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Jean Le Bras, Jacques Muzart

► **To cite this version:**

Jean Le Bras, Jacques Muzart. The Saegusa Oxidation and Related Procedures. John Wiley & Sons, Inc., 98, pp.1-172, 2019, Organic reactions, 10.1002/0471264180.or098.01 . hal-02307204

HAL Id: hal-02307204

<https://hal.science/hal-02307204>

Submitted on 7 Jan 2022

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1 **THE SAEGUSA OXIDATION AND RELATED PROCEDURES**

2
3 Jean Le Bras and Jacques Muzart

4 *Institute of Molecular Chemistry of Reims, UMR 7312*

5 *CNRS - University of Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France*

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INTRODUCTION

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22

α,β -Unsaturated carbonyl compounds are highly useful synthetic materials in organic synthesis, {HK-03}, {ABK-08}, {HHG-08}, {TH-09} and regioselective dehydrogenation of carbonyl compounds to the corresponding α,β -unsaturated carbonyl compounds is an important transformation in synthetic chemistry. {BP-91}, {L-99} One-pot, palladium-mediated dehydrogenation reactions of ketones, aldehydes, esters, lactones, and amides are known, but such reactions are limited primarily to simple substrates. {M-10}, {TCN-16}, {CR-15}, {CT-16}, {DMC-15} Moreover, they suffer from lack of regiocontrol in the case of unsymmetrical ketones. In 1977, Ito, Hirato, and Saegusa reported the conversion of silyl enol ethers to the corresponding α,β -unsaturated ketones and aldehydes using stoichiometric or substoichiometric amounts of palladium(II) salts. {IHS-78} Although silyl enol ethers are easily prepared from saturated ketones or aldehydes, {IHS-78} several years passed before the first

1 application of the Saegusa Reaction was reported. Studies to improve on the original procedure by using
2 lower catalyst loadings have since appeared. A brief review of the Saegusa Reaction concerning the
3 literature up to 1998 is available, {IS-02} and related methods devised primarily by the Tsuji and Larock
4 groups are discussed in reviews {T-86}, {TM-87}, {MNY-87} and books {L-99}, {T-95}, {T-04}, {SD-
5 14}.

6 This review concerns the Saegusa Reaction and related methods. In addition to enol silanes, enol
7 acetates, alkyl enol ethers, allyl enol carbonates, allyl β -keto carboxylates, allyl malonates, and α -chloro
8 ketones have been transformed into α,β -unsaturated carbonyl products. This chapter covers the literature
9 through February 2016.

11 MECHANISM AND STEREOCHEMISTRY

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

17 Silyl Enol Ethers or Silyl Ketene Acetals as Substrates

18 Most palladium-mediated, oxidative dehydrogenation reactions of silyl enol ethers and silyl
19 ketene acetals use a palladium(II) salt. The coordination of the C=C bond to the palladium species
20 results in transmetalation, which leads to loss of the silyl group and formation of a palladium
21 enolate. {IS-02} The latter compound exists as an equilibrium between the oxo- η^3 -allyl palladium and
22 the *C*- and *O*-enolate tautomers (Scheme 1). {AME-99} Subsequent β -hydride elimination affords the
23 α,β -unsaturated carbonyl compound and a hydridopalladium complex. Although the stability of

1 palladium hydrides is ligand-dependent, {HF-04} they are converted, in most cases, to palladium(0)
2 species. Because addition/elimination of hydridopalladium species to olefins is reversible, (*E*)- α,β -
3 unsaturated carbonyl compounds are usually produced selectively from acyclic substrates.

4

5 (1)

6 To achieve a catalytic process, the Saegusa Reaction is carried out in the presence of an
7 oxidant—often 1,4-benzoquinone or oxygen—to regenerate the active palladium(II) species. The
8 proposed catalytic cycle generates AcOSiR₃ and acetic acid (i.e., YSiR₃ and HY of Scheme 1) as the
9 byproducts of the first turnover and hydroquinone or peroxides as the stoichiometric byproducts.
10 However, palladium(0) species can form relatively stable palladium(0)–alkene complexes, which can
11 impede the catalytic cycle (Scheme 2). {PBT-99} Such complexes can be decomposed on heating or
12 treatment with silica gel.

13

(2)

14 **1,4-Benzoquinone as the Oxidant.** Coordination of 1,4-benzoquinone to palladium(0) in the
15 presence of acetic acid generates 4-hydroxyphenoxypalladium acetate (Scheme 3). {GGB-93}, {PTS-06}
16 This intermediate reacts with AcOSiR₃ to regenerate palladium(II) acetate. A mixture of 4-
17 trimethylsilyloxyphenol and 1,4-bis(trimethylsilyloxy)benzene has been isolated. {IHS-78} It is also
18 possible that HPdOAc reacts directly with 1,4-benzoquinone, rather than undergoing reductive
19 elimination to form palladium(0) first. {T-71}

20

(3)

21 **Oxygen, Oxygen and a Copper Salt, or Oxygen and Oxone as the Oxidant.** The use of
22 oxygen as the oxidant in DMSO leads to formation of a peroxopalladacycle. Addition of acetic acid
23 affords a hydroperoxypalladium complex, which reacts with AcOSiR₃ to regenerate palladium(II)

1 acetate (Scheme 4). {LHK-95} The mechanism of the formation of active palladium(II) species from
2 hydridopalladium intermediates and oxygen remains unknown. {GM-06}, {M-06}, {GS-09}, {SG-14}

3 (4)

4 In the presence of both oxygen and a copper salt, the catalyst can be regenerated in a manner
5 analogous to the Wacker oxidation (Scheme 5). {KH-09}

6 (5)

7 A recently developed catalytic procedure involves the use of Oxone under an oxygen or air
8 atmosphere. The exact role of oxygen under these conditions has not been elucidated. {LLL-13}

9 Silica-supported palladium(0) has been used as a catalyst under an oxygen atmosphere primarily
10 in NMP; acetonitrile is a poor solvent for this method. {BNN-89}, {BNN-90} The dispersion of oxygen
11 on palladium(0) is proposed to oxidize part of the supported palladium(0) into palladium(II), and the
12 silyl ether is adsorbed onto the catalytic surface. {BNN-90}

13 **Oxygen and *tert*-Butyl Hydroperoxide as the Oxidant.** Cycloalkenyloxy triisopropylsilyl
14 ethers can be used to prepare cyclic α,β -enones; this process employs palladium(II) hydroxide on carbon
15 as the catalyst and is performed in the presence of oxygen, a base (disodium hydrogen phosphate or
16 triethylamine), and excess amounts of *tert*-butyl hydroperoxide. {YWC-05}, {Y-15} The catalyst is
17 believed to initiate a radical process by palladium-mediated homolytic cleavage of the O–H bond of the
18 hydroperoxide (Scheme 6). However, because *tert*-butyl hydroperoxide is capable of generating active
19 palladium(II) species from palladium(0), {MCM-80} a catalytic cycle similar to that shown in Scheme 1
20 cannot be ruled out.

21 (6)

22 **Allyl Carbonate as the Oxidant.** An alkyl allyl carbonate or a diallyl carbonate reacts with a
23 palladium(0) catalyst to afford an η^3 -allyl palladium complex (Scheme 7, $R^3 = \text{alkyl or allyl}$, $Z =$

1 (R⁴)₃Si). {MTS-86} This palladium(II) species reacts with a silyl enol ether to form the η³-allyl
2 palladium enolate, which provides the unsaturated carbonyl compound and an η³-allyl palladium
3 hydride. The latter complex then releases propene and regenerates palladium(0).

4 (7)

6 Enol Acetates as Substrates

7 Enones can also be obtained from enol acetates using an excess of an alkyl allyl carbonate and
8 catalytic amounts of both palladium(II) acetate and tributyltin methoxide. The proposed mechanism is
9 depicted in Scheme 7 (R³ = alkyl, Z = Bu₃Sn). The role of tributyltin methoxide is to form the tin
10 enolate, which easily transmetalates with the palladium species to afford the η³-allyl palladium enolate
11 with concomitant generation of the tributyltin alkoxide.

12 Oxidative dehydroacetoxylation of enol acetates can also be accomplished with silica-supported
13 palladium(0) in the presence of oxygen (9 atm). Under these conditions, oxygen is dispersed over the
14 heterogeneous catalyst and takes part in the reaction. {BIN-90}

16 Alkyl Enol Ethers and Vinyl Halides as Substrates

17 The palladium-mediated formation of enals from alkyl enol ethers is carried out under aqueous
18 conditions with either stoichiometric or catalytic amounts of palladium(II) acetate. Under catalytic
19 conditions, either copper(II) acetate {TKA-92} or 1,4-benzoquinone {LHA-12} is typically employed as
20 the stoichiometric oxidant. The proposed mechanism parallels the catalytic cycle of the Wacker
21 oxidation, {MSS-14} wherein the key step is addition of water to the C=C bond that is activated by
22 coordination to palladium(II) acetate (Scheme 8). {TKA-92} The resulting intermediate undergoes

1 regioselective β -hydride elimination, in preference to β -OH or β -OR elimination, {M-12} to afford the
 2 enal. A similar reaction is also possible with vinyl halides. {TR-02}

3 (8)

4
 5 **Allyl Enol Carbonates, Allyl β -Keto Carboxylates, or Allyl Malonates as Substrates**

6 The palladium-catalyzed transformation of allyl enol carbonates, allyl β -keto carboxylates, and
 7 allyl malonates into α,β -unsaturated carbonyl compounds also involves a palladium enolate as the key
 8 intermediate (Scheme 9). {ST-82} The latter arises from the initial formation of an η^3 -allyl palladium
 9 carbonate or an η^3 -allyl palladium carboxylate, followed by subsequent decarboxylation. In agreement
 10 with this proposed mechanism, treatment of sodium 2-oxocyclohexanecarboxylate with a stoichiometric
 11 amount of $\text{PdCl}_2(\text{PPh}_3)_2$ and an excess of sodium acetate at room temperature affords cyclohex-2-enone
 12 (Scheme 10). A catalytic process is possible by including copper(II) chloride as the oxidant. {TCN-80}

13 (9)

14 (10)

15
 16 **α -Chloro Ketones as Substrates**

17 The synthesis of enones from α -chloro ketones proceeds by oxidative insertion of palladium(0)
 18 into the C–Cl bond to afford a chloropalladium enolate, which then likely follows the catalytic cycle
 19 shown in Scheme 11. {WBM-12}

20 (11)

21
 22 **SCOPE AND LIMITATIONS**

23 **Silyl Enol Ethers or Silyl Ketene Acetals as Substrates**

1 **Palladium(II) and 1,4-Benzoquinone or Copper Salt (Methods A and B).** The seminal report
 2 by Ito, Hirato, and Saegusa describes the synthesis of α,β -unsaturated ketones and aldehydes from
 3 trimethylsilyl enol ethers using either a stoichiometric amount of palladium(II) acetate (Method A^S) or
 4 0.5 equivalents each of palladium(II) acetate and 1,4-benzoquinone (Method A^C) at room temperature in
 5 acetonitrile. {IHS-78} Both procedures are well documented. Trimethylsilyl enol ethers are obtained
 6 from the corresponding saturated carbonyl compounds (Scheme 12) {HT-98b} and are often used
 7 without purification owing to their hydrolytic instability. More stable silyl enol ethers such as
 8 triethylsilyl (TES) {YSH-09}, {CMM-96}, {HHN-10}, {PDA-12}, {TTI-11}, {HCS-12}, {MYK-09}, {TJJ-
 9 01}, {HMS-09}, {HHN-11}, TBS {PDA-12}, {SNH-01}, {KMM-01a}, {KMM-02}, {ZYX-14}, {IKK-
 10 08}, {CXB-12}, {RZP-09}, {KKW-93}, {LHK-95}, {KKT-01} or TIPS ethers {LHJ-13}, {SSL-
 11 13}, {HLW-11}, {WGL-12}, {HHN-11} can be employed as well, though these products are also
 12 typically used without purification.

(12)

14 Saegusa's original conditions are effective for the synthesis of α,β -unsaturated lactones,
 15 dienones, and heterocyclic 2,3-en-1-ones. Some reactions are, however, carried out with stoichiometric
 16 or excess amounts of both palladium(II) acetate and 1,4-benzoquinone. {HBK-01}, {IKK-08}, {CXB-12}
 17 Saegusa Reactions are compatible with halides {OT-88} and ethers, but acid-catalyzed hydrolysis of the
 18 trimethylsilyl enol ethers may compete with the desired reaction, resulting in isolation of the original
 19 saturated ketones. {NJV-99}

20 Another possible side reaction is cyclization onto a tethered alkene (Scheme 13). {KRS-
 21 82a}, {LM-16} This pathway likely involves the coordination of the tethered alkene to the palladium
 22 enolate {IAH-79}, {IAS-80} or addition of the silyl enol ether to the palladium-complexed pendant
 23 alkene. {KRS-82}, {KW-85} This cyclization reaction is sensitive to crowding around the C=C bond, as

1 shown in the reaction of silyl enol ether **1**, which affords only the enone (Scheme 14).{TL-86} By
 2 comparison, silyl enol ether **2** affords a mixture of cyclohexenones **3–5** (Scheme 15).{TL-86} This
 3 cycloalkenylation procedure has been utilized in the synthesis of a variety of natural products. {KRS-
 4 82},{KS-83},{SMI-86},{TNM-93},{TSF-93},{TWN-95},{TRI-00},{TI-02},{YCM-14}

5 **(13)**

6 **(14)**

7 **(15)**

8 When subjected to the original Saegusa conditions, a number of substrates afford none of the
 9 expected α,β -unsaturated carbonyl compounds or form them only in low yields. These problematic
 10 substrates are summarized in Figure 1. The nature of the silyl group or the troublesome step (silylation
 11 or palladation) is not always specified, and consequently, the problematic substrates may be depicted as
 12 either the silyl enol ether or the carbonyl compound. In some cases, strong complexation of the catalyst
 13 to basic groups such as an isoquinoline moiety precludes the Saegusa Reaction. {NPS-09}

14 **(16)**

15 {FPR-05},{PMS-97},{SON-07},{STF-13},{SHN-04},{KNT-86},{HIS-11},{LGG-13},{LDD-
 16 13},{KHH-06},{SST-04},{SIS-05},{TF-05},{EML-07},{NPS-09},{SSD-00},{BFB-10},{GX-
 17 09},{HMH-04},{RBT-06},{MO-02},{CFI-10},{NMV-05},{BCD-02},{BSG-97},{MRT-98},{SJS-
 18 02},{CD-01}

19 Several modifications of the Saegusa procedure have been reported, such as using stoichiometric
 20 amounts of Pd(OCOCF₃)₂ in MeCN,{DDL-11} CH₂Cl₂/MeCN,{KMF-05} or DMF;{SJS-02} using
 21 stoichiometric amounts of Pd(OAc)₂ in DMSO{NKY-09},{AWD-08},{PP-09},{WM-11},{OFM-
 22 12},{LDD-13},{CGO-14}, DMSO/MeCN,{LDD-13},{MM-03b} or THF {HAC-13}; and using 1–5
 23 equivalents of Pd(OAc)₂ with 0.5–5 equivalents of 1,4-benzoquinone in MeCN{CM-86},{KAP-

1 90}, {CWM-98}, {JYR-98}, {HBK-01}, {FM-06}, {BAW-07}, {IKK-08}, {KMP-10}, {BBC-11}, {CXB-
2 12}, {BBW-13} or CH_2Cl_2 . {SJC-13} The $\text{Pd}(\text{OAc})_2/\text{DMSO}$ procedure appears to furnish the highest
3 yields with small scale reactions. {WM-11}

4 In a footnote, Saegusa and coworkers mention that 6-methyl-2-cyclohexenone is produced
5 quantitatively at room temperature by treating an oxygenated acetonitrile solution of 6-methyl-1-
6 trimethylsilyloxy-1-cyclohexene with catalytic amounts of both palladium(II) acetate and copper(II)
7 acetate. {IAH-79} Under an oxygen atmosphere, superstoichiometric quantities of both palladium(II)
8 acetate and copper(II) acetate at 50° in acetonitrile provide the desired product, {HCS-12} as does
9 catalytic amounts of palladium(II) acetate. Alternative reaction conditions include the use of
10 palladium(II) acetate and copper(I) chloride in the presence of HMPA (0.5 equivalents) in THF at room
11 temperature (Method B, Scheme 16) {HNT-92}. The α -hydroxy ketone can be formed as the major
12 product if traces of water are present in the reaction mixture. {HNT-92}

13 (17)

14 **Palladium Acetate, DMSO, and Oxygen (Method C).** The use of anhydrous DMSO as the
15 solvent under an oxygen atmosphere at room temperature is particularly effective for the Saegusa
16 Reaction, {LHK-95} likely due to the ability of DMSO to coordinate to palladium species. {GM-06}, {M-
17 06}, {GS-09}, {SG-14}, {BHL-95}, {SFS-02}, {S-04}, {ZP-05}, {PS-09}, {M-14} Under these conditions,
18 traces of water or an increase of the reaction temperature to 80° leads to the concomitant formation of
19 large amounts of the saturated ketone. Switching the solvent from DMSO to acetonitrile results in the
20 formation of no enone product. {LHK-95}

21 A variety of silyl groups may be used in this procedure: trimethyl-, triethyl-, triisopropyl-, and
22 *tert*-butyldimethylsilyl enol ethers are all viable substrates. However, substitution on the enol itself is
23 problematic, and trisubstituted enoxysilanes afford low yields. The method is effective for the

1 preparation of α,β -unsaturated ketones and aldehydes, but extension to α,β -unsaturated esters is only
 2 moderately successful. {LHK-95} For less reactive substrates, heating in DMSO under oxygen with
 3 catalytic {LHK-95} or superstoichiometric {YMM-11}, {CFO-13} amounts of palladium(II) acetate can
 4 be successful, but desilylation of the starting material can become a significant side reaction. {LHK-95}
 5 This desilylation appears to depend on the batch of palladium(II) acetate used and on the scale of the
 6 reaction. {FHM-13} Another possible side reaction is the formation of unsaturated lactones by a Baeyer–
 7 Villiger-type oxidation in the reaction of cyclic silyl enol ethers (Scheme 17). {TTI-11}

8 **(18)**

9 Silyl enol ethers bearing tethered alkenes cyclize to form bridged bicyclic products using
 10 palladium(II) acetate and oxygen in DMSO (Scheme 18). {TI-02}, {TRI-02}, {TWK-98}, {VM-
 11 09}, {YCM-14}, {LM-16}

12 **(19)**

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

15 **(20)**

16 {LDD-13}, {DXW-11}, {STF-13}, {CFI-10}, {BMO-13}, {GKS-98}

17 **Palladium(0)/SiO₂ and Oxygen (Method D).** The trimethylsilyl enol ethers of cyclopentanone
 18 and cyclohexanone are converted to the corresponding cycloalk-2-en-1-ones by employing a
 19 heterogeneous catalyst—palladium(0)/SiO₂—under an oxygen atmosphere at 60° in NMP. {BNN-89}
 20 To date, this procedure has been used only for these two substrates.

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

1 contains disodium hydrogen phosphate. Enones and enals are formed in good yields, {LLL-13} and this
 2 protocol is compatible with the presence of a cyclic acetal, or an OTBS group.

3 **Palladium(II) Hydroxide, *tert*-Butyl Hydroperoxide, Oxygen, and a Base (Method F).**

4 Triisopropylsilyl enol ethers of cycloalkanones may be converted to the corresponding enones by using
 5 20 mol % of palladium(II) hydroxide on carbon (Pearlman's catalyst), either disodium hydrogen
 6 phosphate or triethylamine, and an excess of *tert*-butyl hydroperoxide in CH₂Cl₂ at room temperature
 7 under oxygen. {YWC-05} Interestingly, β-silyloxy-α,β-enones are obtained when cesium carbonate is
 8 used as the base (Scheme 19).

