* **2008**, *130*, 6716.
[658] Yamato, T.; Fujita, K.; Abe, T.; Tsuzuki, H. *New J. Chem.* **2001**, *25*, 728.
[659] Marshall, J. A.; Black, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 7581.
[660] Aukauloo, M. A.; Guilard, R. *New J. Chem.* **1994**, *18*, 1205.
[661] Sessler, J. L.; Brucker, E. A.; Weghorn, S. J.; Kisters, M.; Schäfer, M.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2308.
[662] Kozaki, M.; Parakka, J. P.; Cava, M. P. *J. Org. Chem.* **1996**, *61*, 3657.
[663] Vogel, E.; Binsack, B.; Hellwig, Y.; Erben, C.; Heger, A.; Lex, J.; Wu, Y.-D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2612.
[664] Eguchi, T.; Terachi, T.; Kakinuma, K. *Tetrahedron Lett.* **1993**, *34*, 2175.

[665] Lin, H.-C.; Lin, W.-Y.; Bai, H.-T.; Chen, J.-H.; Jin, B.-Y.; Luh, T.-Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 897.
[666] Rajakumar, P.; Gayatri Swaroop, M. *Tetrahedron Lett.* **2005**, *46*, 8543.
[667] Suzuki, T.; Tanaka, S.; Higuchi, H.; Kawai, H.; Fujiwara, K. *Tetrahedron Lett.* **2004**, *45*, 8563.
[668] Eguchi, T.; Terachi, T.; Kakinuma, K. *J. Chem. Soc., Chem. Commun.* **1994**, 137.
[669] Eguchi, T.; Arakawa, K.; Terachi, T.; Kakinuma, K. *J. Org. Chem.* **1997**, *62*, 1924.
[670] Arakawa, K.; Eguchi, T.; Kakinuma, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2419.
[671] Merner, B. L.; Dawe, L. N.; Bodwell, G. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 5487.
[672] Lhoták, P.; Zieba, R.; Hromádko, V.; Stibor, I.; Sykora, J. *Tetrahedron Lett.* **2003**, *44*, 4519.
[673] Rojanathanes, R.; Pipoosananakaton, B.; Tuntulani, T.; Bhanthumnavin, W.; Orton, J. B.; Cole, S. J.; Hursthouse, M. B.; Grossel, M. C.; Sukwattanasinitt, M. *Tetrahedron* **2005**, *61*, 1317.
[674] Sukwattanasinitt, M.; Rojanathanes, R.; Tuntulani, T.; Sritana-Anant, Y.; Ruangpornvisuti, V. *Tetrahedron Lett.* **2001**, *42*, 5291.
[675] Eguchi, T.; Kano, H.; Kakinuma, K. *Chem. Commun.* **1996**, 365.
[676] Vogel, E.; Bröring, M.; Weghorn, S. J.; Scholz, P.; Deponte, R.; Lex, J.; Schmickler, H.; Schaffner, K.; Braslavsky, S. E.; Müller, M.; Pörting, S.; Fowler, C. J.; Sessler, J. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1651.
[677] Eguchi, T.; Ibaragi, K.; Kakinuma, K. *J. Org. Chem.* **1998**, *63*, 2689.
[678] Okarma, P. J.; Caringi, J. J. *Org. Prep. Proced. Int.* **1985**, *17*, 212.
[679] Clive, D. L. J.; Murthy, K. S. K.; Zhang, C.; Hayward, W. D.; Daigneault, S. *J. Chem. Soc., Chem. Commun.* **1990**, 509.
[680] Nakayama, J.; Machida, H.; Hoshino, M. *Tetrahedron Lett.* **1985**, *26*, 1981.
[681] Nakayama, J.; Ikuina, Y.; Murai, F.; Hoshino, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1072.
[682] Paquette, L. A.; Dressel, J.; Pansegrau, P. D. *Tetrahedron Lett.* **1987**, *28*, 4965.
[683] Pauw, J. E.; Weedon, A. C. *Tetrahedron Lett.* **1982**, *23*, 5485.