9 **(21)**

10 These reaction conditions cannot be used with trimethylsilyl enol ethers or with the substrates
 11 depicted in Figure 3. An allylic peroxide intermediate is thought to be involved (Scheme 6), and the
 12 presence of radicals may limit the reaction scope. However, the survival of the cyclopropyl unit of
 13 substrate **6** under the experimental conditions (Scheme 20) is “an indication that the reaction of the
 14 allylic radical with molecular oxygen or *t*-BuOO• is fast relative to cleavage of the three-membered
 15 ring”. {YWC-05}, {Y-15}, {MFI-76}, {BM-80}, {MW-86}

16 **(22){DLY-08}, {TDV-10}**

17 **(23)**

18 **Palladium(0) Complexes and Diallyl Carbonate (Method G).** When palladium(0) reacts with
 19 an allyl carbonate, the resulting palladium(II) species can participate in the Saegusa Reaction with a
 20 trimethylsilyl enol ether formed from a ketone, aldehyde, ester, or lactone. This method relies on the
 21 allyl carbonate to generate the reactive η³-allyl palladium(II) complex (Scheme 9), usually in either
 22 acetonitrile or benzonitrile. However, the optimal experimental conditions depend on the type of
 23 substrates. For the synthesis of enones and enals, Pd(OAc)₂/dppe (1:1) and diallyl carbonate appear to be

1 best, whereas dppe-free Pd(OAc)₂ with allyl methyl carbonate is superior for preparing α,β -unsaturated
 2 esters and lactones. Typical conditions involve 0.01–0.1 equivalents of the catalyst and 1.4–2
 3 equivalents of an allyl carbonate in a solvent at reflux. {TMS-83}, {TMS-84}, {TTM-84}, {MTS-86} The
 4 importance of the solvent is clearly seen in reactions carried out with Pd₂(dba)₃•CHCl₃/dppe: selective
 5 formation of the α -allyl ketones or aldehydes (the Tsuji–Trost reaction) is observed in THF (Scheme
 6 21), whereas the Saegusa Reaction is observed in acetonitrile. {TMS-83b} The use of a silica-supported
 7 palladium catalyst favors the C-allylation reaction pathway in a variety of solvents, including
 8 acetonitrile. {BNN-90a}, {BNS-91}

9 (24)

10 Some silyl protecting groups are removed under the reaction conditions. The TBS enol ether in
 11 substrate **7** is unaffected by the use of diallyl carbonate and Pd₂(dba)₃•CHCl₃ in acetonitrile at room
 12 temperature {OXT-02}, {OXT-04}, {HGT-05}, {MKY-06}, {MD-07}, {NLE-09} (Scheme 22). {NLE-09}
 13 However, the TMS protecting group in substrate **8** is cleaved with Pd(OAc)₂/dppe in benzonitrile at
 14 reflux (Scheme 23). {TMS-83}

15 (25)

16 (26)

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

19 (27)

20 {TF-05}, {CBL-06}, {PMS-97}, {TNK-10}, {SR-14}, {SST-04}, {SIS-05}, {ZLF-11}

21 **Atypical Dehydrogenation Reactions.** In the course of the synthesis of (–)-platyphyllide, the
 22 expected product **10** is obtained from TES enol ether **9** with Method A^S, whereas a mixture of
 23 constitutional isomers **10** and **11** is produced with Method C (Scheme 24). {HHN-10} The unexpected

1 isomer forms only in the presence of the free hydroxyl group on the side chain and is favored by a bulky
 2 silyl ether, as exemplified by the different reactivities of silyl enol ethers **12**, **13**, **14**, and **15** (Schemes 25
 3 and 26). {HHN-11} A substituent at the 3-position of the cyclohex-1-en-1-yloxysilyl unit appears to be
 4 indispensable to the formation of the isomeric enone, which becomes the sole product when the 3-
 5 position is blocked (Scheme 27). The participation of the hydroxyl group in the palladium-mediated
 6 isomerization of the silyl enol ether appears to promote the atypical constitutional site selectivity. {HHN-
 7 11}

8
 9 (28)

10 (29)

11 (30)

12 (31)

13 When the TIPS enol ether of α -dihydronaphthol is subjected to Method F, aromatization occurs
 14 without cleavage of the silyl protecting group (Scheme 28). {YWC-05}, {Y-15}

15 (32)

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

18 (33)

19 {LHJ-13}, {KMM-01}, {QST-04}, {QSR-04}, {NLE-06}, {NLE-09}, {PP-09}, {WKS-98}, {TMS-
 20 83}, {MTS-86}, {LHK-95}, {MD-07}, {CBL-06}, {OXT-02}, {OXT-04}, {TMS-83}, {MTS-86}, {IHS-
 21 78}, {TTI-11}, {HHN-10}, {IHS-78}, {LHK-95}, {HHN-11}, {BMO-13}, {IHS-78}, {BNN-89}, {TMS
 22 84}, {HNT-92}, {CGM-12}, {IHS-78}, {LHK-95}, {MTS-86}, {HNT-92}, {LLL-13}, {IHS-78}, {YWC-
 23 05}, {Y-15}

Enol Acetates as Substrates

The initial report on the formation of α,β -unsaturated cycloalkenones from enol acetates involves allyl carbonate in refluxing acetonitrile with catalytic amounts of tributyltin methoxide and either Pd(OAc)₂ or Pd(OAc)₂/dppe. {TMS-83a} Since this report, the reaction has been found to be highly dependent on the purity of the reagents, {ACH-01} and the most effective palladium catalyst appears to be substrate-dependent. {MTS-86} The transformation of (*S*)-enol acetate **16** under the aforementioned conditions produces (*S*)-enone **17** without loss of enantiomeric purity (analyzed by specific rotation), {GSR-91}, {SGU-91}, {WK-02} but reinvestigation by chiral stationary phase HPLC analysis has since indicated partial racemization (Scheme 29). {KKS-14} An increase in racemization at a longer reaction time is attributed to the formation of an (η^3 -allyl)PdH species derived from product **17**. {KKS-14} The formation of the enones from (*S*)-enol acetates **18** {CBS-97} and **19** proceeds without racemization (Scheme 30), as evidenced by chiral stationary phase HPLC analysis. {ACH-01} This preservation of enantiopurity is consistent with the racemization mechanism described, since substitution at the 4-position precludes the formation of a (η^3 -allyl)PdH complex.

(34)

(35)

Although this method is ineffective for the synthesis of enals, {MTS-86} it can be used for the synthesis of dienones and cycloalkenones and is compatible with cyano, chloroaryl, and ether groups.

Alkyl Enol Ethers as Substrates

α,β -Unsaturated aldehydes can be prepared from methyl enol ethers, and a typical procedure employs palladium(II) acetate (0.5 equivalents), copper(II) acetate monohydrate (1 equivalent), and

1 sodium bicarbonate (0.5 equivalents) in acetonitrile. {TKA-92} By changing the solvent to water/acetic
2 acid or acetic acid/dichloromethane, the catalyst loading can be lowered to 0.01–0.05 equivalents of
3 palladium(II) acetate. This reaction takes place between room temperature and 40° and uses 1,4-
4 benzoquinone as the oxidant. {LHA-12} Because these reactions involve a Wacker-type addition, alkyl
5 enol ethers containing pendant OH groups afford 2,5-dihydrofurans instead of α,β -unsaturated
6 aldehydes (Scheme 31). {LHA-12} Common functional groups such as alkenes, silyl ethers, acetates,
7 benzyl groups, vinylsilanes, and dioxolanes are compatible with these reaction conditions.

8 (36)

9 This method is effective for the synthesis of α,β -unsaturated aldehydes, but there are no
10 literature examples for the synthesis of α,β -unsaturated ketones from alkyl enol ethers. However, traces
11 of cyclohexenone **20** were formed from the reaction of 1-methoxy-6,6-dimethylcyclohex-1-ene with a
12 stoichiometric amount of palladium(II) acetate in acetonitrile (Scheme 32). {KRS-82}

13
14 (37)

15
16 **Allyl Enol Carbonates, Allyl β -Keto Carboxylates, or Allyl Malonates as Substrates**

17 α,β -Unsaturated ketones can be prepared from allyl β -keto carboxylates or allyl enol carbonates
18 by treatment with Pd(OAc)₂/dppe in refluxing acetonitrile (Scheme 33). {ST-82} This approach is very
19 sensitive to the nature of the catalyst and experimental conditions. For example, at room temperature or
20 with solvents such as acetone or *tert*-butanol, the main product is either the saturated ketone or the α -
21 allyl ketone, {ST-82}, {SMT-83} the latter compound being selectively obtained from the Pd(PPh₃)₄
22 catalyzed reaction of allyl β -keto carboxylates in DMF. {TCN-80}

23 (38)

1 With respect to catalyst, palladium(II) acetate or Pd₂(dba)₃ (with or without PPh₃) is sometimes
 2 preferred to Pd(OAc)₂/dppe, {TMS-84}, {MNY-87}, {MMA-91}, {RMK-94}, {MMP-97}, {YKT-
 3 00}, {WRG-02}, {SMG-10} depending on the substrate. {SMT-83} This method has been used to prepare
 4 isoflavones {DFR-93} and α,β-unsaturated esters, {KKK-09}, {KK-10}, {HKS-12} but has rarely been
 5 used to make α,β-unsaturated aldehydes {SMT-83}, {MNY-87} owing to decarboxylative
 6 allylation. {AT-14} The procedure is compatible with the presence of phenol and cyano groups, as well
 7 as alkyl, benzyl, aryl, and silyl ethers, but is ineffective for substrates having an indole or a carbamate-
 8 protected indolyl group (Figure 6). {KK-10}

9 **(39)**{KK-10}

10 The substitution pattern of the substrate affects its reactivity. In general, allyl β-keto carboxylates
 11 generate 2-substituted cyclopent-2-enones in yields up to 90%. {ST-82}, {TMS-84}, {MNY-87}, {WRG-
 12 02}, {SMG-10} However, the synthesis of unsubstituted cyclopent-2-enone is problematic; neither allyl
 13 carboxylate **21** nor allyl carbonate **22** furnishes the desired enone product in a useful yield. Instead, the
 14 major product is 2-allylcyclopentanone, which results from decarboxylative allylation (Scheme
 15 34). {SMT-83}, {TB-05}

16 **(40)**

17 As depicted in Scheme 9, a Pd–H species is involved in the dehydrogenation reaction. When
 18 carbon–palladium(II) intermediates have both a hydrogen and an acetate in the β-position, competition
 19 can occur between β-H and β-OAc elimination. {LM-12} Favoring the latter pathway provides an
 20 effective synthesis of α-methylene ketones, esters, lactones, and lactams from allyl acetoxymethyl
 21 carboxylates such as substrate **23** (Scheme 35). The same reaction is observed from substrates **24** and **25**
 22 which bear a carbonate or a benzoate instead of an acetate group. {TNM-86}, {TNM-87} On the other

1 hand, substrates **26** and **27**, which bear a methoxy or a hydroxyl group, respectively, afford the α -allyl
2 carbonyl compounds as the major products. {TNM-86}

3 **(41)**

4 **α -Chloro Ketones as Substrates**

5 α -Chloro ketones undergo palladium-catalyzed dehydrohalogenation to form the corresponding
6 enones. {GLP-12}, {WBM-12} Attempts to effect a methoxycarbonylation of 2-chloro-1-tetralone afford
7 70% of 1-naphthol and only 5% of the β -keto ester (Scheme 36). {WBM-12}

8 **(42)**

9 This method for preparing enones by palladium-catalyzed dehydrohalogenation of α -halo
10 ketones has not seen synthetic applications. Simpler reaction conditions than those documented {GLP-
11 12}, {WBM-12} may be effective but remain uninvestigated.

12 **APPLICATIONS TO SYNTHESIS**

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

16 **Desymmetrization/Palladium-Mediated Dehydrosilylation Reaction Sequence**

17 Enantioselective deprotonation of prochiral cyclic ketones {WF-80}, {S-86}, {CCC-90}, {ATN-
18 97}, {SW-13} provides convenient access to non-racemic, 4-substituted cyclohex-2-en-1-ones (Scheme
19 37). {STK-86}, {CS-91}, {SYK-01}, {TH-12}, {CVP-11}, {RVS-05}, {NAN-15} This method involves
20 quenching with chlorotrimethylsilane {CG-84} followed by palladium-catalyzed dehydrosilylation.
21
22
23

(43)

Enones as Intermediates in Natural Product Synthesis

Enones are useful intermediates in the total synthesis of natural products, wherein they are often prepared by the Saegusa Reaction. Representative examples include the syntheses of gambierol (Schemes 38 and 39), {FHH-10}, {FHM-09}, {M-10a}, {MCJ-06}, {KTS-03}, {KTS-03b}, {FSS-02}, {FKT-02}, {SF-14}, {SF-04} (\pm)-preussomerins F, K and L (Scheme 40), {QSR-04}, {QST-04}, zoanthamine, {M-07}, {YSH-09} zoanthenol, {YTT-11} norzoanthamine (Scheme 41), {MSH-04}, {M-07}, {YSH-09}, {YMH-09} gochnatiolides, {LDZ-12} and methyl (\pm)-jasmonate (Scheme 42). {KYG-87}

(44)

(44a)

{FHM-09}, {FHH-10}, {M-10a}, {KTS-03}, {KTS-03b}, {FSS-02}, {FKT-02}

(45){QST-04}, {QSR-04}

(46)

(47)

Tandem Reactions Involving Enones

Saegusa Reaction products have been used as intermediates in various tandem reactions. For example, sonication of a DMSO solution of silyl enol ether **28** in the presence of palladium(II) acetate under an atmosphere of air generates dienone **29**, which undergoes a cross-Diels–Alder reaction with enone **30** to produce intermediate **31** (Scheme 43). {LDZ-12} Isomerization of compound **31** yields gochnatiolide C, and allylic oxidation of the latter compound affords gochnatiolides A and B. Also

1 isolated is compound **33**, which arises from a homo-Diels–Alder reaction of dienone **29** to form
2 intermediate **32**, followed by isomerization and allylic oxidation (Scheme 44).

3 **(48)**

4 **(48a)**

5 Scheme 45 depicts a spontaneous intramolecular Diels–Alder reaction of a Saegusa product en
6 route to the methyl ester of sordaricin. {KKW-93}

7 **(49)**

8 The synthesis of 3-arylacrylate **36** involves decarboxylative palladation of acid **34** and oxidative
9 dehydrogenation of enol silane **35**, followed by a Heck-type coupling (Scheme 46). {FHK-10}. Notably,
10 all three steps of this tandem reaction are catalyzed by the same palladium species, palladium(II) acetate.

11 **(50)**

12 **Saegusa Reaction on an Industrial Scale**

14 Because the Saegusa Reaction is a reliable method for enone synthesis, it has found application
15 in industrial syntheses. The synthesis of a receptor agonist involves a phenol intermediate that can be
16 accessed from enone **37** by palladium-mediated, oxidative dehydrogenation (Scheme 47). {HAC-
17 13} {TM-87} Up to 11.5 kg of palladium(II) acetate is used in this stoichiometric dehydrogenation
18 reaction, resulting in kilogram quantities of the desired intermediate. Elaborate workup procedures are
19 used to recover the palladium metal; in one example, 10.3 kg of palladium metal was recovered from a
20 reaction that employed 10.5 kg of palladium(II) acetate.

21 **(51)**

22 **COMPARISON WITH OTHER METHODS**

23

1 Because of the well-known utility of α,β -unsaturated carbonyl compounds in increasing molecular
 2 complexity in organic synthesis, their preparation has been the subject of a large number of studies and
 3 many different approaches are available. In this section, the Saegusa Reaction is compared with
 4 alternative methods for the dehydrogenation of carbonyl compounds and related substances to the
 5 corresponding α,β -unsaturated carbonyl compounds. Included in this discussion are bromination–
 6 dehydrobromination, {SH-73}, {MW-72}, {GMO-72}, {BW-91}, {BC-83} thiolation–oxidation–
 7 elimination, {TSH-76} and selenation–oxidation–elimination {RRR-73}, {RRR-75}, {SLT-73}, {RW-
 8 93}, {BLL-78}, {BLL-80} reaction sequences. In addition, palladium, {M-10}, {TCN-16}, {DS-
 9 11}, {GHQ-12}, {DWS-12} iodine, {NZB-00}, {NMB-02}, {NGM-02}, {NMB-02a}, {NMBZ-02}, {SHR-
 10 10} *N-tert*-butyl benzenesulfinimidoyl chloride, {MMK-00}, {MA-05} and 2,3-dichloro-5,6-dicyano-
 11 1,4-benzoquinone (DDQ) {RMH-78} chemistry are discussed as well, as is dye-sensitized
 12 photooxygenation. {RLC-78} Examples of products that are best prepared by methods other than the
 13 Saegusa Reaction are summarized in Table A, whereas Table B depicts substrates for which the Saegusa
 14 Reaction was most efficient. Table C depicts the examples of the α,β -unsaturated carbonyl compounds
 15 that have been obtained in similar yields by the Saegusa Reaction and by another method. The
 16 relationships between the method, substrate, and yield are not obvious within these datasets, and
 17 therefore, identifying the best reaction sequence for a given substrate remains a largely empirical
 18 process.

19 **(52)**

20 {RFZ-12}, {GKS-98}, {CBL-06}, {STF-13}, {CMM-96}, {HML-06}, {TF-05}, {TDV-10}, {KDY-
 21 00}, {BFB-10}, {D-99}, {XWZ-15}, {PMS-97}, {SSD-00}, {HMH-04}, {O-01}, {O-02}, {DLY-
 22 08}, {LGG-13}, {BAW-07}, {D-99}, {BSG-97}, {HSI-11}, {BCD-02}, {GX-09}, {CFI-10}, {NKV-
 23 06}, {RZP-09}, {KNT-86}, {FPR-05}, {SHN-04}, {NPS-09}, {LDD-13}

(53)

{JDV-14},{MMA-97},{IZM-01},{HGC-02},{GFB-00},{CBL-06},{D-99},{HZ-96},{PP-09},{D-99},{D-99},{RS-79},{D-99},{BMO-13},{WT-07},{FPK-15},{G-08},{DWJ-14},{SIF-02},{FKT-02},{NKV-06},{YMM-11},{QST-04},{QSR-04},{JW-97b},{DD-15},{DDH-15}

(54)

{CBL-06},{NPT-08},{BBW-13},{FTF-05},{NPS-09},{NKV-06}

The dehydrogenation of bis(trimethylsilyl enol ether) **38** is an interesting case, because multiple reaction pathways are possible (Scheme 48). {NJV-99} Chemoselective dehydrogenation of substrate **38** is observed in the presence of two equivalents of palladium(II) acetate (Method A^S). On the other hand, both enol ethers react with phenylselenenyl chloride, and the products that are isolated depend on the nature of the oxidant, which can also promote a Pummerer-type reaction prior to the desired dehydrogenation reaction.

(55)

All of the methods discussed herein involve a metal (either catalytic or stoichiometric), but there is one example of a metal-free dehydrogenation of a silyl enol ether. 3-(Trimethylsilyl)cyclohex-2-enone is formed by aerobic oxidation of 1-(trimethylsilyloxy)-3-(trimethylsilyl)cyclohex-1-ene in the absence of a metal (Scheme 49). {HCH-08}

(56)**EXPERIMENTAL CONDITIONS**

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

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

4 **Silyl Enol Ethers as Substrates**

6 When diallyl carbonate is used to regenerate the catalyst, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ produces higher
7 yields than $\text{Pd}(\text{OAc})_2$ (with or without dppe) at room temperature and at reflux. {OXT-04} In the case of
8 Method C, side reactions may occur to varying degrees depending on the batch of $\text{Pd}(\text{OAc})_2$ and on the
9 scale. {FHM-12}, {FHM-13}

11 **Enol Acetates as Substrates**

12 Product yields are very sensitive to the purity of the reagents when $\text{Pd}(\text{OAc})_2/\text{dppe}$ and allyl
13 methyl carbonate are employed. {ACH-01} In some cases, the use of dppe lowers the yields. {TMS-
14 84}, {MTS-86}

16 **Allyl Enol Carbonates as Substrates**

17 α,β -Unsaturated ketones are obtained in better yields using $\text{Pd}(\text{OAc})_2/\text{dppe}$ than with
18 $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ at 80° . The decarboxylation/allylation pathway predominates at room temperature or
19 with $\text{Pd}_2(\text{dba})_3/\text{dppe}$ or $\text{Pd}(\text{PPh}_3)_4/\text{dppe}$. {SMT-83} Both $\text{Pd}(\text{OAc})_2$ and $\text{Pd}_2(\text{dba})_3$ in MeCN are effective
20 in the absence of phosphine ligands. {TMS-84}

22 **Allyl β -Keto Carboxylates as Substrates**

1 The use of Pd(OAc)₂/dppe is slightly more efficient in MeCN than in DMF, whereas the use of
2 acetone or *t*-BuOH as solvent provides mainly the decarboxylation/allylation product. {ST-82}
3 Decarboxylative allylation also predominates when PPh₃ is employed instead of dppe. {ST-82}, {MDC-
4 15} With Pd₂(dba)₃ as the catalyst, the reaction may stop prematurely in DMF. {KK-10}

6 EXPERIMENTAL PROCEDURES

7 (57)

8 **5,5-Dimethyl-3a',4'-dihydro-1'*H*-spiro[[1,3]dioxane-2,2'-pentalen]-5'(3'*H*)-one**

9 **[Stoichiometric Dehydrogenation of a Ketone via a Silyl Enol Ether].{D-00}** To a stirred solution of
10 the cyclopentanone (1.80 g, 8.0 mmol, 1 equiv) in dry CH₂Cl₂ (100 mL) at -78° under an argon
11 atmosphere were added Et₃N (3.44 mL, 24 mmol, 3 equiv) and Me₃SiI (2.35 mL, 16 mmol, 2 equiv).
12 After the mixture had been stirred at -78° for 30 min, saturated aqueous NaHCO₃ (10 mL) was added,
13 and the mixture was allowed to warm to rt. The phases were separated, and the aqueous phase was
14 extracted with Et₂O (3 × 10 mL). The organic extracts were combined and dried over anhydrous MgSO₄.
15 Evaporation of the solvent gave the silyl enol ether (2.19 g, 92%) as a colorless oil. The silyl enol ether
16 was used without further purification.

17 To a solution of Pd(OAc)₂ (1.59 g, 7.1 mmol, 1.0 equiv) in dry MeCN (90 mL) at rt was added a
18 solution of the unpurified silyl enol ether (2.09 g, 7.1 mmol, 1 equiv) in dry MeCN (10 mL). After the
19 mixture had been stirred at rt for 2 h, it was filtered through a short column of Florisil. The column was
20 washed with Et₂O, and the combined filtrates were concentrated under reduced pressure. Colum
21 chromatography on silica gel (4 cm × 25 cm; petroleum ether/EtOAc, 2:1) of the residue gave the

1 product (1.29 g, 72%) as a white solid: mp 84–86° (after recrystallization from hexane); IR (KBr) 2959,
2 1704, 1635, 1103 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 0.94 (s, 3H), 1.01 (s, 3H), 1.40 (dd, *J* = 6.2, 6.2
3 Hz, 1H), 2.08 (dd, *J* = 9.0, 1.7 Hz, 1H), 2.60 (dd, *J* = 9.0, 3.0 Hz, 1H), 2.65 (dd, *J* = 6.2, 4.0 Hz, 1H),
4 2.87 (d, *J* = 9.0 Hz, 1H), 2.99 (d, *J* = 9.0 Hz, 1H), 3.12 (m, 1H), 3.47 (dd, *J* = 5.0 Hz, 2H), 3.52 (dd, *J* =
5 5.0 Hz, 2H), 5.89 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 22.3, 22.4, 30.1, 38.1, 42.0, 42.1, 43.4, 71.6,
6 72.5, 109.0, 125.8, 185.6, 209.6; HRMS (*m/z*): [M]⁺ calcd for C₁₃H₁₈O₃, 222.1256; found, 222.1255.
7 Anal. Calcd. for C₁₃H₁₈O₃: C, 70.25; H, 8.16. Found: C, 70.36; H, 8.30

8 (58)

9 **4-Isopropylcyclohex-2-enone [Dehydrogenation of a Ketone in the Presence of**

10 **Benzoquinone via a Silyl Enol Ether].{FSM-08}** A 2.3 M solution of *n*-BuLi (1.93 mL, 4.49 mmol,
11 2.1 equiv) was added to a solution of *i*-Pr₂NH (0.660 mL, 4.71 mmol, 2.2 equiv) in THF (8 mL) at -78°.
12 The mixture was warmed to 0° over 30 min and then cooled to -78°. A solution of 4-
13 isopropylcyclohexanone (0.300 g, 2.14 mmol, 1 equiv) in THF (2 mL) was added dropwise, and the
14 reaction mixture was stirred at -78° for 1 h. TMSCl (0.410 mL, 3.21 mmol, 1.5 equiv) was added
15 dropwise, and the resulting mixture was stirred at rt for 18 h before being quenched with saturated
16 aqueous NaHCO₃ solution (8 mL). The reaction mixture was diluted with Et₂O (8 mL), and the aqueous
17 layer was extracted with Et₂O (2 × 10 mL). The combined organic layers were washed with saturated
18 aqueous NaCl (30 mL), dried over Na₂SO₄, and concentrated in vacuo to yield 4-isopropylcyclohex-1-
19 enyloxytrimethylsilane (0.590 g, 2.79 mmol) as a yellow oil that was used without further purification.

20 A solution of 4-isopropylcyclohex-1-enyloxytrimethylsilane (0.590 g, 2.79 mmol, 1 equiv) in
21 MeCN (3 mL) was added dropwise to a solution of Pd(OAc)₂ (0.440 g, 1.95 mmol, 0.7 equiv) and 1,4-

1 benzoquinone (0.210 g, 1.95 mmol, 0.7 equiv) in MeCN (8 mL) at rt. The reaction mixture was stirred at
2 rt for 16 h, and then was filtered through a pad of Celite. The pad of Celite was washed with Et₂O (30
3 mL), and the filtrates were concentrated in vacuo. This material was purified by silica gel column
4 chromatography (petroleum ether/EtOAc, 9:1) to yield the product (0.270 g, 1.96 mmol, 92% over two
5 steps) as a pale-yellow oil: IR (liquid film) 2960, 2872, 1676, 1419, 1389, 1187, 1145 cm⁻¹; ¹H NMR
6 (CDCl₃, 500 MHz) δ 0.97 (app t, *J* = 7.1 Hz, 6H), 1.72–1.87 (m, 2H), 1.97–2.05 (m, 1H), 2.27–2.39 (m,
7 2H), 2.51 (dt, *J* = 16.7, 4.1 Hz, 1H), 6.15 (dd, *J* = 10.4, 2.5 Hz, 1H), 6.90 (dt, *J* = 10.4, 1.9 Hz, 1H); ¹³C
8 NMR (CDCl₃, 125 MHz) δ 19.4, 19.6, 25.2, 31.5, 37.4, 42.5, 129.6, 154.4, 200.1; EIMS (*m/z*): [M + H]⁺
9 139 (49), 94 (100), 81 (48), 64 (81), 52 (60), 40 (45); HRMS (*m/z*): [M]⁺ calcd for C₉H₁₄O, 138.1039;
10 found, 138.1039.

11 (59)

12 **1,4-Dioxaspiro[4.5]dec-6-en-8-one [Catalytic Dehydrogenation of a Silyl Enol Ether in the**
13 **Presence of an Allyl Carbonate].{KMM-01}** A solution of Pd(OAc)₂ (36.0 mg, 0.16 mmol, 0.05
14 equiv) and dppe (58.0 mg, 0.14 mmol, 0.04 equiv) in MeCN (50 mL) was heated to reflux, and then
15 diallyl carbonate (0.64 g, 4.51 mmol, 1.4 equiv) and the silyl enol ether (0.74 g, 3.24 mmol, 1 equiv)
16 were added. The mixture was heated at reflux for 40 h. The solvent was then evaporated under reduced
17 pressure to furnish a residue, which was purified by filtration through a column of silica gel (Et₂O/light
18 petroleum, 1:1). The filtrate was evaporated under reduced pressure to provide the product (0.41 g, 82%)
19 as a pale-yellow oil: IR (film) 1683 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.20 (t, *J* = 6.5, 2H), 2.63 (t, *J*
20 = 6.5, 2H), 4.05 (m, 4H), 6.00 (d, *J* = 10.2, 1H), 6.61 (d, *J* = 10.2, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ
21 33.0, 35.4, 65.2, 104.1, 130.6, 146.6, 198.8; HRMS (*m/z*): [M + H]⁺ calcd for C₈H₁₁O₃, 155.0708; found,
22 155.0710. Anal. Calcd for C₈H₁₀O₃: C, 62.30; H, 6.50. Found: C, 62.31; H, 6.35.

(60)

Bicyclo[4.1.0]hept-3-en-2-one [Catalytic Dehydrogenation of a Silyl Enol Ether in the Presence of *tert*-Butyl Hydroperoxide and Oxygen].{YWC-05},{Y-15} Under an atmosphere of air, a 50-mL, round-bottomed flask equipped with a magnetic stirring bar was charged with Pd(OH)₂/C (20% Pd) (17 mg, 0.032 mmol, 0.05 equiv), NEt₃ (0.86 mL, 6.4 mmol, 10 equiv), CH₂Cl₂ (2 mL), and the silyl enol ether (69 mg, 0.64 mmol, 1 equiv). The flask was purged with pure oxygen gas and was kept under an oxygen atmosphere with a balloon. To this mixture was added *tert*-butyl hydroperoxide (40 μL, 0.40 mmol, 5 equiv) [sic] in 4 portions every 2 h with vigorous stirring. The resulting mixture was stirred at rt for 72 h, at which point TLC analysis indicated that the reaction was complete. The mixture was then filtered through a short pad of silica gel, and the pad was washed with CH₂Cl₂. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/Et₂O, 1:1) to provide the product as a clear oil (48 mg, 70%): IR (neat) 2923, 1704, 1664, 1362, 1258, 864 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.28–1.34 (m, 2H), 1.72–1.78 (m, 1H), 1.86–1.90 (m, 1H), 2.64–2.77 (m, 2H), 5.88–5.90 (m, 1H), 6.47–6.51 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 12.3, 21.9, 25.4, 51.1, 127.0, 143.3, 197.7; HRMS (70 eV) (*m/z*): [M + H]⁺ calcd for C₇H₉O, 109.0653; found, 109.0658.

(61)

(4*R*,5*S*)-5-Ethyl-4,5-dihydroxycyclohex-2-enone [Catalytic Dehydrogenation of a Silyl Enol Ether in the Presence of Oxygen].{HLW-11} A 500-mL, round-bottomed flask was charged sequentially with a Teflon-coated stirring bar, the starting diol (9.60 g, 30.6 mmol, 1 equiv), and DMSO (15.3 mL). Pd(OAc)₂ (685 mg, 3.06 mmol, 0.1 equiv) was then added. The reaction flask was purged

1 with oxygen by three evacuation–refill cycles, using a balloon of oxygen to fill the flask. The resulting
2 mixture was stirred under a balloon of oxygen for 10 h at rt. The reaction flask was then purged again
3 three times with oxygen, and stirring was continued for an additional 7 h at rt under a balloon of oxygen.
4 The product mixture was purified by column chromatography on silica gel (hexanes/acetone, 55:45) to
5 afford the product as a viscous, colorless oil (4.41 g, 92%): TLC R_f 0.20 (ethyl acetate/hexanes, 7:3,
6 SiO₂); IR (film) 3407, 1675, 1463, 1385 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 0.97 (t, J = 8.0 Hz, 3H),
7 1.72 (app q, J = 7.5 Hz, 2H), 2.26 (s, 1H), 2.48 (d, J = 16.5 Hz, 1H), 2.64 (dd, J = 16.5, 0.5 Hz, 1H),
8 2.76 (d, J = 8.5 Hz, 1H), 4.38 (dt, J = 9.0, 2.5 Hz, 1H), 6.04 (ddd, J = 11.0, 2.0, 1.0 Hz, 1H), 6.74 (dd, J
9 = 10.0, 2.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz), δ 7.9, 31.2, 46.1, 70.1, 76.8, 128.9, 149.8, 198.3;
10 HRMS–CI (m/z): [M + H]⁺ calcd for C₈H₁₃O₃, 157.0859; found, 157.0855.

11 **(62)**

12 **(1*R*,5*R*)-1-(((1,1-Dimethylethyl)dimethylsilyloxy)methyl)bicyclo[3.1.0]hex-3-en-2-one**
13 **[Catalytic Dehydrogenation of a Ketone in the Presence of Oxygen via a Silyl Enol Ether].{JDV-**
14 **14}** To a solution of the ketone (0.647 g, 2.69 mmol, 1 equiv) in CH₂Cl₂ (13.5 mL) was added TBSOTf
15 (0.742 mL, 3.23 mmol, 1.2 equiv). Triethylamine (1.12 mL, 8.07 mmol, 3 equiv) was added dropwise.
16 The reaction mixture was stirred at rt for 1 h and then was diluted with a saturated aqueous NaHCO₃
17 solution. The organic layer was removed, and the aqueous layer was extracted with CH₂Cl₂. The
18 combined extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue
19 was passed through a short column of silica gel (pretreated with 3% triethylamine in hexanes). The
20 residue was eluted with 1% triethylamine in hexanes. Concentration of the fractions in vacuo yielded a
21 colorless liquid that was dissolved in DMSO (26.9 mL).

1 To the solution of the silyl enol ether in DMSO was added Pd(OAc)₂ (60.4 mg, 0.269 mmol, 0.1
2 equiv). The reaction flask was purged with molecular oxygen before attaching a balloon filled with
3 oxygen. The reaction mixture was heated to 55° and stirred at that temperature for 48 h. The reaction
4 mixture was allowed to cool to rt and was extracted with hexanes. The combined extracts were dried
5 over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography
6 on silica gel (hexanes/ethyl acetate, 97:3 to 92:8) to provide the product as a colorless oil (0.495 g, 77%
7 over two steps): ¹H NMR (C₆D₆, 400 MHz) δ 0.02 (s, 6H), 0.82–0.93 (m, 10H), 1.11 (app dd, *J* = 6.9,
8 3.3 Hz, 1H), 2.02 (ddd, *J* = 6.8, 2.9, 2.9, 1H), 3.68 (d, *J* = 10.5 Hz, 1H), 4.22 (d, *J* = 10.5 Hz, 1H), 5.42
9 (d, *J* = 5.7 Hz, 1H), 6.90 (dd, *J* = 5.7, 2.8 Hz, 1H); ¹³C NMR (C₆D₆, 100 MHz) δ –5.34, –5.27, 18.5,
10 26.1, 26.3, 36.1, 37.6, 60.0, 128.8, 162.0, 204.5; HRMS–ESI (*m/z*): [M + Na]⁺ calcd for C₁₃H₂₂O₂NaSi,
11 261.1287; found, 261.1300.

12

(63)

13 **4-Cyano-4-(3,4-dichlorophenyl)cyclohex-2-enone [Catalytic Dehydrogenation of an Enol**
14 **Acetate in the Presence of an Allyl Carbonate].{ACH-01}** To a solution of 4-cyano-4-(3',4'-dichloro-
15 phenyl)cyclohex-1-enyl acetate (150 mg, 0.4 mmol, 1 equiv) in dry MeCN (5 mL) were added Pd(OAc)₂
16 (6.7 mg, 0.03 mmol, 0.075 equiv), dppe (12 mg, 0.03 mmol, 0.075 equiv), and allyl methyl carbonate
17 (0.07 mL, 0.62 mmol, 1.55 equiv). The mixture was stirred for 30 min at rt, and then tributyltin
18 methoxide (0.03 mL, 0.12 mmol, 0.3 equiv) was added. The reaction mixture was heated at reflux for 18
19 h, cooled to rt, and filtered through a pad of Celite. After CH₂Cl₂ (15 mL) was added, the organic layer
20 was washed with a saturated aqueous NH₄Cl solution (3 × 15 mL), dried over MgSO₄, and concentrated
21 in vacuo. The crude product was purified by column chromatography on silica gel (hexane; then
22 hexane/Et₂O, 1:1) to yield the product (77.4 mg, 65%) as a colorless oil: TLC R_f 0.62 (hexane/EtOAc,

1 1:1); IR (film) 2239, 1693 cm^{-1} ; ^1H (CDCl_3 , 300 MHz) δ 2.13–2.86 (m, 4H), 6.33 (d, $J = 9.9$ Hz, 1H),
2 6.80 (d, $J = 9.9$ Hz, 1H), 7.24–7.54 (m, 3H); ^{13}C (CDCl_3 , 75 MHz) δ 34.65, 37.63, 42.25, 118.41,
3 125.48, 128.31, 131.52, 132.49, 133.73, 134.03, 137.91, 143.61, 195.22; EIMS (m/z): $[\text{M}]^+$ 265 (44),
4 237 (82), 202 (23), 267 (32), 239 (57), 174 (100); HRMS–ESI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{13}\text{H}_9\text{Cl}_2\text{NO}$,
5 265.0061; found 265.0065.

6 (64)

7 **(4*R*,5*S*)-2-Allyl-4,5-bis((benzyloxy)methyl)-4,5-dimethylcyclopent-2-enone [Catalytic**
8 **Decarboxylative Dehydrogenation of an Allyl β -Keto Carboxylate].{SMG-10}** A solution of
9 (3*S*,4*R*)-allyl 1-allyl-3,4-bis((benzyloxy)methyl)-3,4-dimethyl-2-oxocyclopentanecarboxylate (5.0 g,
10 10.5 mmol, 1 equiv) in MeCN (20 mL) was added slowly to a solution of $\text{Pd}(\text{OAc})_2$ (117 mg, 0.525
11 mmol, 0.05 equiv) and PPh_3 (37 mg, 0.525 mmol, 0.05 equiv) in MeCN at 90° under Ar. The reaction
12 mixture was then stirred at 90° for 3 h before being allowed to cool to rt. Filtration of the reaction
13 mixture through a plug of silica, removal of solvent, and column chromatography on silica gel
14 (hexanes/EtOAc, 20:1) furnished the product (3.6 g, 90%) as a colorless oil: IR (film) 3064, 3030, 2979,
15 2858, 1705, 1454, 1360, 1093, 914, 737, 698 cm^{-1} ; ^1H NMR (CDCl_3 , 360 MHz) δ 1.13 (s, 3H), 1.15 (s,
16 3H), 2.91 (ddd, $J = 6.6, 2.7, 1.3$ Hz, 1H), 3.48 (d, $J = 9.0$ Hz, 1H), 3.50 (d, $J = 9.0$ Hz, 1H), 3.56 (d, $J =$
17 9.4 Hz, 1H), 3.59 (d, $J = 9.4$ Hz, 1H), 4.33 (s, 2H), 4.33 (d, $J = 11.9$ Hz, 1H), 4.38 (d, $J = 11.9$ Hz, 1H),
18 5.01–5.10 (m, 2H), 5.83 (tdd, $J = 16.8, 10.1, 6.6$ Hz, 1H), 6.97 (t, $J = 1.4$ Hz, 1H), 7.17–7.31 (m, 10H);
19 ^{13}C NMR (CDCl_3 , 90 MHz) δ 19.8, 20.1, 29.1, 49.5, 54.3, 72.8, 73.1, 73.5, 74.7, 116.4, 127.2, 127.3,
20 127.4, 128.1, 128.2, 134.5, 138.2, 138.3, 140.6, 161.5, 210.9; HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd for
21 $\text{C}_{36}\text{H}_{31}\text{O}_3$, 391.2268; found, 391.2273.

(65)

6-[(Z)-7-[(Tetrahydropyranyl)oxy]hept-1,5-diyne-3-ene]-6-[(tert-butyl)dimethylsilyl]oxy]cyclohex-2-en-1-one [Catalytic Decarboxylative Dehydrogenation of an Allyl Enol Carbonate].{MMP-97} To a solution of the carbonate (41.7 g, 83.3 mmol, 1 equiv) in anhydrous MeCN (420 mL) heated at reflux under argon was added Pd(OAc)₂ (375 mg, 1.67 mmol, 0.02 equiv). The reaction mixture was heated at 80° for 4 h until TLC (hexanes/Et₂O, 4:1) showed that the reaction was complete. Celite 545 (15 g) was added, and the mixture was allowed to cool over 30 min with vigorous stirring. The solution was filtered through a pad of Celite, and the solvent was evaporated in vacuo. The residue was immediately purified by column chromatography on silica gel (hexanes/Et₂O, 4:1) to provide the product as a colorless oil (26.2 g, 76%): IR (film) 2928, 2854, 1706, 1620 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.18 (s, 3H), 0.20 (s, 3H), 0.86 (s, 9H), 1.50–1.83 (m, 6H), 2.17–2.41 (m, 2H), 2.35–2.47 (m, 1H), 2.50–2.66 (m, 1H), 3.46–3.55 (m, 1H), 3.78–3.84 (m, 1H), 4.32–4.46 (m, 2H), 4.78 (bt, 1H), 5.77–5.88 (m, 2H), 5.95 (bd, 1H), 6.84–6.89 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ -3.2, -3.1, 18.3, 19.0, 25.1, 25.3, 25.8, 30.2, 38.8, 54.7, 62.0, 73.2, 82.9, 84.4, 93.2, 94.4, 96.9, 118.9, 120.2, 126.9, 149.8, 193.6; HRMS (*m/z*): [M + H]⁺ calcd for C₂₄H₃₅O₄Si, 415.2315; found, 415.2305.

(66)

(E)-6-Oxohex-4-en-1-yl Acetate [Catalytic Dehydrogenation of an Alkyl Enol Ether in the Presence of Benzoquinone].{LHA-12} To a 4-mL borosilicate glass vial containing 6-methoxyhex-5-en-1-yl acetate (172 mg, 1.00 mmol, 1 equiv), 1,4-benzoquinone (130 mg, 1.2 mmol, 1.2 equiv), water (20.0 μL, 1.11 mmol, 1.1 equiv), and AcOH (240 μL, 4.19 mmol, 4 equiv) was added Pd(OAc)₂ (2.4

1 mg, 0.02 mmol, 0.01 equiv), followed by CH₂Cl₂ (1 mL). The reaction mixture was stirred at rt until
2 completion (12 h), as indicated by GC analysis. The reaction mixture was then diluted with CH₂Cl₂ (50
3 mL) and washed with water (50 mL). The organic layer was dried over Na₂SO₄ and concentrated in
4 vacuo. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 9:1) to
5 provide the product (125 mg, 80%) as a clear, colorless oil: FTIR (film) 2955, 1734, 1686, 1367, 1242,
6 1045 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.87 (quint, *J* = 6.4 Hz, 2H), 2.06 (s, 1H), 2.41–2.47 (m, 2H),
7 4.12 (t, *J* = 6.4 Hz, 2H), 6.87 (dt, *J* = 15.6, 6.8 Hz, 1H), 9.52 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃, 100
8 MHz) δ 20.8, 26.8, 29.1, 63.2, 133.3, 156.9, 170.9, 193.7; HRMS (*m/z*): [M + Na]⁺ calcd for
9 C₈H₁₂NaO₃, 179.0679; found, 179.0671.

10 (67)

11 **(*E*)-4-Phenyl-2-butenal [Catalytic Dehydrogenation of an Alkyl Enol Ether in the Presence**
12 **of Cu(II)].{TKA-92}** To a stirred suspension of Pd(OAc)₂ (30 mg, 0.134 mmol, 0.5 equiv) in MeCN
13 (0.6 mL) at rt were added 5% aqueous NaHCO₃ (0.05 mL, 0.05 equiv) and Cu(OAc)₂•H₂O (54 mg,
14 0.268 mmol, 1.0 equiv). After the mixture was cooled to 0°, a solution of (4-methoxybut-3-en-1-
15 yl)benzene (43 mg, 0.268 mmol, 1 equiv) in MeCN (0.35 mL) was added. The resulting mixture was
16 stirred vigorously at 0° for 1 h and then at rt for 1 h. The mixture was poured into saturated aqueous
17 NH₄Cl solution, and the aqueous layer was extracted with CHCl₃. The organic extract was dried over
18 MgSO₄ and concentrated. The residue was purified by column chromatography on silica gel
19 (hexane/EtOAc, 7:1) to provide the product (45 mg, 83%): UV (EtOH) λ_{max} 217 nm; IR (CHCl₃) 1690
20 cm⁻¹; ¹H NMR (270 MHz) δ 3.65 (dd, *J* = 6.4, 1.7 Hz, 2H), 6.11 (ddt, *J* = 15.8, 7.7, 1.7 Hz, 1H), 6.97
21 (dt, *J* = 15.8, 6.4 Hz, 1H), 9.53 (d, *J* = 7.7 Hz, 1H); EIMS (*m/z*): [M]⁺ 146 (84), 117 (100), 115 (61), 91
22 (51); HRMS (*m/z*): [M]⁺ calcd for C₁₀H₁₀O, 146.0730; found, 146.0730.