[684] Dang, Y.; Chen, Y. *J. Org. Chem.* **2007**, *72*, 6901.
[685] Dang, Y.; Chen, Y. *Eur. J. Org. Chem.* **2007**, 5661.
[686] Disanayaka, B. W.; Weedon, A. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1282.
[687] Chen, Y.; Zeng, D. X.; Fan, M. G. *Org. Lett.* **2003**, *5*, 1435.
[688] Huang, Z.-N.; Xu, B.-A.; Jin, S.; Fan, M.-G. *Synthesis* **1998**, 1092.
[689] Venkataiah, B.; Ramesh, C.; Ravindranath, N.; Das, B. *Phytochemistry* **2003**, *63*, 383.
[690] Honda, T.; Namiki, H.; Nagase, H.; Mizutani, H. *ARKIVOC* **2003**, 188.
[691] Lucas, L. N.; de Jong, J. J. D.; van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Eur. J. Org. Chem.* **2003**, 155.
[692] Lucas, L. N.; van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Chem. Commun.* **1998**, 2313.
[693] Lucas, L. N.; van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Tetrahedron Lett.* **1999**, *40*, 1775.
[694] Baumstark, A. L.; Bechara, E. J. H.; Semigran, M. J. *Tetrahedron Lett.* **1976**, 3265.
[695] Paquette, L. A.; Gardlik, J. M.; McCullough, K. J.; Hanzawa, Y. *J. Am. Chem. Soc.* **1983**, *105*, 7644.
[696] Han, Y.; Zhang, Z. B.; Xiao, J. P.; Yan, W. P.; Fan, M. G. *Chin. Chem. Lett.* **2005**, *16*, 175.
[697] Zeng, D. X.; Chen, Y. *Synlett* **2006**, 490.
[698] Marshall, J. A.; Constantino, M.; Black, T. H. *Synth. Commun.* **1980**, *10*, 689.
[699] McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* **1984**, *106*, 5018.
[700] Vogel, E.; Neumann, B.; Klug, W.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1046.
[701] Reitz, D. B.; Li, J. J.; Norton, M. B.; Reinhard, E. J.; Collins, J. T.; Anderson, G. D.; Gregory, S. A.; Koboldt, C. M.; Perkins, W. E.; Seibert, K.; Isakson, P. C. *J. Med. Chem.* **1994**, *37*, 3878.
[702] Yamato, T.; Fujita, K.; Tsuzuki, H. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2089.
[703] Yamato, T.; Miyamoto, S.; Hironaka, T.; Miura, Y. *Org. Lett.* **2005**, *7*, 3.
[704] Rathore, R.; Weigand, U.; Kochi, J. K. *J. Org. Chem.* **1996**, *61*, 5246.
[705] Jenny, L.; Borschberg, H.-J. *Helv. Chim. Acta* **1995**, *78*, 715.
[706] Krayushkin, M. M.; Yarovenko, V. N.; Semenov, S. L.; Zavarzin, I. V.; Martynkin, A. Y.; Uzhinov, B. M. *Russ. J. Org. Chem.* **2003**, *39*, 1656.

[707] Yamato, T.; Saisyo, T.; Hironaka, T.; Miyamoto, S. *J. Chem. Res.* **2006**, 558.
[708] Reitz, D. B.; Huang, H.-C.; Li, J. J.; Garland, D. J.; Manning, R. E.; Anderson, G. D.; Gregory, S. A.; Koboldt, C. M.; Perkins, W. E.; Seibert, K.; Isakson, P. C. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 867.
[709] Rybalkin, V. P.; Shepelenko, E. N.; Popova, L. L.; Dubonosov, A. D.; Metelitsa, A. V.; Makarova, N. I.; Bren, V. A.; Minkin, V. I. *Russ. J. Org. Chem.* **2006**, *42*, 619.
[710] Huang, Z.; Yang, Q.-Z.; Kucharski, T. J.; Khvostichenko, D.; Wakeman, S. M.; Boulatov, R. *Chem.—Eur. J.* **2009**, *15*, 5212.