TABULAR SURVEY

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

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

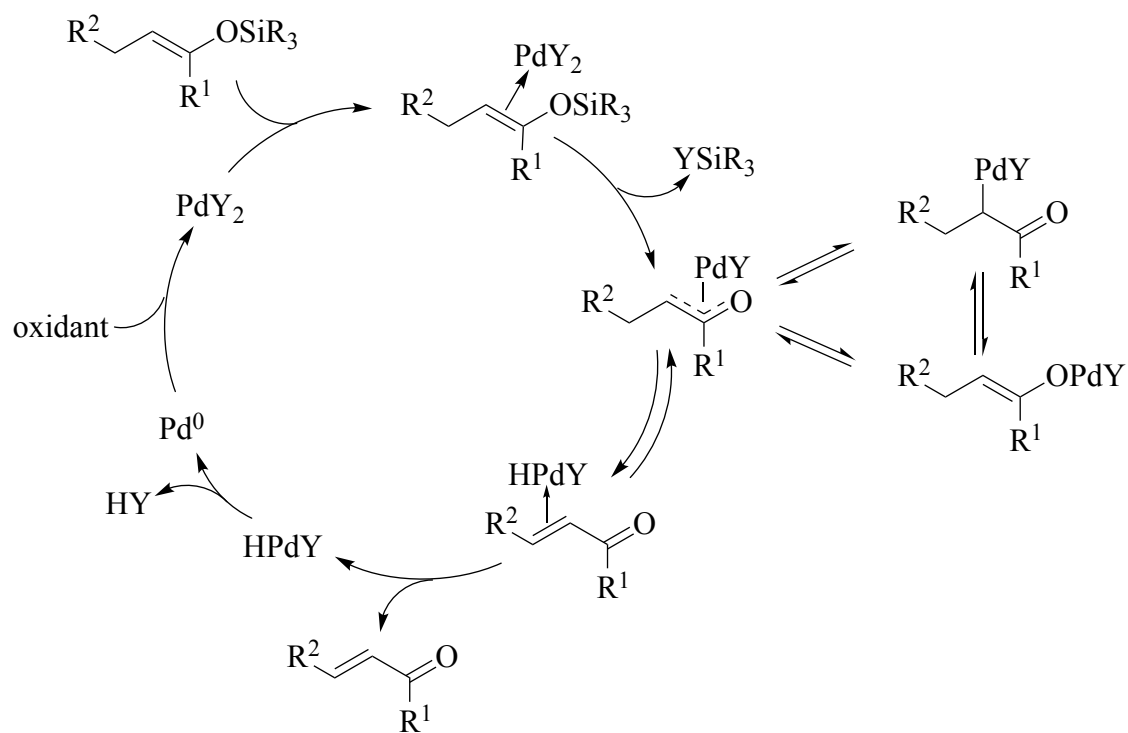
Table 1 presents oxidative dehydrogenation reactions leading to enones, cross-conjugated dienones, and phenols. Tables 2 and 3 concern the synthesis of α,β -unsaturated aldehydes and esters, respectively. Table 4 shows oxidative dehydrogenations leading to unsaturated lactones and lactams. Table 5 contains the synthesis of $\alpha,\beta,\gamma,\delta$ -unsaturated ketones, esters, and amides.

Some dehydrogenation reactions, which were used to prepare key intermediates starting from the silyl enol ethers, were reported without experimental details and yields, and consequently are not included in Tables. These compounds include 2-methoxy-14,15-dehydro-estrone, {MDG-09} 2-cyclooctenone, {LZH-09}, {OH-11} and 8,9-dihydro-5*H*-benzo[7]annulen-5-one {OH-11} prepared by Methods A; 6-phenyl-cyclohex-2-en-1-one {SSY-08} by Method G; {TMS-83} and (*R*)-4-((*tert*-butyldimethylsilyl)oxy)cyclohex-2-enone, {MAO-10} 4-*tert*-butylcyclohexenone, {S-11} and 3-nonen-5-one {S-11} using Method C. {LHK-95}

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

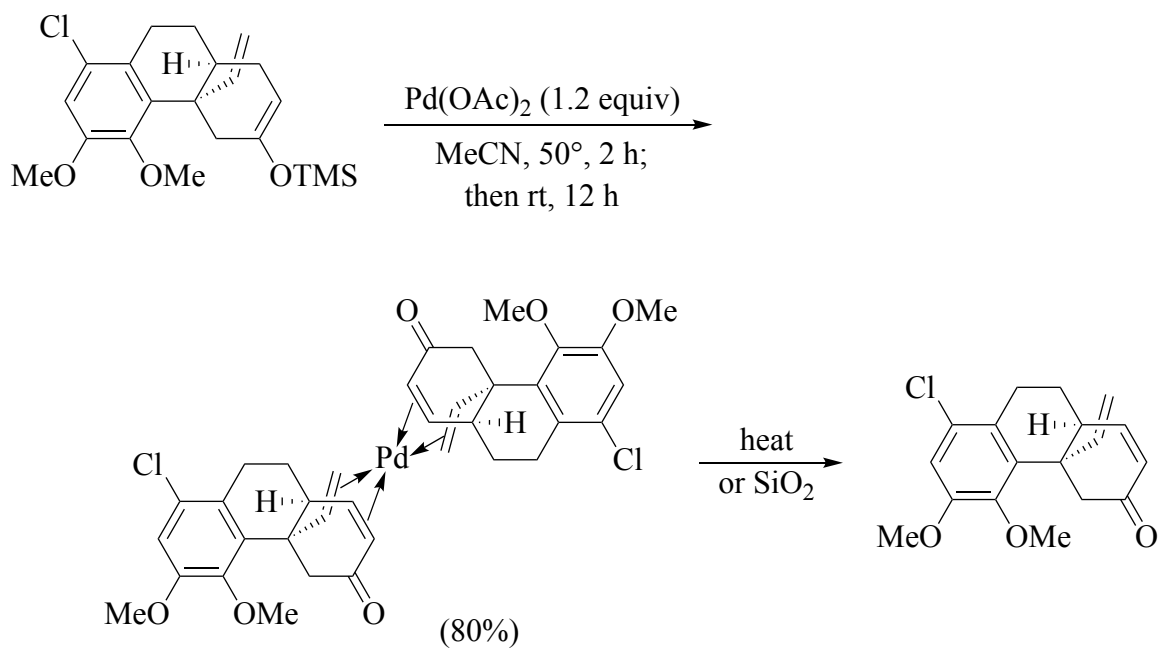
1	BOM	benzyloxymethyl
2	C ₄ H ₃ S	thienyl
3	CSA	camphorsulfonic acid
4	dba	dibenzylideneacetone
5	dppe	1,2-bis(diphenylphosphino)ethane
6	HMDS	hexamethyldisilazane
7	MPM	4-methoxybenzyl
8	MS	molecular sieves
9	PMP	4-methoxyphenyl
10	TBDPS	<i>tert</i> -butyldiphenylsilyl
11	TES	triethylsilyl
12	TPAP	tetra- <i>n</i> -propylammonium perruthenate
13	Xantphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene
14		
15		

1



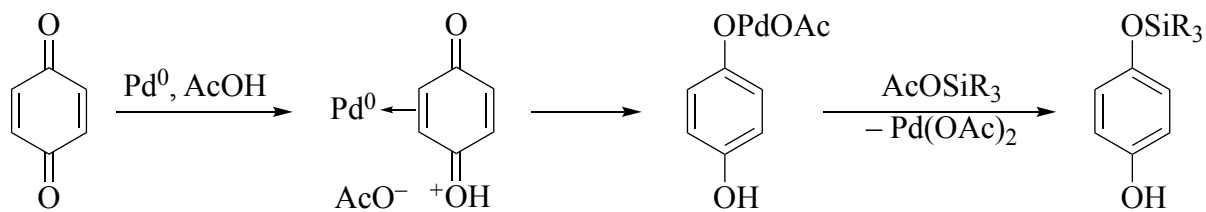
Scheme 1

2



Scheme 2

3



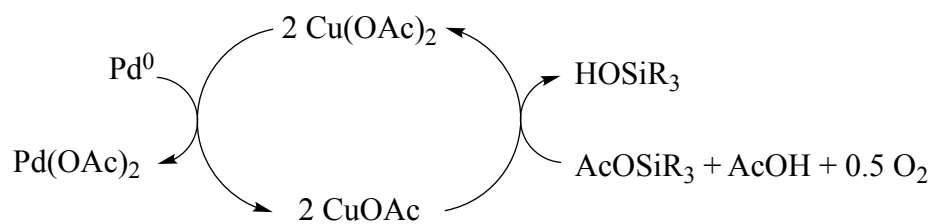
Scheme 3

4



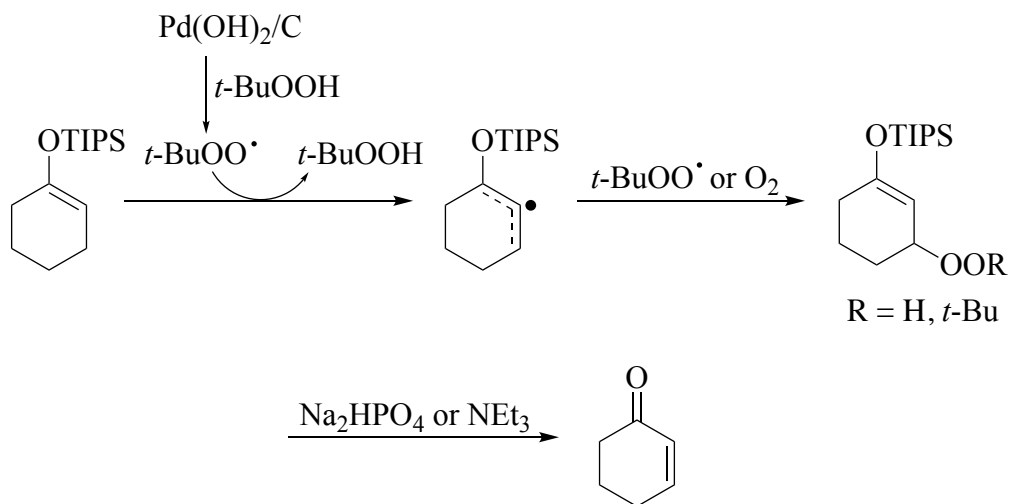
Scheme 4

5



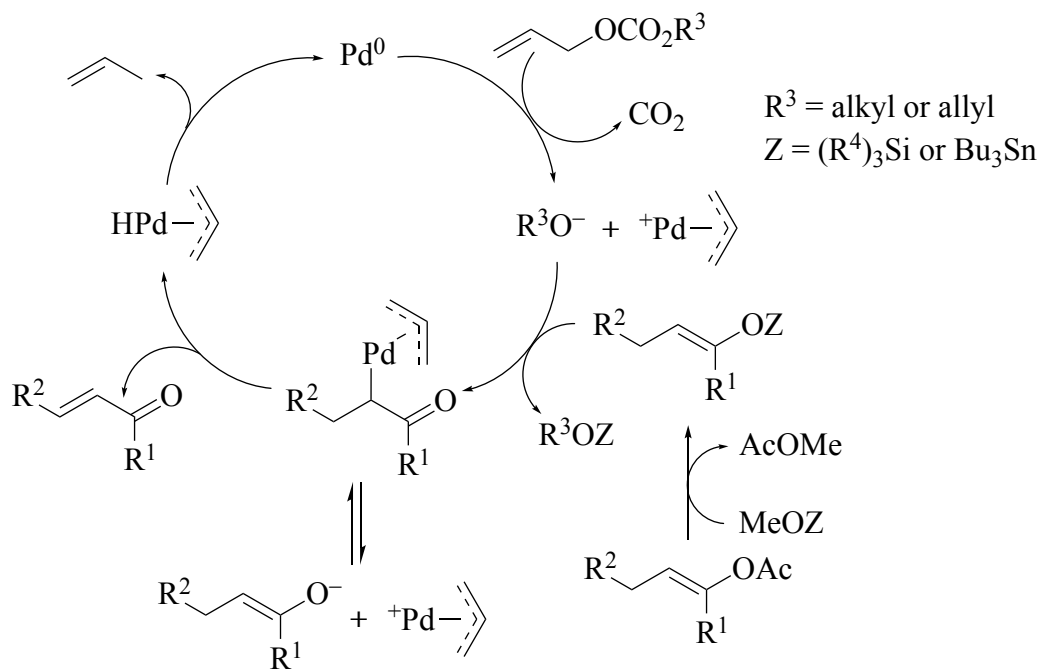
Scheme 5

6



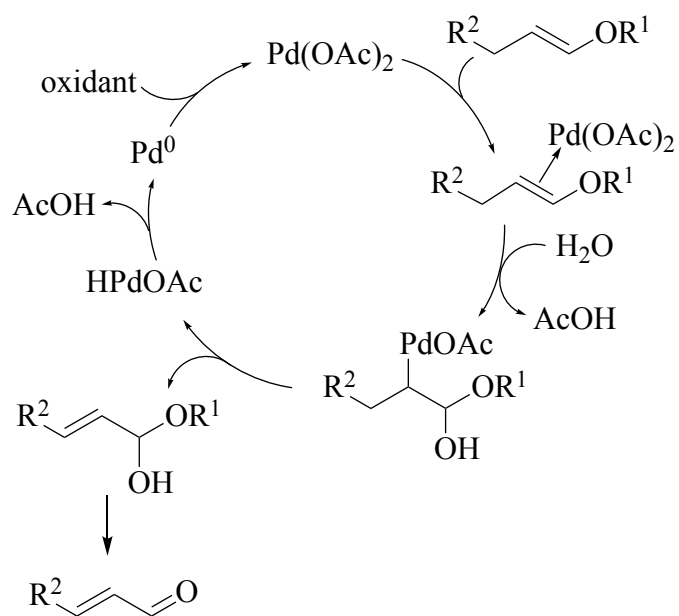
Scheme 6

7



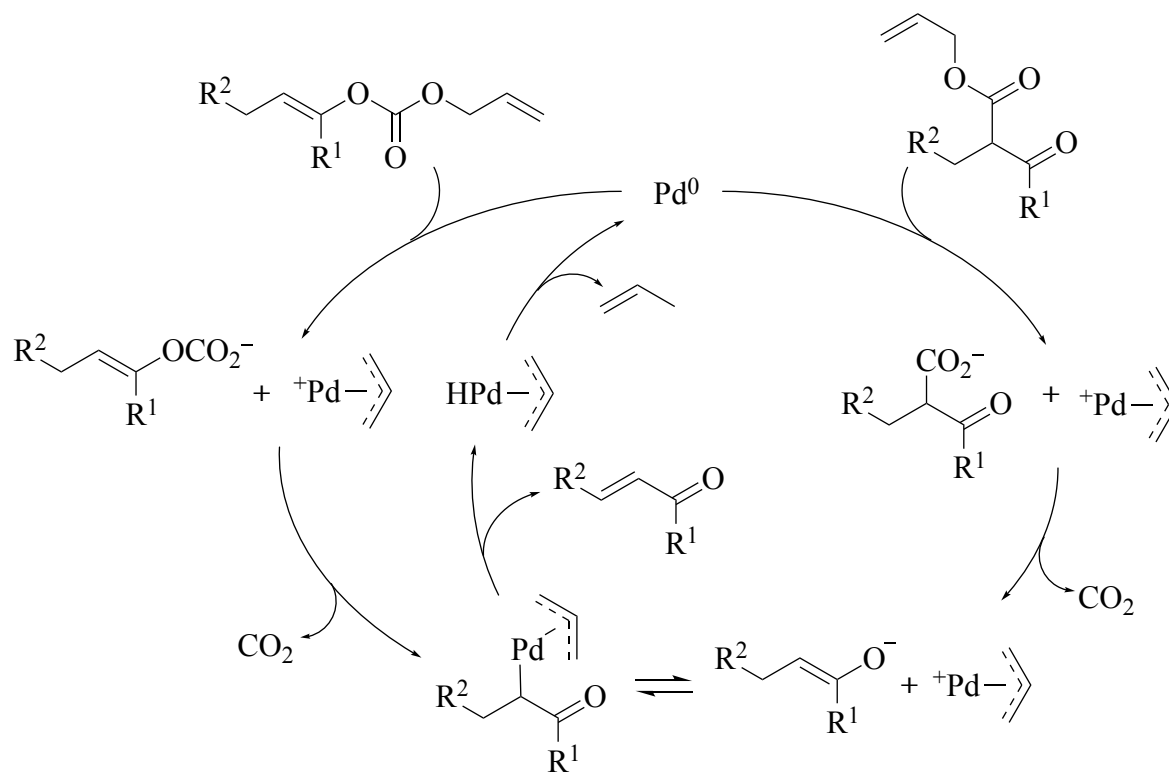
Scheme 7

8



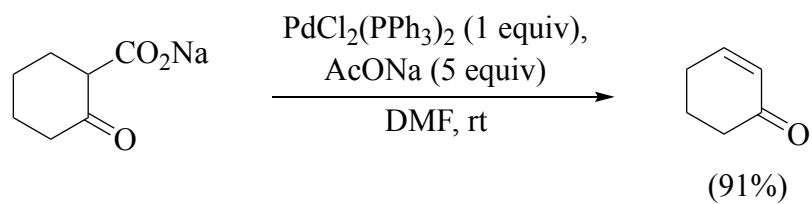
Scheme 8

9



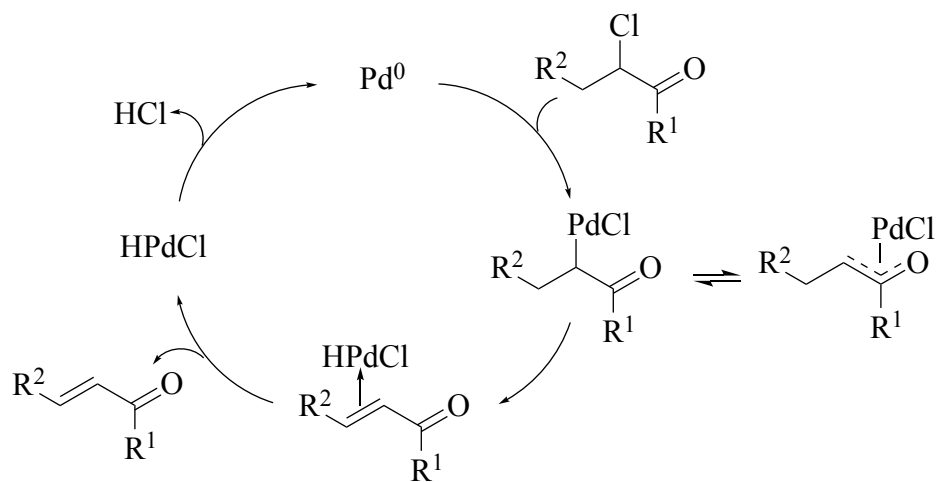
Scheme 9

10



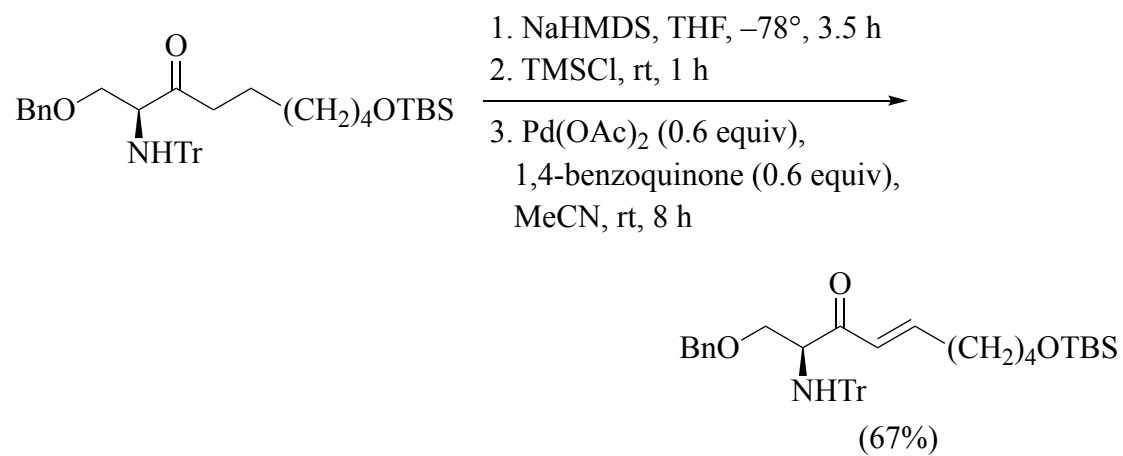
Scheme 10

11



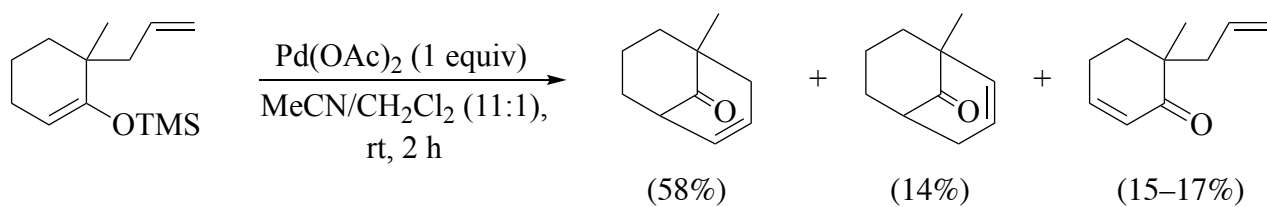
Scheme 11

12



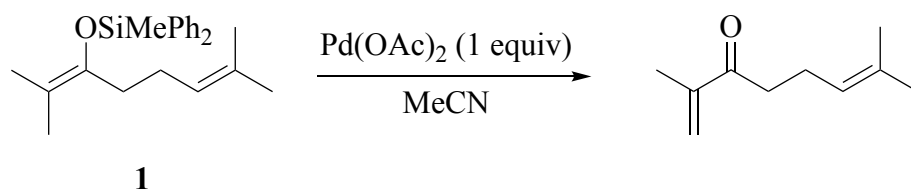
Scheme 12

13



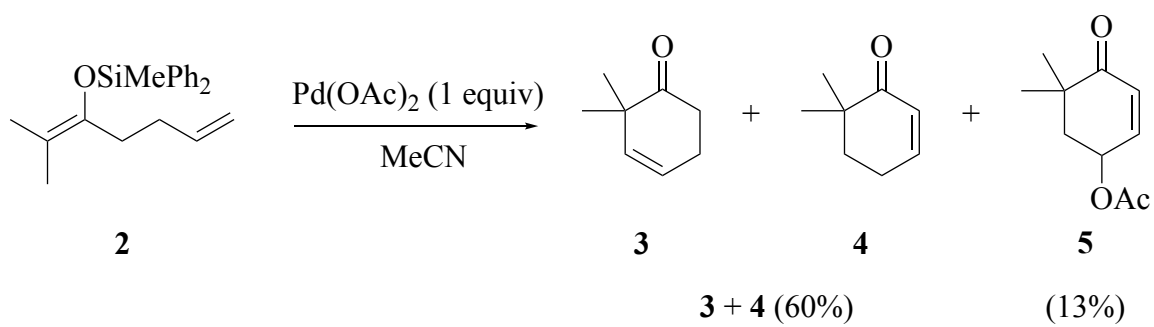
Scheme 13

14

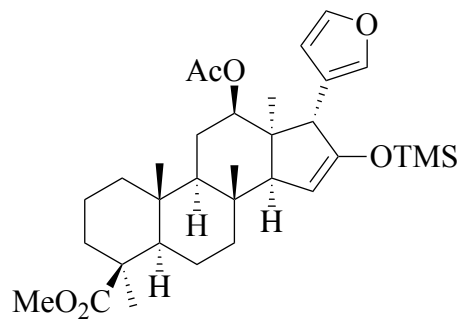


Scheme 14

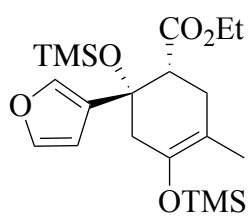
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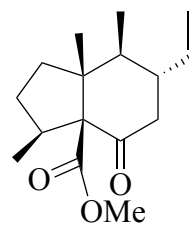
Scheme 15



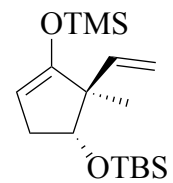
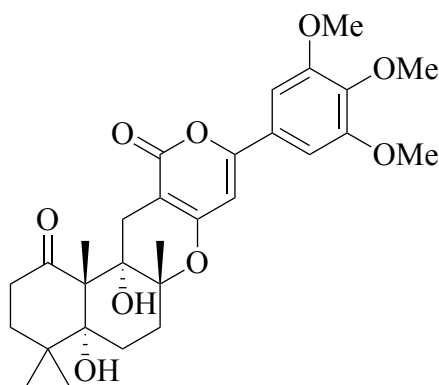
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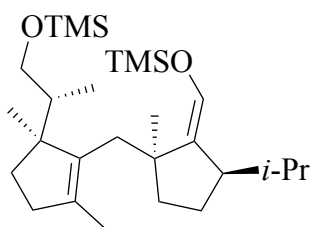
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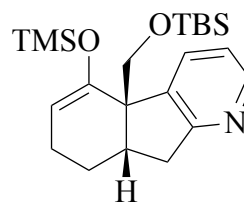
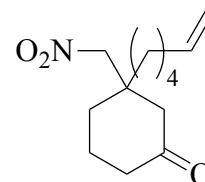
Ref. SON-07

Ref. STF-13^a

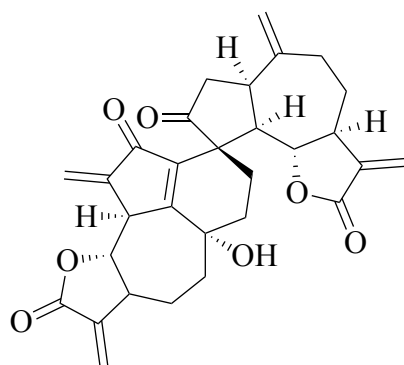
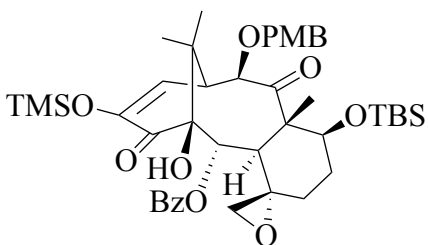
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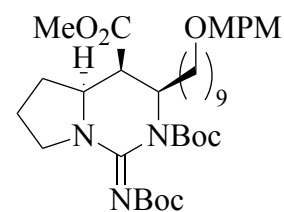
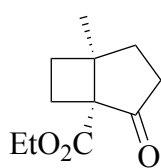
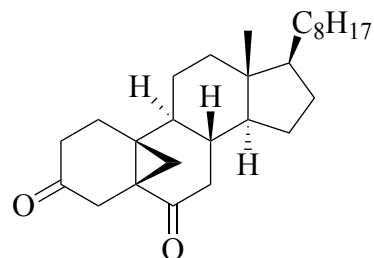
Ref. KNT-86

Ref. HIS-11^a

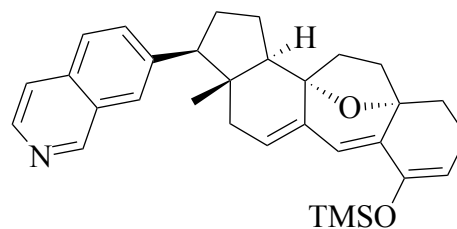
Ref. LGG-13

Ref. LDD-13^a

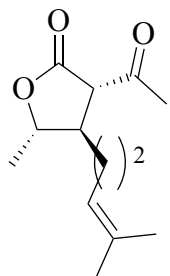
Ref. KHH-06

Ref. SST-0405^bRef. TF-05^a

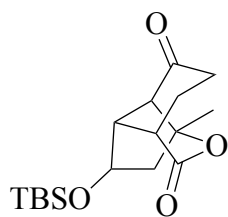
Ref. EML-07



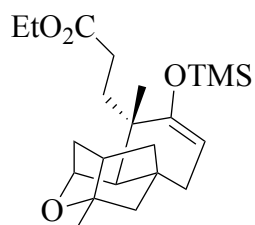
Ref. NPS-09



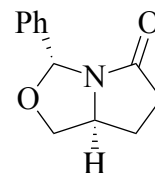
Ref. SSD-00



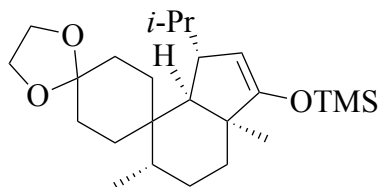
Ref. BFB-10



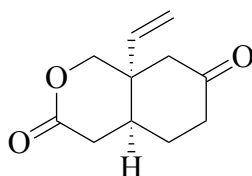
Ref. GX-09^a



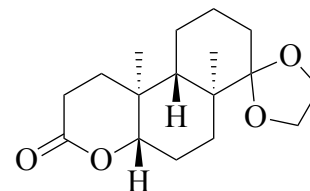
Ref. HMM-04



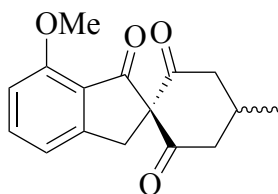
Ref. RBT-06^a



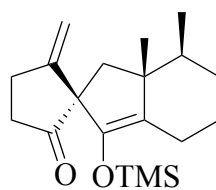
Ref. MO-02



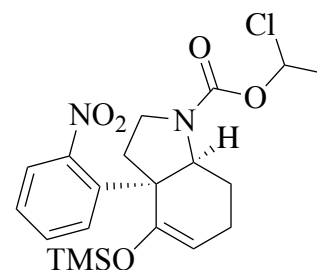
Ref. CFI-10



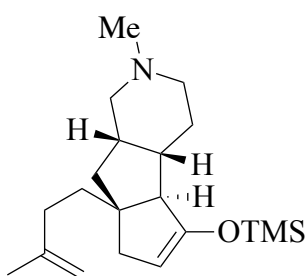
Ref. NMV-05



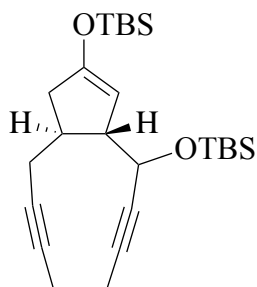
Ref. BCD-02^a



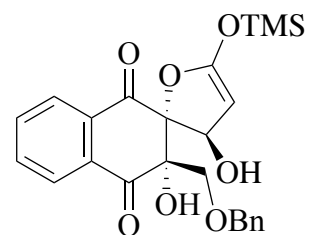
Ref. BSG-97



Ref. MRT-98



Ref. SJS-02



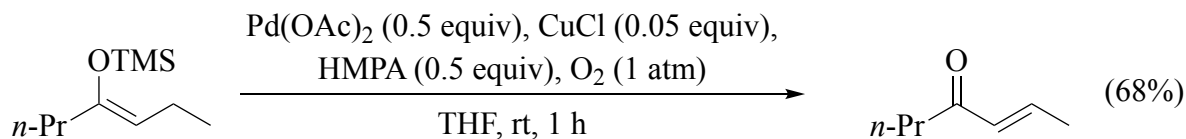
Ref. CD-01

^a A low yield of the enone product was obtained.

^b The silylation reaction was unsuccessful.

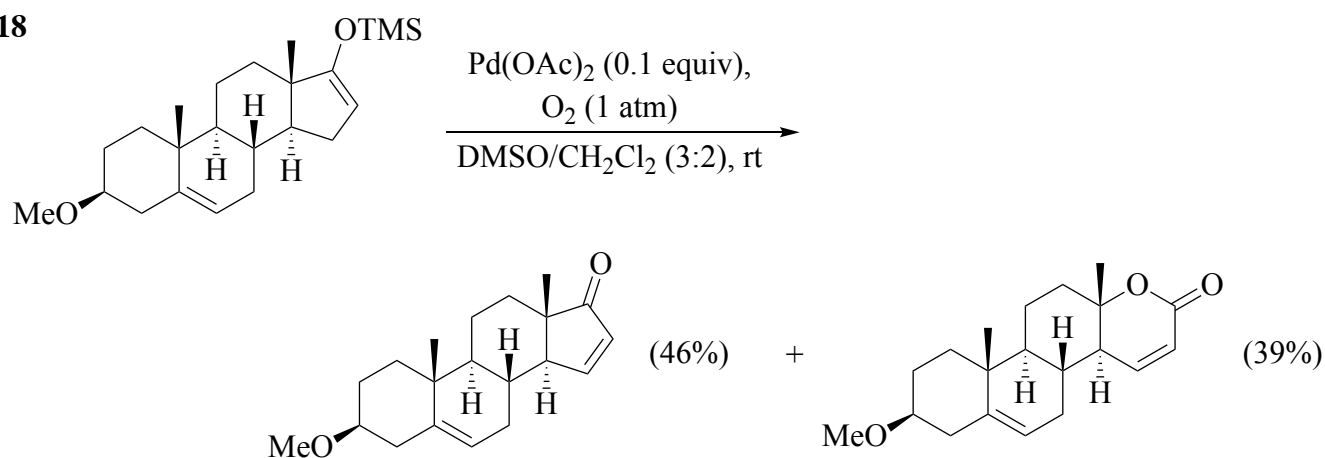
Figure 1. Substrates leading to inefficient reactions under Saegusa's conditions.

17



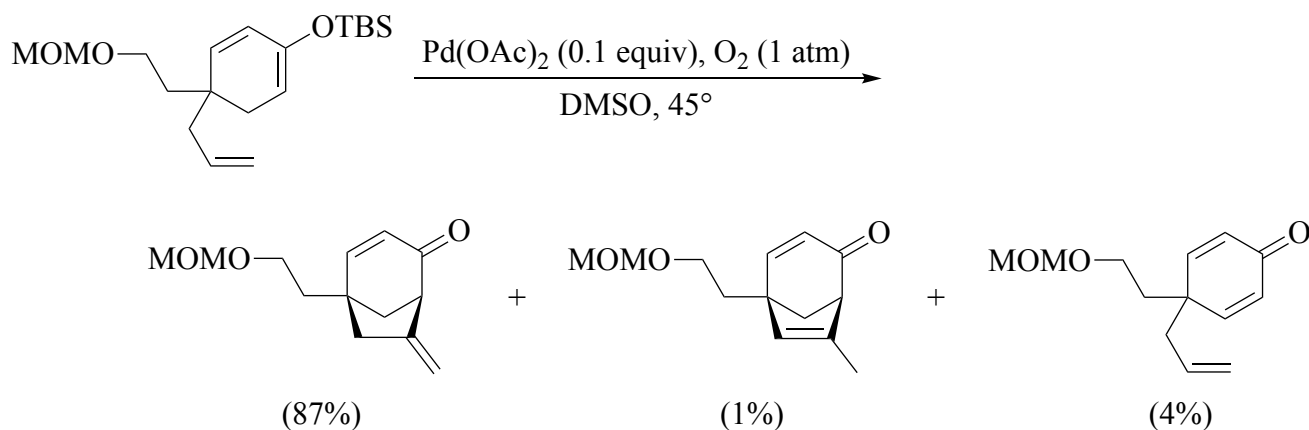
Scheme 16

18

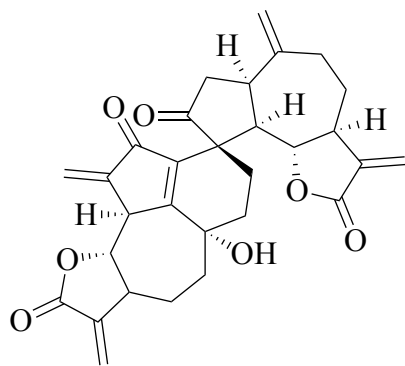
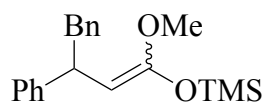


Scheme 17

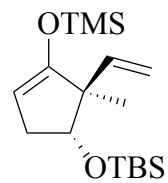
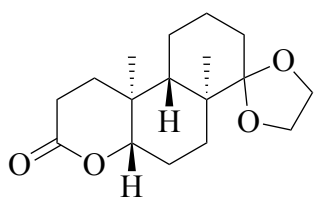
19



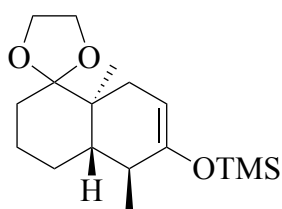
Scheme 18

Ref. LDD-13^a

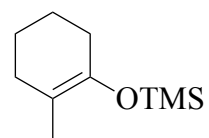
Ref. DXW-11

Ref. STF-13^a

Ref. CFI-10



Ref. BMO-13

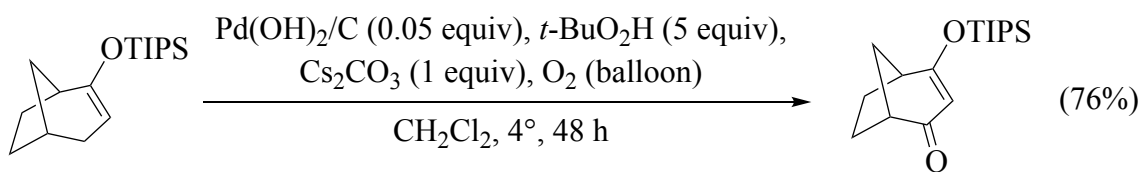


Ref. GKS-98

^a A low yield of the enone product was obtained.

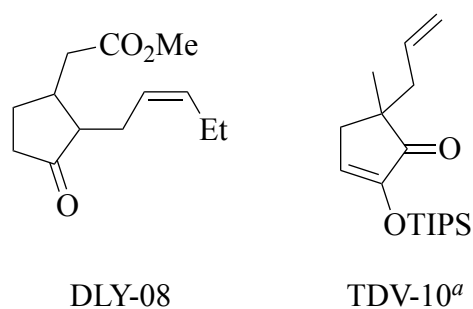
Figure 2. Substrates leading to inefficient Pd(OAc)₂/O₂/DMSO reactions.

21



Scheme 19

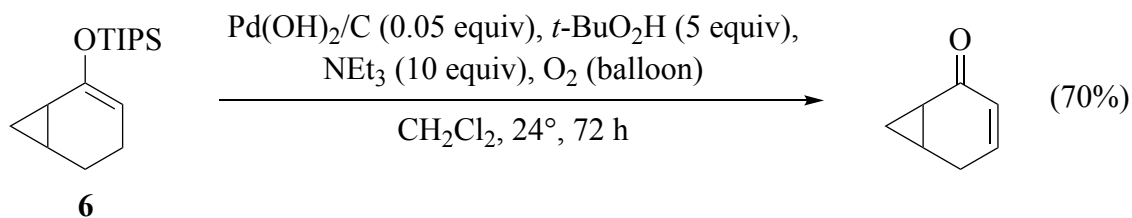
22



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

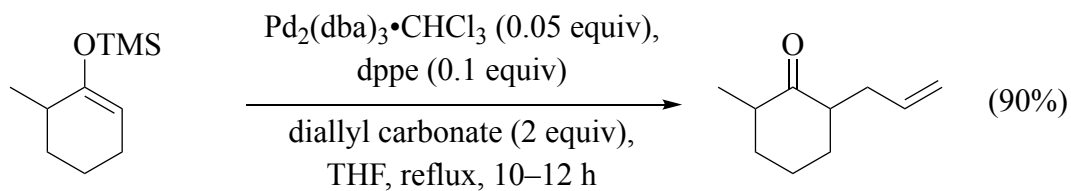
Figure 3. Substrates leading to inefficient reactions under $\text{Pd(OH)}_2/t\text{-BuOOH}$ conditions.

23



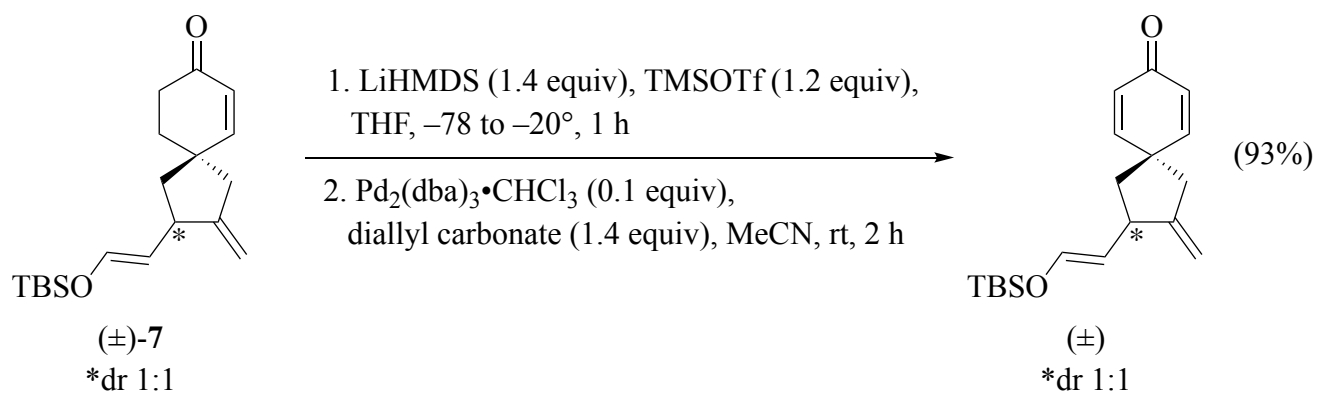
Scheme 20

24



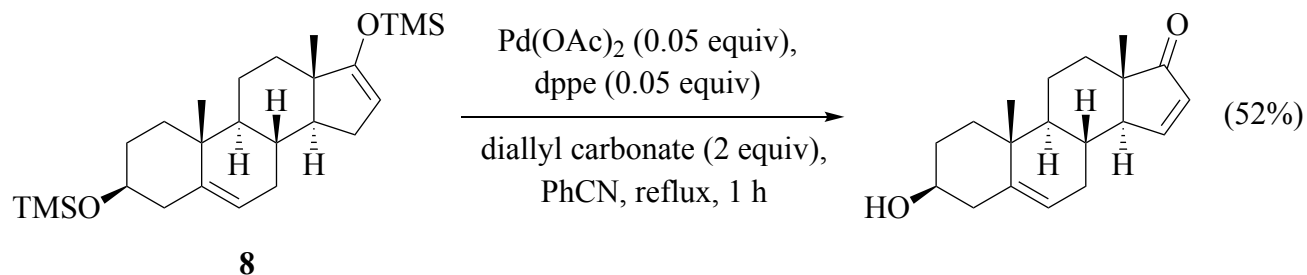
Scheme 21

25

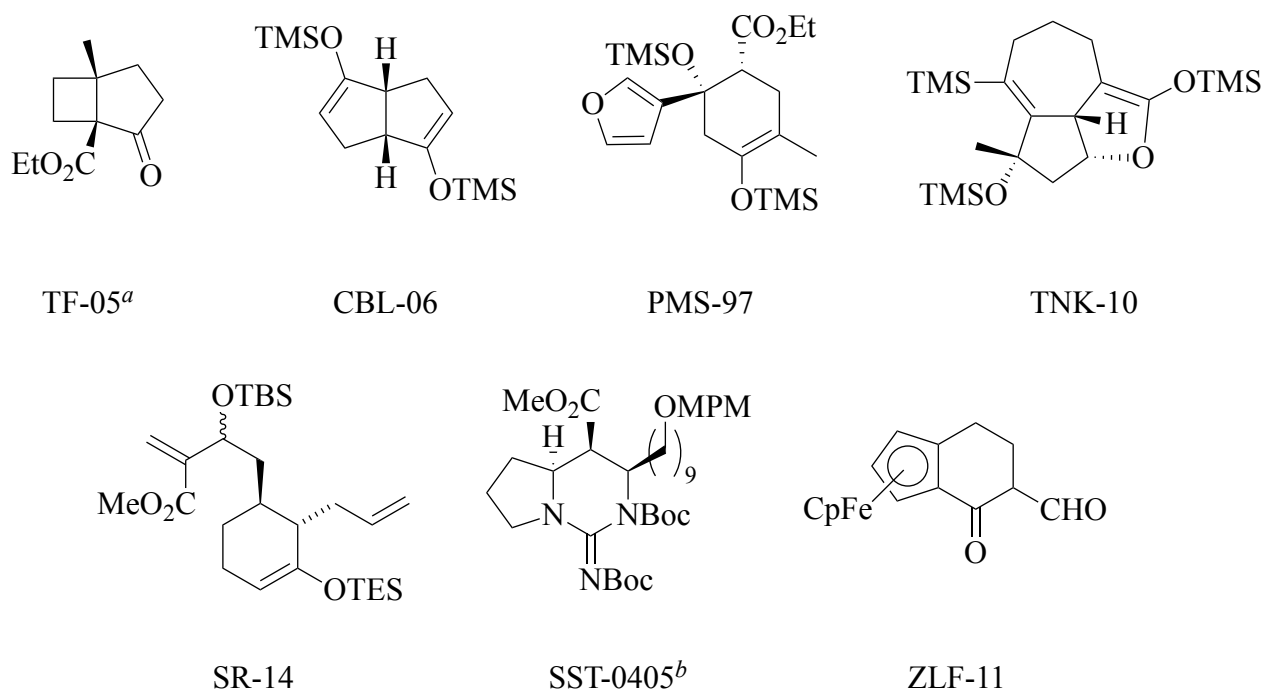


Scheme 22

26



Scheme 23

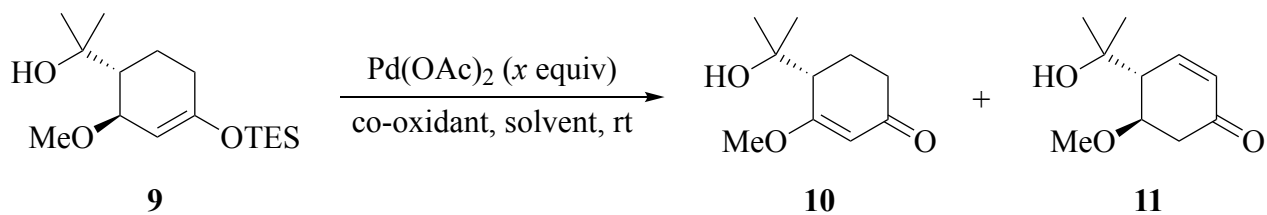


^a A low yield of the enone product was obtained.