[711] Shepelenko, E. N.; Rybalkin, V. P.; Karamov, O. G.; Makarova, N. I.; Metelitsa, A. V.; Popova, L. L.; Bren, V. A. *Russ. J. Org. Chem.* **2006**, *42*, 1727.
[712] Hu, J.; Jiang, X.; He, T.; Zhou, J.; Hu, Y. F.; Hu, H. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1820.
[713] Krayushkin, M. M.; Migulin, V. A.; Yarovenko, V. N.; Barachevskii, V. A.; Vorontsova, L. G.; Starikova, Z. A.; Zavarzin, I. V.; Bulgakova, V. N. *Mendeleev Commun.* **2007**, *17*, 125.
[714] Huang, Z. N.; Jin, S.; Fan, M. G. *Chin. Chem. Lett.* **1997**, *8*, 7.
[715] Walko, M.; Feringa, B. L. *Chem. Commun.* **2007**, 1745.
[716] Rajca, A.; Pink, M.; Xiao, S.; Miyasaka, M.; Rajca, S.; Das, K.; Plessel, K. *J. Org. Chem.* **2009**, *74*, 7504.
[717] Knapp, K. M.; Goldfuss, B.; Knochel, P. *Chem.—Eur. J.* **2003**, *9*, 5259.
[718] Huang, Z.; Yang, Q.-Z.; Khvostichenko, D.; Kucharski, T. J.; Chen, J.; Boulatov, R. *J. Am. Chem. Soc.* **2009**, *131*, 1407.
[719] Myers, A. G.; Condroski, K. R. *J. Am. Chem. Soc.* **1993**, *115*, 7926.
[720] Yamato, T.; Hironaka, T.; Shiino, M.; Saisyo, T.; Miyamoto, S. *J. Chem. Res.* **2006**, 110.
[721] Yamato, T.; Hironaka, T.; Miyamoto, S. *J. Chem. Res.* **2006**, 393.
[722] Kuroda, S.; Obata, Y.; Thanh, N. C.; Miyatake, R.; Horino, Y.; Oda, M. *Tetrahedron Lett.* **2008**, *49*, 552.
[723] Lee, W. Y.; Park, C. H. *J. Org. Chem.* **1993**, *58*, 7149.
[724] Lee, W. Y.; Park, C. H.; Kim, H.-J.; Kim, S. *J. Org. Chem.* **1994**, *59*, 878.
[725] Emond, S. J.; Debroy, P.; Rathore, R. *Org. Lett.* **2008**, *10*, 389.
[726] Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238.
[727] Komatsu, K.; Murata, Y. *Chem. Lett.* **2005**, *34*, 886.
[728] Murata, M.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2006**, *128*, 8024.
[729] Komatsu, K. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2285.
[730] Anderson, P. C.; Clive, D. L. J.; Evans, C. F. *Tetrahedron Lett.* **1983**, *24*, 1373.
[731] Raubo, P.; Kulagowski, J. J.; Chicchi, G. G. *Synlett* **2006**, 271.
[732] Corey, E. J.; Palani, A. *Tetrahedron Lett.* **1997**, *38*, 2397.
[733] Saunders, M.; Krause, N. *J. Am. Chem. Soc.* **1990**, *112*, 1791.
[734] McMurry, J. E.; Hodge, C. N. *J. Am. Chem. Soc.* **1984**, *106*, 6450.
[735] McMurry, J. E.; Lectka, T.; Hodge, C. N. *J. Am. Chem. Soc.* **1989**, *111*, 8867.
[736] Rank, E.; Brückner, R. *Eur. J. Org. Chem.* **1998**, 1045.
[737] Eckhardt, M.; Brückner, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1093.
[738] Trehan, I. R.; Kad, G. L.; Seth, V. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **1991**, *30*, 793.
[739] Mikami, K.; Takahashi, K.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 4035.
[740] Zeelen, F. J. *Nat. Prod. Rep.* **1994**, *11*, 607.
[741] Nickon, A.; Hrnjez, B. *Tetrahedron* **1988**, *44*, 1905.