^b The silylation reaction was unsuccessful.

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

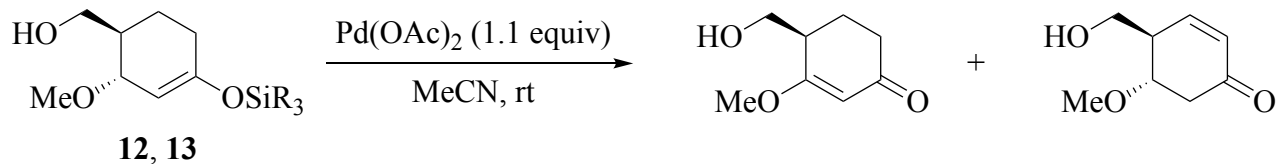
28



<i>x</i>	Co-oxidant	Solvent	Time (h)	Yield (%)	
				10	11
1	—	MeCN	3	90	—
0.1	O ₂ (1 atm)	DMSO	8	62	22

Scheme 24

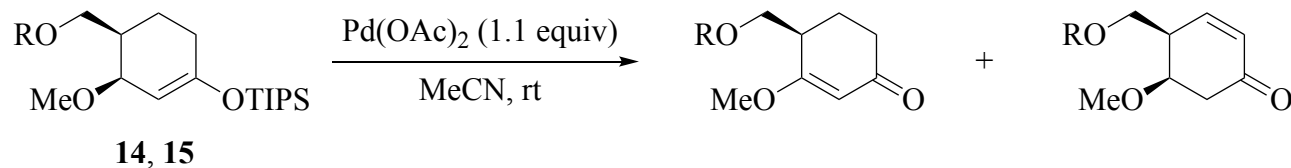
29



	R	Time (h)	Yield (%)	
			α,β -unsaturated ester	α,β -unsaturated ketone
12	Et	6	73	2
13	<i>i</i> -Pr	18	25	45

Scheme 25

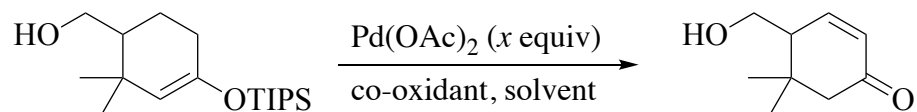
30



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

Scheme 26

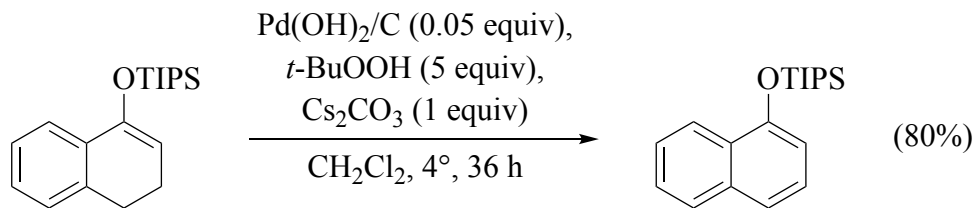
31



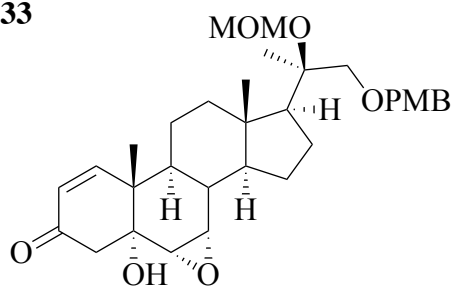
<i>x</i>	Co-oxidant	Solvent	Temp (°)	Time (h)	
1.1	—	MeCN	rt	23	(51%)
0.2	O ₂ (1 atm)	DMSO	80	—	(39%)

Scheme 27

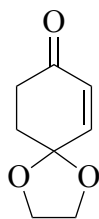
32



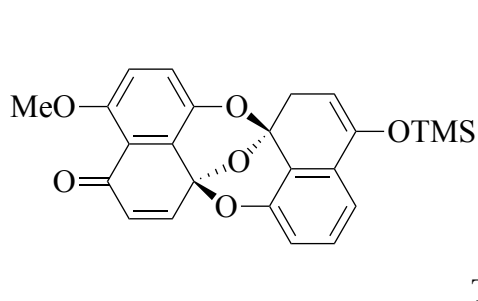
Scheme 28



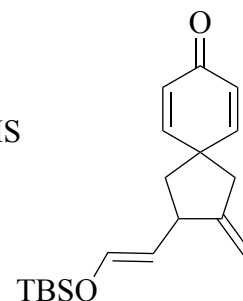
A^S (54%) > A^C (poor yield) A^S (92%) > G (82%)
LHJ-13



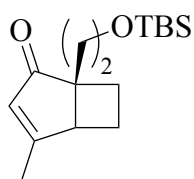
KMM-01



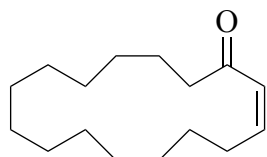
A^S (91%) > C (0%)
QST-04, QSR-04



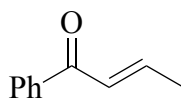
G (>93%) > A^S (>68%)
NLE-06, NLE-09



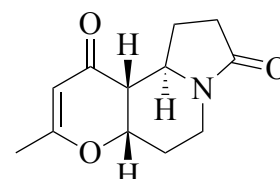
A^S (88%) > C
PP-09



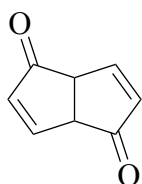
A^S (87%) > A^C (70%)
WKS-98



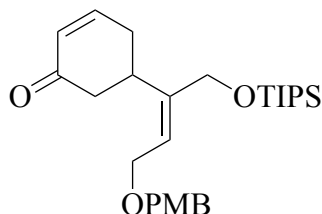
C (74%) > G (66%)
TMS-83, MTS-86,
LHK-95



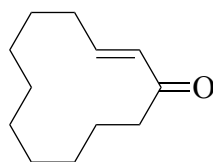
G (>70%) > A^S , C
MD-07



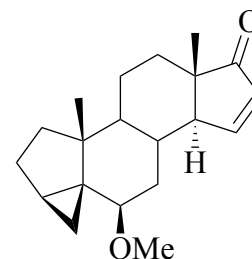
A^C (41%) > G (0%)
CBL-06



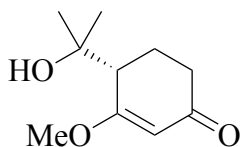
G (>90%) > A^S (79%)
OXT-02, OXT-04



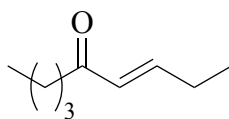
A^C (94%) > G (78%)
TMS-83, MTS-86,
IHS-78



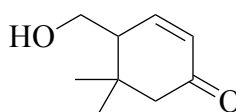
$A^C \sim C$ (75–77%)
TTI-11



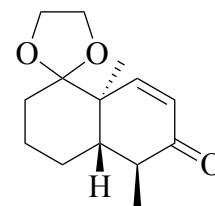
A^S (90%) > C (63%)
HHN-10



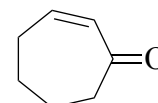
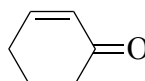
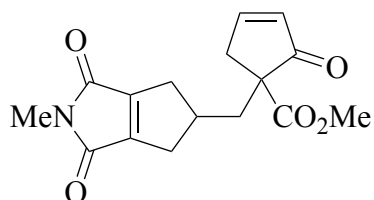
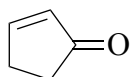
A^C (97%) > C (67%)
IHS-78, LHK-95



A^S (51%) > C (39%)
HHN-11



A^S (>82%) > C (0%)
BMO-13



$A^C \sim D$ (98%) > $B \sim G$ (80%) IHS-78, BNN-89, TMS 84, HNT-92	A^S (87%) > A^C (53%) > C (25%) CGM-12	$A^C \sim E \sim G$ (93%) > B (89%) > C (58%) IHS-78, LHK-95, MTS-86, HNT-92, LLL-13	A^C (91%) > F (74%) IHS-78, YWC-05
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Method A^C : Pd(OAc)₂ (cat.), benzoquinone, MeCN.

Method A^S : Pd(OAc)₂ (1 equivalent or more), with or without benzoquinone, MeCN.

Method $A^?$: Pd(OAc)₂ (unspecified amount), benzoquinone, MeCN.

Method B: PdCl₂(MeCN)₂ or Pd(OAc)₂ (cat.), CuCl (0.05 equivalent), HMPA (0.5 equivalent), O₂, THF.

Method C: Pd(OAc)₂ (cat.), O₂, DMSO.

Method D: Pd(0)/SiO₂ (cat.), O₂, *N*-methyl-2-pyrrolidone.

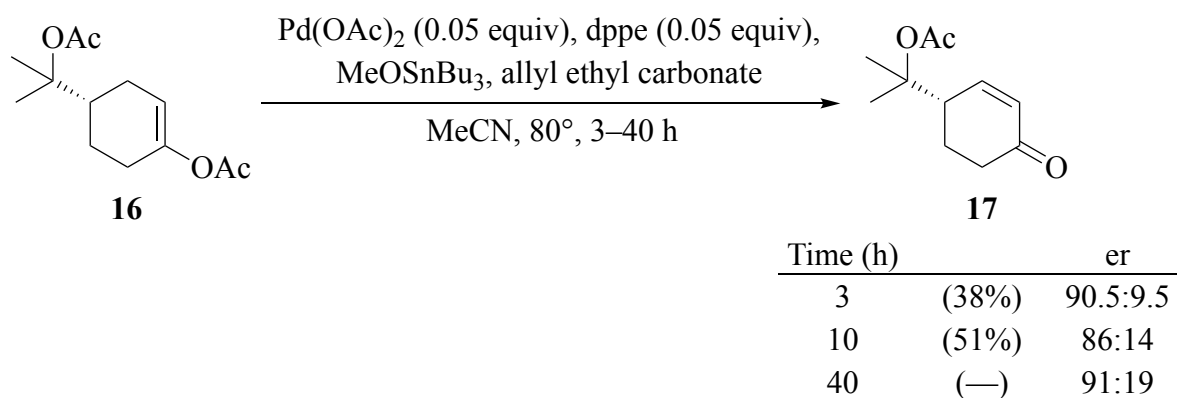
Method E: Pd(OAc)₂ (cat.), Oxone (1 equivalent), Na₂HPO₄ (1 equivalent), O₂, MeCN.

Method F: Pd(OH)₂ (cat.), *t*-BuOOH (2.5 equivalent), Na₂HPO₄ or NEt₃ (0.1–10 equivalent), O₂, CH₂Cl₂.

Method G: Pd(0)L_{*n*} (cat.), allyl carbonate (2 equivalent), MeCN or PhCN.

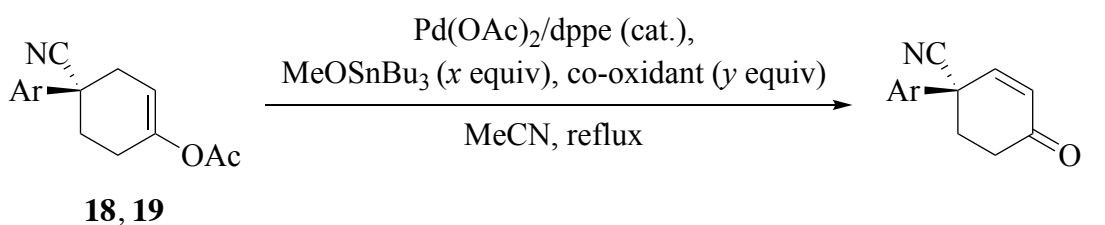
Figure 5. α,β -Enones obtained from silyl enol ethers using Methods A–G.

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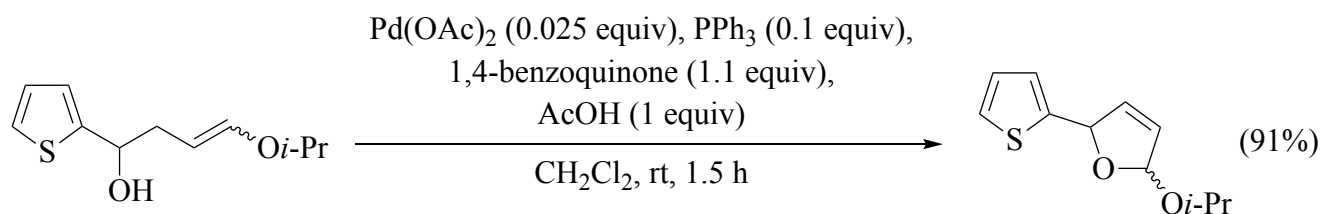
Scheme 29

35



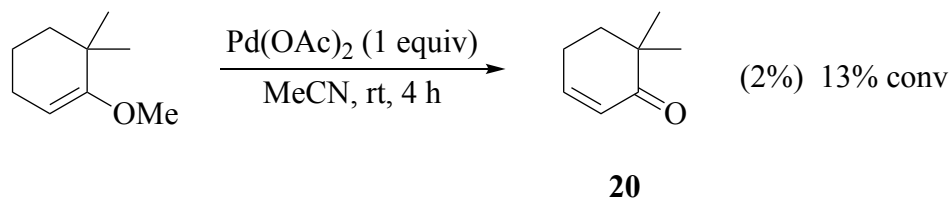
Scheme 30

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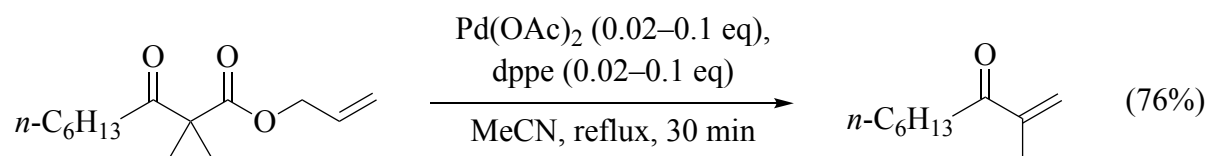
Scheme 31

37



Scheme 32

38



Scheme 33

39

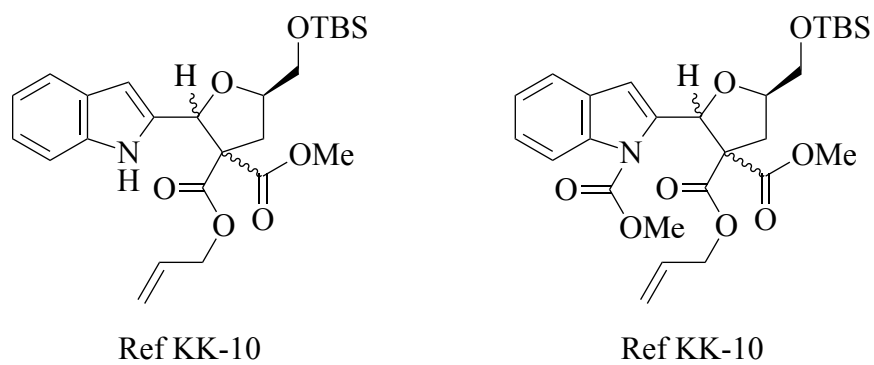
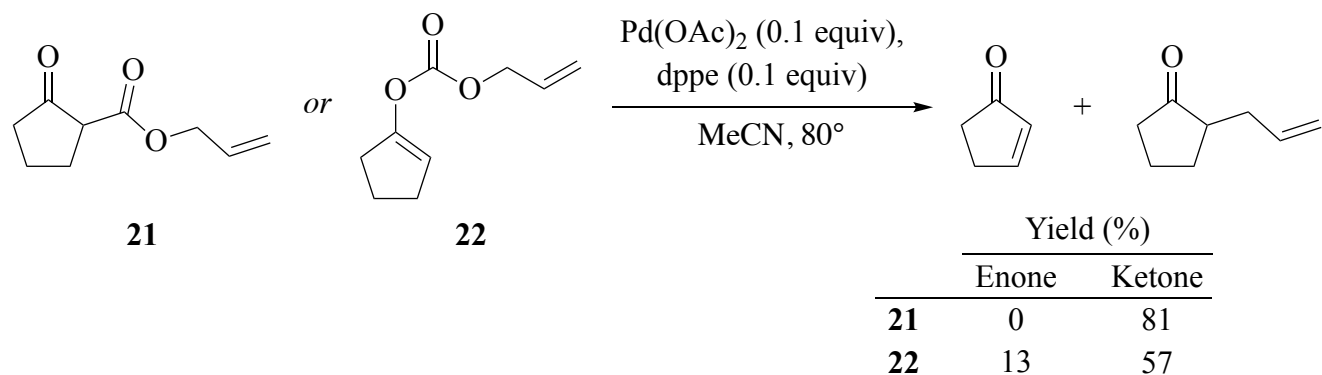


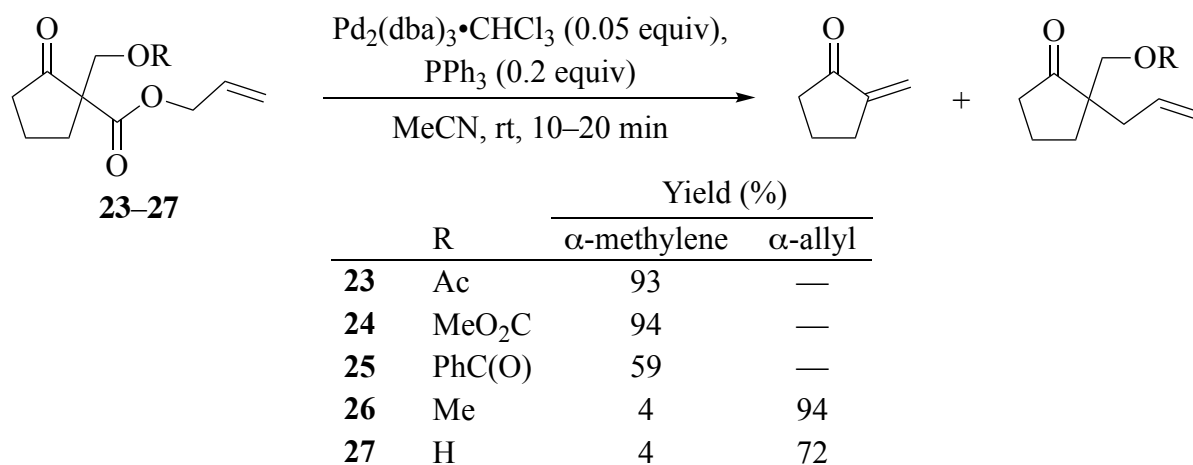
Figure 6. Allyl malonates leading to inefficient reactions.

40

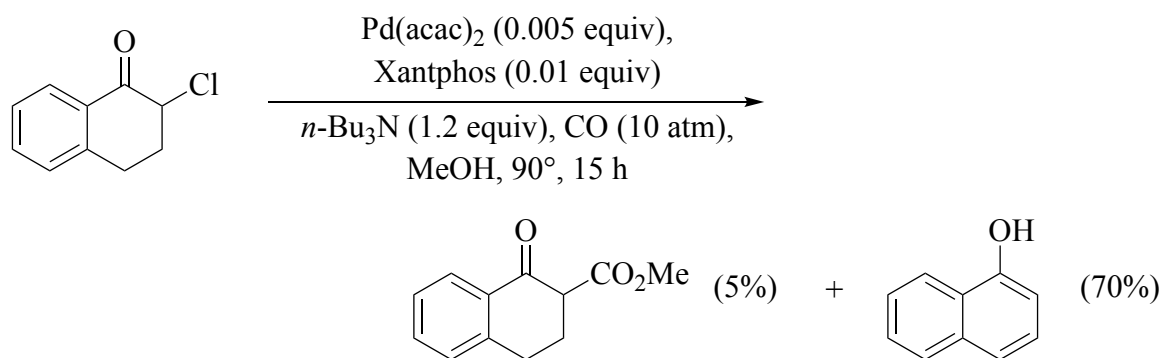


Scheme 34

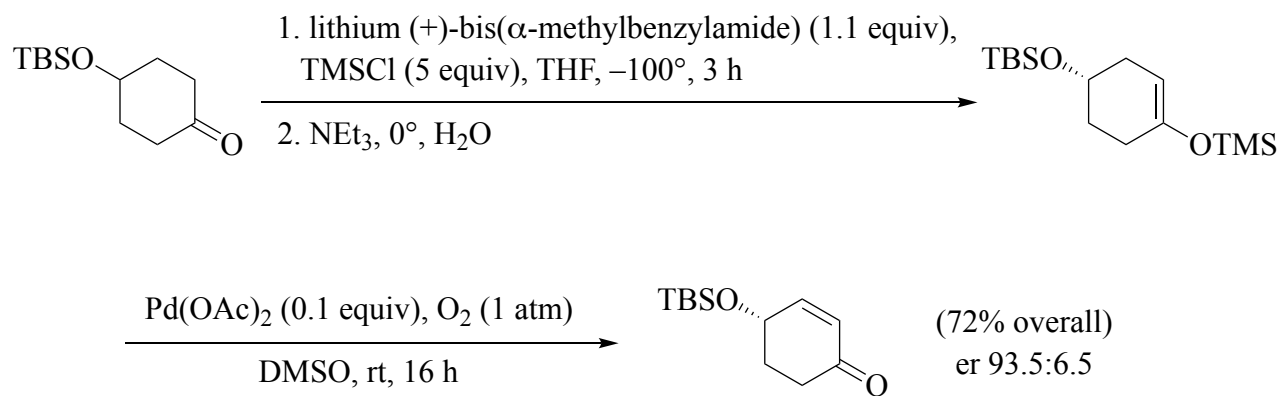
41



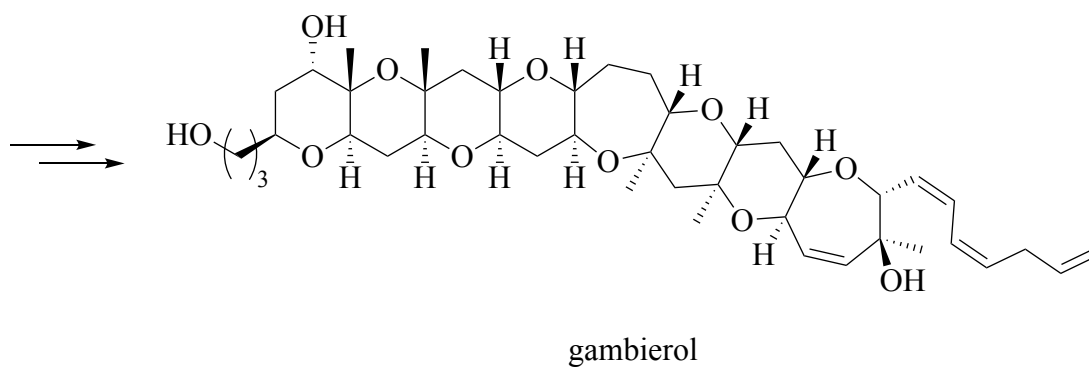
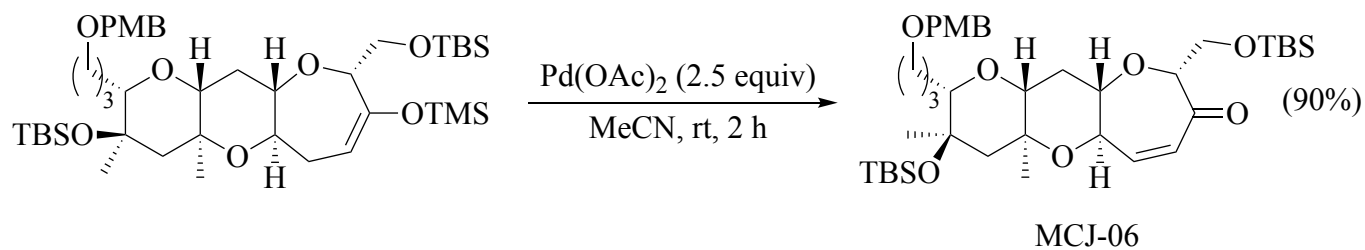
Scheme 35



Scheme 36

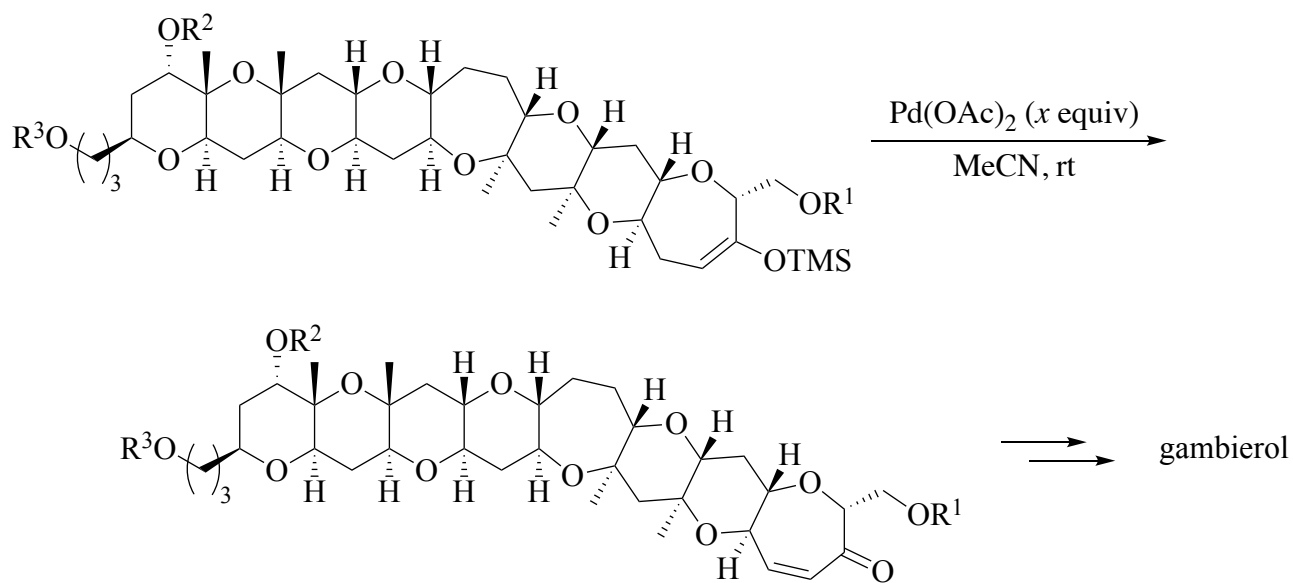


Scheme 37



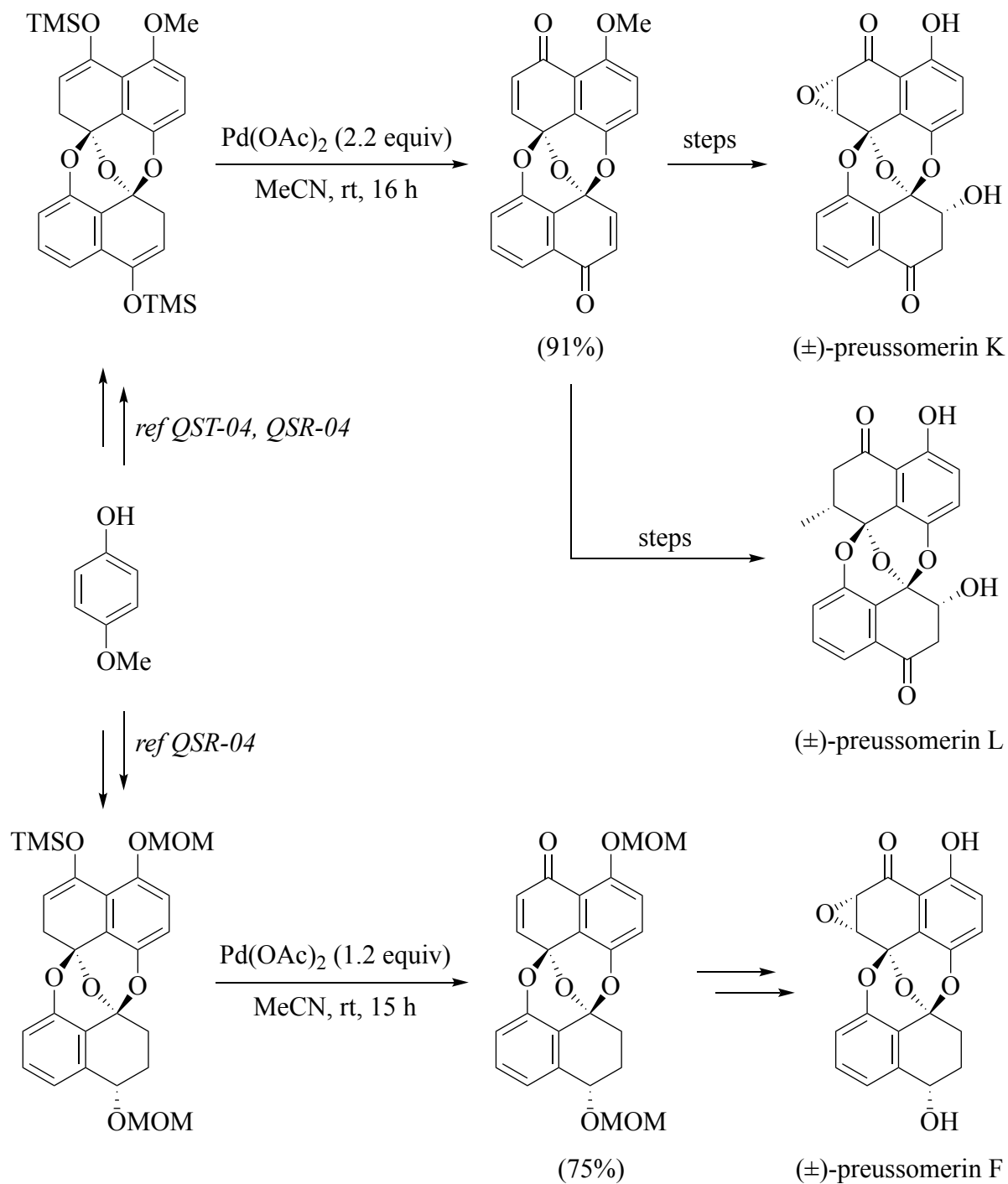
Scheme 38

44a



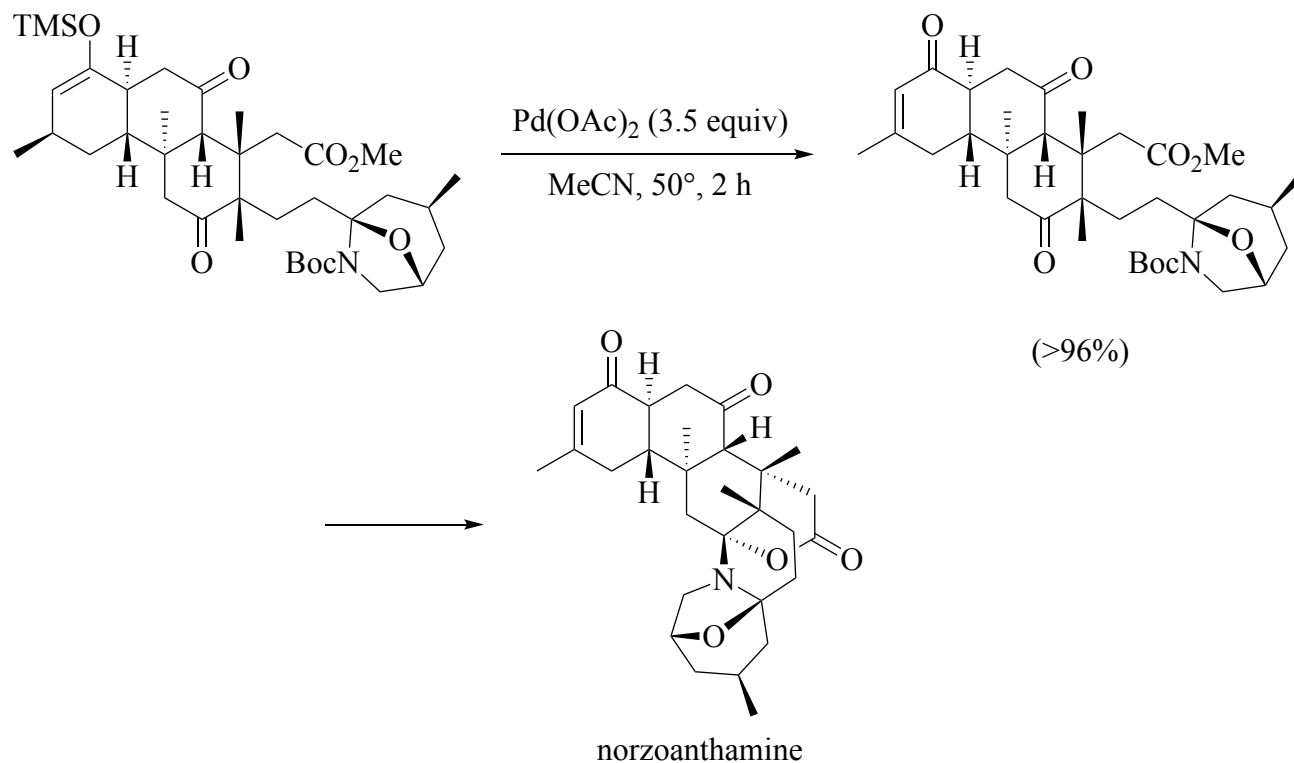
R ¹	R ²	R ³	x	Time (min)		Ref
TBDPS	Bn	Bn	5	75	(98%)	FHM-09, FHH-10, M-10a
TBS	TIPS	Piv	3	60	(92%)	KTS-03, KTS-03b
TBS	Bn	Bn	5.2	75	(>94%)	FSS-02, FKT-02