[742] Ferri, F.; Brückner, R. *Liebigs Ann./Recl.* **1997**, 961.
[742a] Rucker, M.; Brückner, R. *Tetrahedron Lett.* **1997**, *38*, 7353.
[743] Yue, X.; Li, Y. *Bull. Soc. Chim. Belg.* **1995**, *104*, 69.
[744] Jing, L.; Jiong, L.; Zuosheng, L.; Ying, L.; Yulin, L. *Tetrahedron: Asymmetry* **1996**, *7*, 2851.
[745] Lan, J.; Liu, Z.; Cen, W.; Xing, Y.; Li, Y. *Tetrahedron Lett.* **1999**, *40*, 1963.
[746] Li, Y.; Li, W.; Li, Y. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2953.
[747] Liu, Z.; Li, W. Z.; Peng, L.; Li, Y.; Li, Y. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4250.
[748] Hinkley, S. F. R.; Perry, N. B.; Weavers, R. T. *Tetrahedron* **2005**, *61*, 3671.

[749] Clive, D. L. J.; Murthy, K. S. K.; George, R.; Poznansky, M. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2099.
[750] Gao, F.; Burnell, D. J. *Tetrahedron Lett.* **2007**, *48*, 8185.
[751] Fürstner, A.; Ernst, A.; Krause, H.; Ptock, A. *Tetrahedron* **1996**, *52*, 7329.
[752] Fürstner, A.; Ernst, A. *Tetrahedron* **1995**, *51*, 773.
[753] Matsumoto, M.; Watanabe, N.; Kasuga, N. C.; Hamada, F.; Tadokoro, K. *Tetrahedron Lett.* **1997**, *38*, 2863.
[754] Fürstner, A.; Weintritt, H.; Hupperts, A. *J. Org. Chem.* **1995**, *60*, 6637.
[755] Ding, F.; Zhang, Y.; Qu, B.; Li, G.; Farina, V.; Lu, B. Z.; Senanayake, C. H. *Org. Lett.* **2008**, *10*, 1067.
[756] Li, W.; Li, Y.; Li, Y. *Bull. Soc. Chim. Belg.* **1993**, *102*, 503.
[757] Banerji, A.; Nayak, S. K. *J. Chem. Soc., Chem. Commun.* **1990**, 150.
[758] Fan, X.; Zhang, X. *J. Chem. Res. (S)* **2003**, 696.
[758a] Fan, X.; Zhang, Y. *Tetrahedron* **2003**, *59*, 1917.
[759] Watanabe, N.; Nagashima, Y.; Yamazaki, T.; Matsumoto, M. *Tetrahedron* **2003**, *59*, 4811.
[760] Ogawa, A.; Nanke, T.; Takami, N.; Ryu, I.; Kambe, N.; Sonoda, N. *Kidorui* **1994**, *24*, 212.
[761] Cozzi, P. G.; Prati, G. P.; Umani-Ronchi, A. *Gazz. Chim. Ital.* **1997**, *127*, 403.
[762] Li, W.; Li, Y.; Li, Y. *Chem. Lett.* **1994**, 741.
[763] Hu, W. H.; Guo, Z. R.; Bai, A. P.; Xu, Z. B. *Chin. Chem. Lett.* **2002**, *13*, 296.
[764] Hu, W.; Guo, Z.; Chu, F.; Bai, A.; Yi, X.; Cheng, G.; Li, J. *Bioorg. Med. Chem.* **2003**, *11*, 1153.
[765] Hu, W.; Guo, Z.; Yi, X.; Guo, C.; Chu, F.; Cheng, G. *Bioorg. Med. Chem.* **2003**, *11*, 5539.
[766] Fürstner, A.; Ptock, A.; Weintritt, H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 678.
[767] Yang, W.; He, H.; Drueckhammer, D. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1714.
[768] Fürstner, A.; Domostoj, M. M.; Scheiper, B. *J. Am. Chem. Soc.* **2005**, *127*, 11620.
[769] Fürstner, A.; Domostoj, M. M.; Scheiper, B. *J. Am. Chem. Soc.* **2006**, *128*, 8087.
[770] Vogel, E.; Jux, N.; Rodriguez-Val, E.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1387.
[771] Nußbaumer, T.; Krieger, C.; Neidlein, R. *Eur. J. Org. Chem.* **2000**, 2449.
[772] Vogel, E.; Sicken, M.; Röhrig, P.; Schmickler, H.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 411.
[773] Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257.
[774] Munno, G. D.; Lucchesini, F.; Neidlein, R. *Tetrahedron* **1993**, *49*, 6863.
[775] Ellinger, F.; Gieren, A.; Hübner, T.; Lex, J.; Lucchesini, F.; Merz, A.; Neidlein, R.; Salbeck, J. *Monatsh. Chem.* **1993**, *124*, 931.
[776] Dahlmann, U.; Krieger, C.; Neidlein, R. *Eur. J. Org. Chem.* **1998**, 525.
[777] Hu, Z.; Cava, M. P. *Tetrahedron Lett.* **1994**, *35*, 3493.
[778] Michels, H.-P.; Nieger, M.; Vögtle, F. *Chem. Ber.* **1994**, *127*, 1167.
[779] Zimmermann, K.; Haenel, M. W. *Synlett* **1997**, 609.
[780] Märkl, G.; Ehrl, R.; Kreitmeier, P.; Burgemeister, T. *Helv. Chim. Acta* **1998**, *81*, 93.
[781] Märkl, G.; Sauer, H.; Kreitmeier, P.; Burgemeister, T.; Kastner, F.; Adolin, G.; Nöth, H.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1151.
[782] Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 928.
[783] Vogel, E.; Köcher, M.; Lex, J.; Ermer, O. *Isr. J. Chem.* **1989**, *29*, 257.
[784] Kawase, T.; Darabi, H. R.; Uchimiya, R.; Oda, M. *Chem. Lett.* **1995**, 499.
[785] Song, Y.; Di, C.; Yang, X.; Li, S.; Xu, W.; Liu, Y.; Yang, L.; Shuai, Z.; Zhang, D.; Zhu, D. *J. Am. Chem. Soc.* **2006**, *128*, 15940.
[786] Song, Y.; Di, C.-a.; Xu, W.; Liu, Y.; Zhang, D.; Zhu, D. *J. Mater. Chem.* **2007**, *17*, 4483.
[787] Märkl, G.; Knott, T.; Kreitmeier, P.; Burgemeister, T.; Kastner, F. *Tetrahedron* **1996**, *52*, 11763.
[787a] Märkl, G.; Knott, T.; Kreitmeier, P.; Burgemeister, T.; Kastner, F. *Helv. Chim. Acta* **1998**, *81*, 1480.
[787b] Märkl, G.; Knott, T.; Kreitmeier, P.; Burgemeister, T.; Kastner, F. *Helv. Chim. Acta* **2000**, *83*, 592.

[788] Sargent, A. L.; Hawkins, I. C.; Allen, W. E.; Liu, H.; Sessler, J. L.; Fowler, C. J. *Chem.—Eur. J.* **2003**, *9*, 3065.
[789] Memminger, K.; Oeser, T.; Müller, T. J. J. *Org. Lett.* **2008**, *10*, 2797.
[790] Rajakumar, P.; Kanagalatha, R. *Tetrahedron Lett.* **2007**, *48*, 8496.
[791] Hu, Z.; Scordilis-Kelley, C.; Cava, M. P. *Tetrahedron Lett.* **1993**, *34*, 1879.
[792] Märkl, G.; Stiegler, J.; Kreitmeier, P.; Burgemeister, T.; Kastner, F.; Dove, S. *Helv. Chim. Acta* **1997**, *80*, 14.
[793] Matsumoto, K.; Minami, H.; Kawase, T.; Oda, M. *Org. Biomol. Chem.* **2004**, *2*, 2323.
[794] Darabi, H. R.; Kawase, T.; Oda, M. *Tetrahedron Lett.* **1995**, *36*, 9525.
[795] Kawase, T.; Ueda, N.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1556.
[796] Kawase, T.; Hosokawa, Y.; Kurata, H.; Oda, M. *Chem. Lett.* **1999**, 745.
[797] Guilard, R.; Aukauloo, M. A.; Tardieux, C.; Vogel, E. *Synthesis* **1995**, 1480.
[798] Vogel, E.; Koch, P.; Hou, X.-L.; Lex, J.; Lausmann, M.; Kisters, M.; Aukauloo, M. A.; Richard, P.; Guilard, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1600.
[799] Nussbaumer, T.; Neidlein, R. *Helv. Chim. Acta* **2000**, *83*, 1161.
[800] Kurata, H.; Haruki, K.; Nakaminami, H.; Kawase, T.; Oda, M. *Chem. Lett.* **2003**, *32*, 422.
[801] Kurata, H.; Nakaminami, H.; Matsumoto, K.; Kawase, T.; Oda, M. *Chem. Commun.* **2001**, 529.
[802] Märkl, G.; Bruns, D.; Dietl, H.; Kreitmeier, P. *Helv. Chim. Acta* **2001**, *84*, 2220.
[803] Jux, N.; Koch, P.; Schmickler, H.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1385.
[804] Johnson, M. R.; Miller, D. C.; Bush, K.; Becker, J. J.; Ibers, J. A. *J. Org. Chem.* **1992**, *57*, 4414.
[805] Kawase, T.; Nakamura, T.; Utsumi, K.; Matsumoto, K.; Kurata, H.; Oda, M. *Chem. Asian J.* **2008**, *3*, 573.
[806] Mártire, D. O.; Jux, N.; Aramendía, P. F.; Negri, R. M.; Lex, J.; Braslavsky, S. E.; Schaffner, K.; Vogel, E. *J. Am. Chem. Soc.* **1992**, *114*, 9969.
[807] Sawada, T.; Morita, M.; Chifuku, K.; Kuwahara, Y.; Shosenji, H.; Takafuji, M.; Ihara, H. *Tetrahedron Lett.* **2007**, *48*, 9051.
[808] Paek, K.-S.; Cram, D. J. *Bull. Korean Chem. Soc.* **1989**, *10*, 568.
[809] Sánchez-García, D.; Borrell, J. I.; Nonell, S. *Org. Lett.* **2009**, *11*, 77.
[810] Stępień, M.; Donnio, B.; Sessler, J. L. *Chem.—Eur. J.* **2007**, *13*, 6853.
[811] Kawase, T.; Daifuku, Y.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *C. R. Hebd. Sceances Acad. Sci., Ser. IIc*, **2009**, *12*, 403.
[812] Nonell, S.; Borrell, J. I.; Borrós, S.; Colominas, C.; Rey, O.; Rubio, N.; Sánchez-García, D.; Teixidó, J. *Eur. J. Org. Chem.* **2003**, 1635.
[813] Paek, K.-S.; Cram, D. J. *Bull. Korean Chem. Soc.* **1989**, *10*, 572.
[814] Kurata, H.; Haruki, K.; Oda, M. *Chem. Lett.* **2005**, *34*, 484.
[815] Piwoński, H.; Hartschuh, A.; Urbańska, N.; Pietraszkiewicz, M.; Sepiol, J.; Meixner, A. J.; Waluk, J. *J. Phys. Chem. C* **2009**, *113*, 11514.
[816] Nakao, K.; Nishimura, M.; Tamachi, T.; Kuwatani, Y.; Miyasaka, H.; Nishinaga, T.; Iyoda, M. *J. Am. Chem. Soc.* **2006**, *128*, 16740.
[817] Liu, W.-J.; Zhou, Y.; Zhou, Q.-F.; Ma, Y.; Pei, J. *Org. Lett.* **2008**, *10*, 2123.
[818] Miller, D. C.; Johnson, M. R.; Ibers, J. A. *J. Org. Chem.* **1994**, *59*, 2877.
[819] Miller, D. C.; Johnson, M. R.; Becker, J. J.; Ibers, J. A. *J. Heterocycl. Chem.* **1993**, *30*, 1485.