Scheme 39



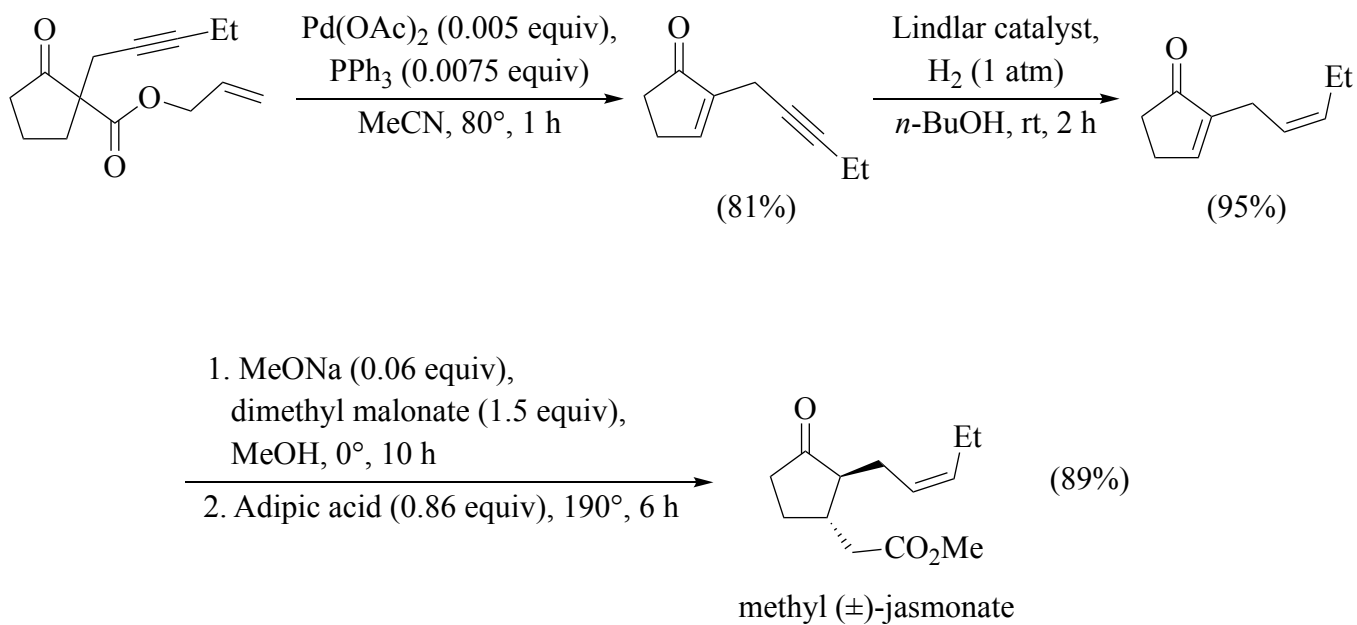
Scheme 40

46

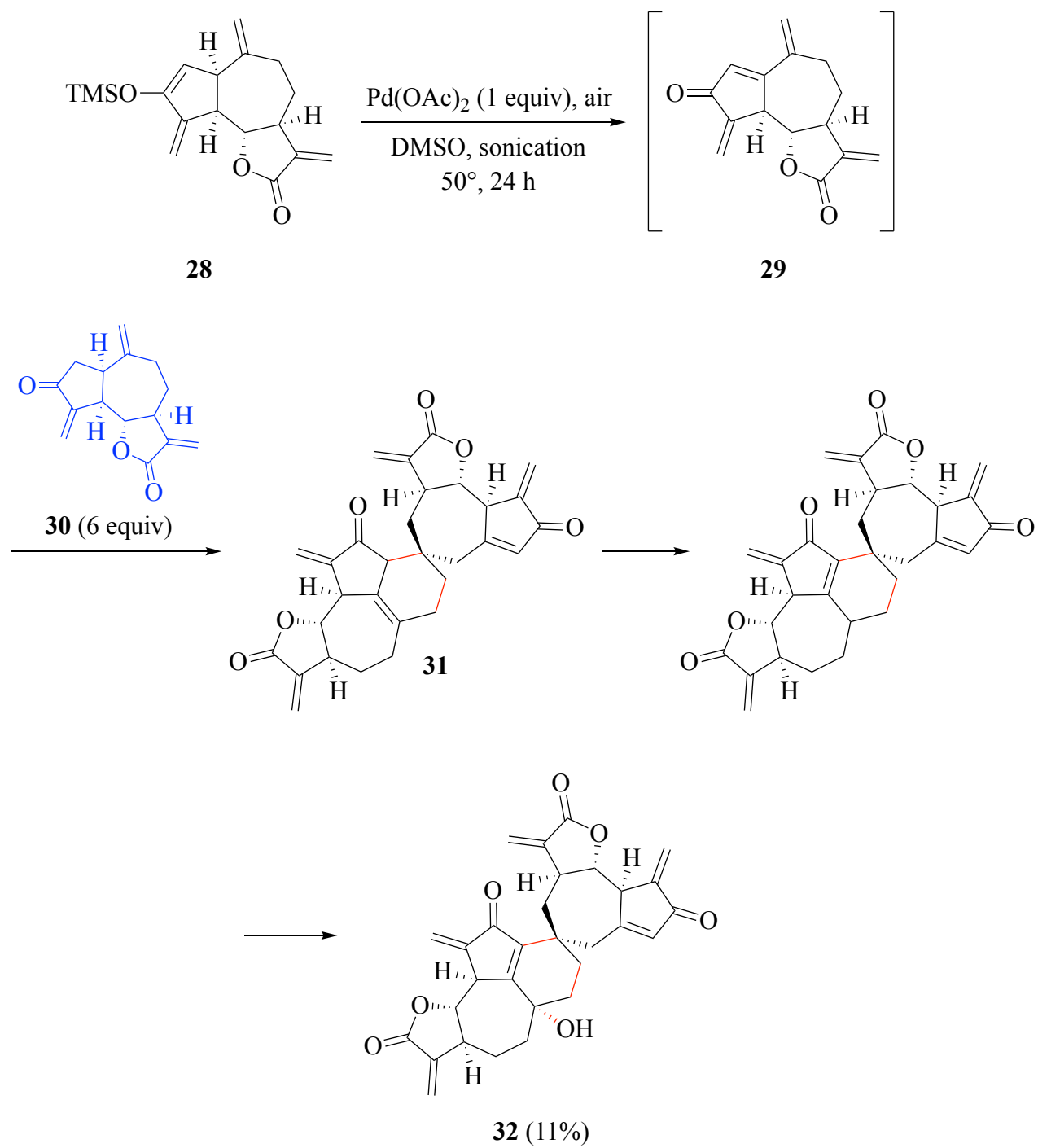


Scheme 41

47

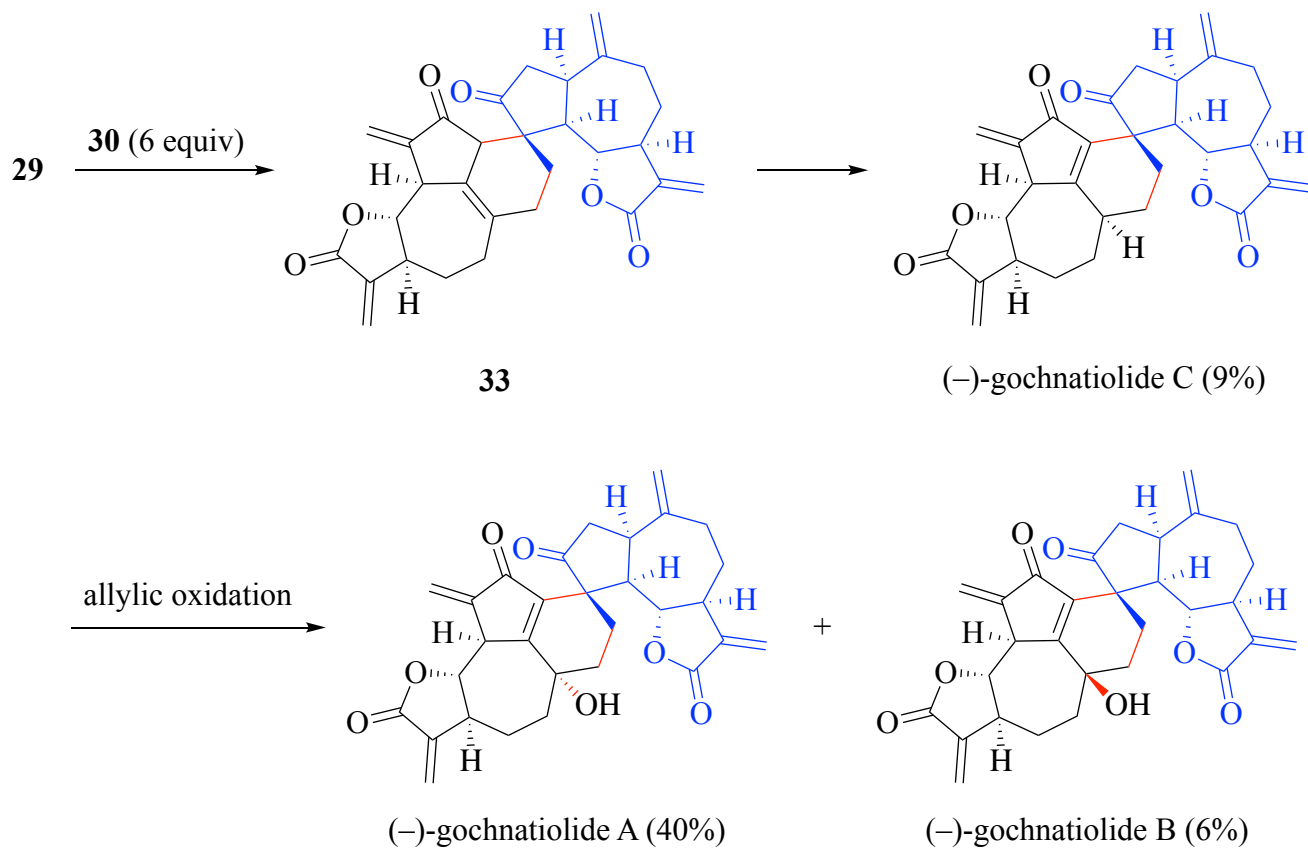


Scheme 42



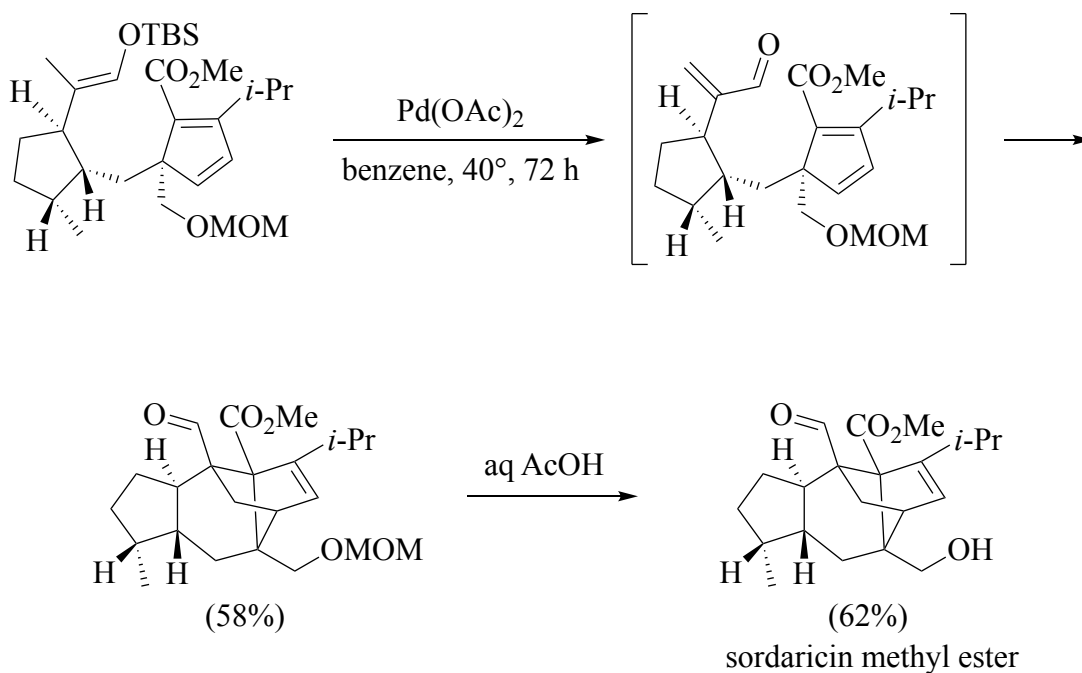
Scheme 43

48a



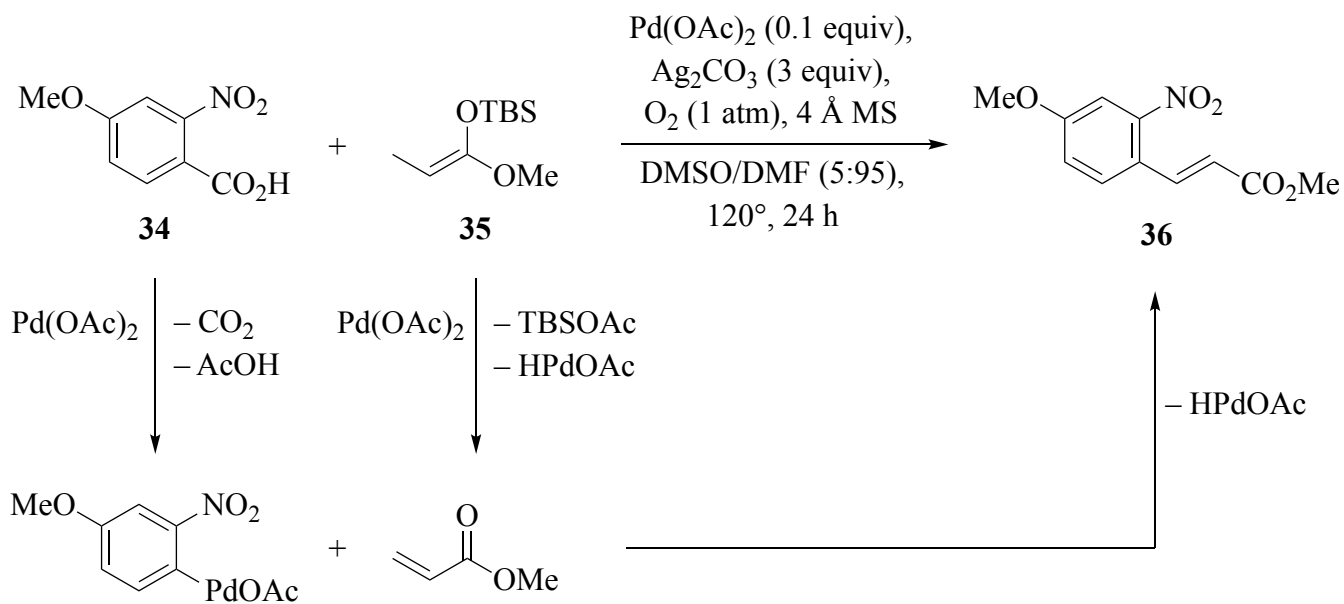
Scheme 44

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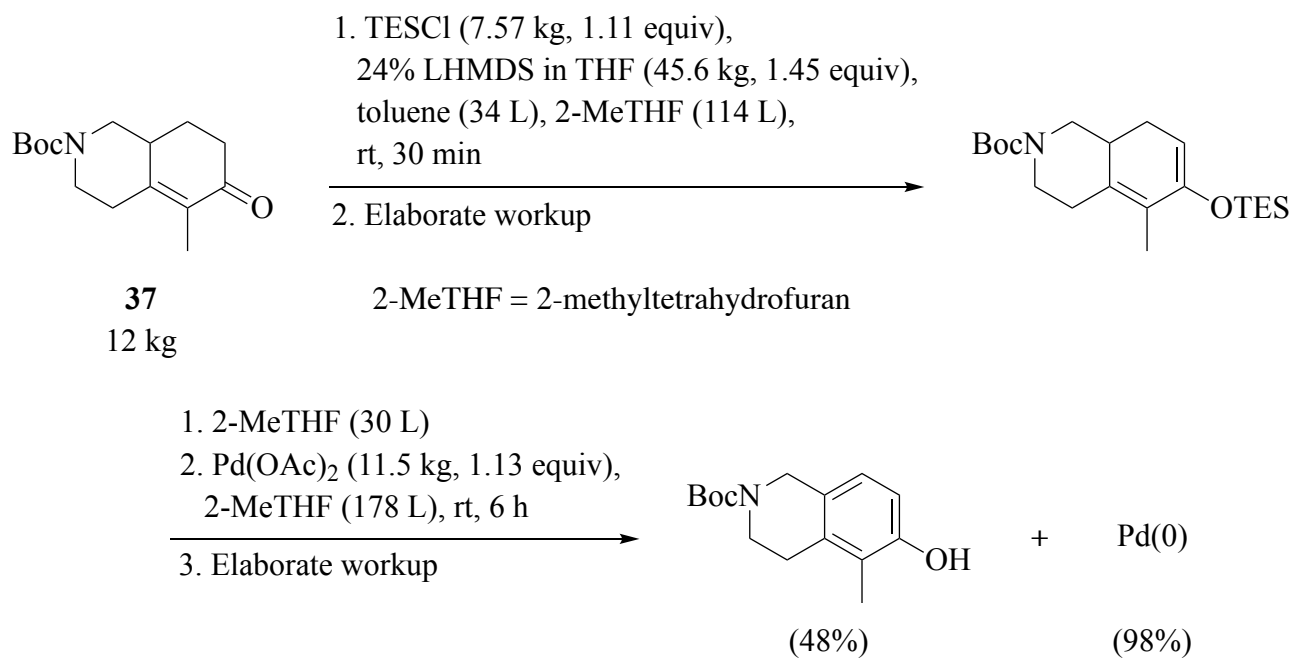


Scheme 45

50

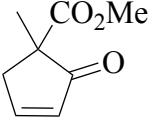
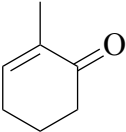
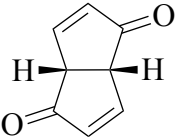
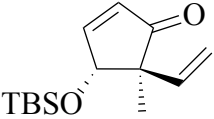
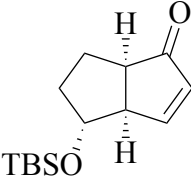
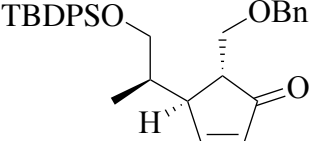
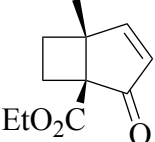


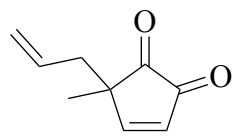
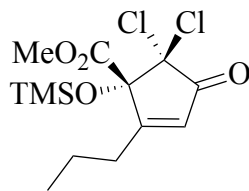
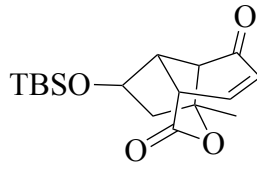
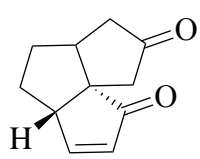
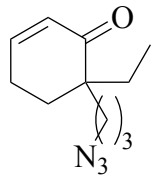
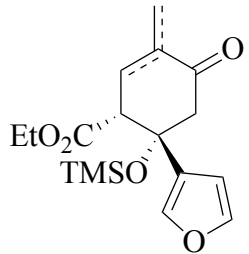
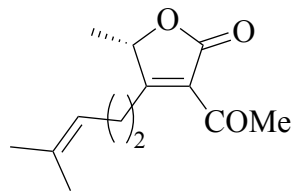
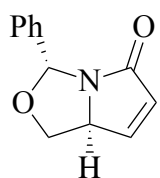
Scheme 46

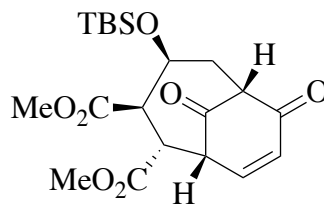
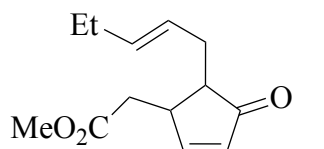
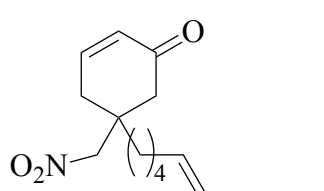
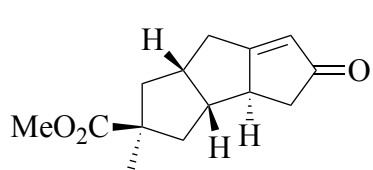
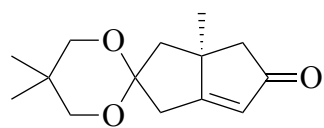
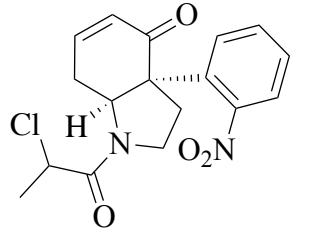
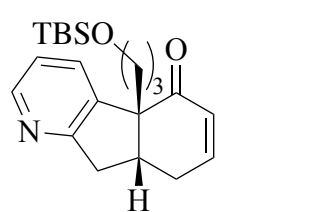
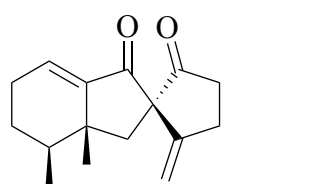


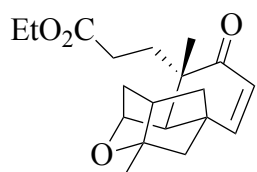
Scheme 47

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

α,β -Unsaturated Carbonyl Product	Pd-Mediated Oxidative Dehydrogenation Conditions	Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Ref
	C	CS: 2-iodoxybenzoic acid/DMSO	RFZ-12
	C	SS: phenylselenation, oxidative elimination	GKS-98
	A [?]	CS: bromination, ketalisation, dehydrobromination, deprotection	CBL-06
	A [?] , C	SS: bromination, dehydrobromination	STF-13
	A [?]	CS: sulfenylation, dehydrosulfenylation	CMM-96
	A ^S	CS: phenylselenation, oxidative elimination	HML-06
	A [?] , G	CS: bromination, dehydrobromination	TF-05

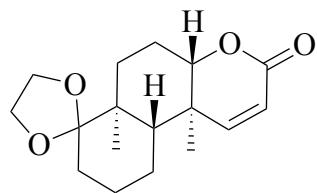
	F	CS: Pd(OAc) ₂	TDV-10
	A [?]	CS: SeO ₂	KDY-00
	A [?]	CS: bromination, dehydrobromination, phenylselenation, oxidative elimination	BFB-10
	A ^S	CS: benzeneseleninic anhydride	D-99
	C	CS: 2-iodoxybenzoic acid/DMSO	XWZ-15
	A [?] , G	SS: phenylselenation, oxidative elimination	PMS-97
	A [?]	CS: NaH, PhSe(O)Cl, warming	SSD-00
	A [?]	CS: LDA, <i>N</i> - <i>t</i> -butyl phenylsulfonimidoyl chloride	HMH-04

	A [?]	CS: 2-iodoxybenzoic acid/DMSO	O-01 O-02
	F	CS: 2-iodoxybenzoic acid/DMSO, CF ₃ CO ₂ H	DLY-08
	A [?]	CS: 2-iodoxybenzoic acid/NMO/DMSO	LGG-13
	A ^S	CS: 2-iodoxybenzoic acid/DMSO, TsOH	BAW-07
	A ^S	CS: benzeneseleninic anhydride	D-99
	A [?]	SS: phenylselenation, oxidative elimination	BSG-97
	A ^S	SS: 2-iodoxybenzoic acid/NMO/DMSO	HSI-11
	A [?]	CS: phenylselenation, oxidative elimination	BCD-02



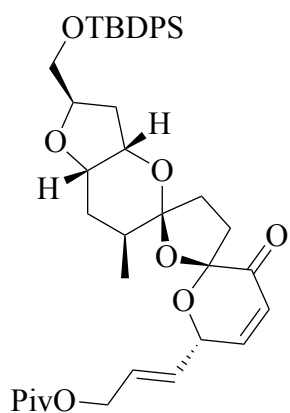
A[?]

CS: phenylselenation, oxidative elimination GX-09



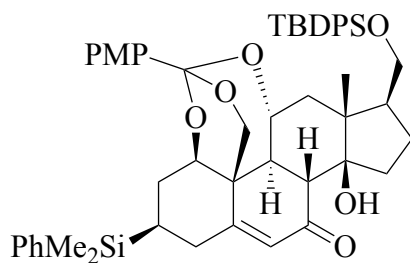
A[?], C

CS: LDA, *N-t*-butyl phenylsulfonimidoyl chloride CFI-10



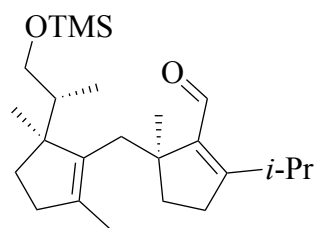
A^S

SS: phenylselenation, oxidative elimination NKV-06



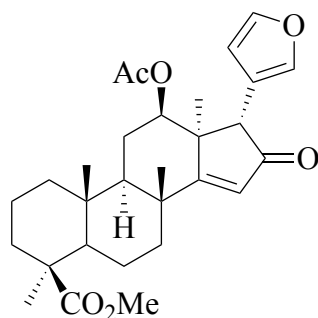
A[?]

SS: DDQ, 2,6-di-*t*-butyl-4-methylpyridine RZP-09



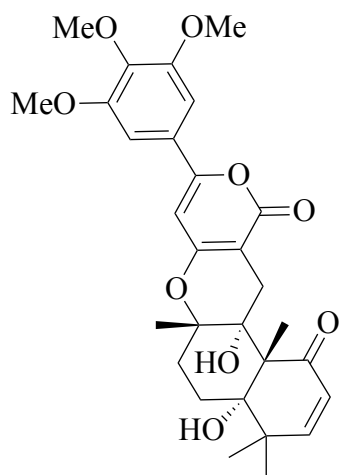
A^S

SS: singlet oxygen, PPh₃ KNT-86



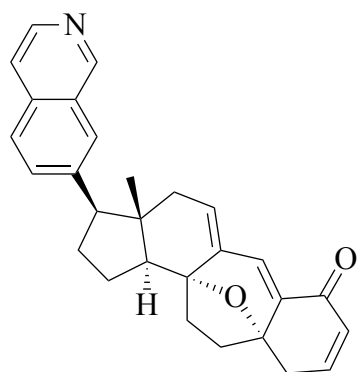
A[?]

CS: epoxidation, TsOH FPR-05



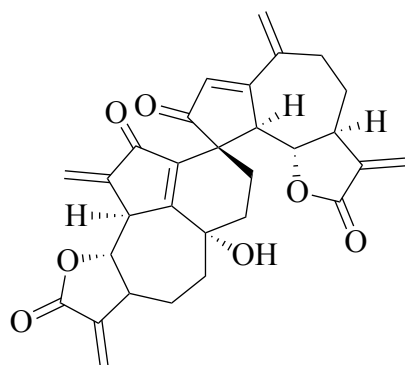
A[?]

CS: phenylselenation, oxidative elimination SHN-04



A[?]

CS: 2-iodoxybenzoic acid/
4-methoxypyridine *N*-oxide/DMSO NPS-09



A[?], C

CS: Pd(OAc)₂ LDD-13

Method A^S: Pd(OAc)₂ (1 equivalent or more), with or without benzoquinone, MeCN.

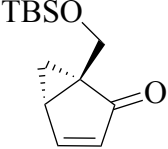
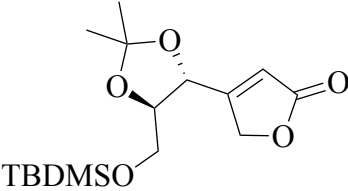
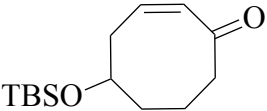
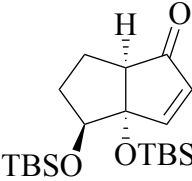
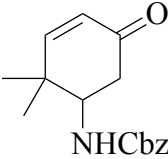
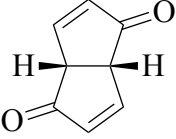
Method A[?]: Pd(OAc)₂ (unspecified amount), benzoquinone, MeCN.

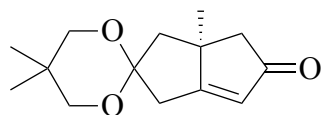
Method C: Pd(OAc)₂ (cat.), O₂, DMSO.

Method F: Pd(OH)₂ (cat.), *t*-BuOOH (2.5 equivalent), Na₂HPO₄ or NEt₃ (0.1–10 equivalent), O₂, CH₂Cl₂.

Method G: Pd(0)Ln (cat.), allyl carbonate (2 equivalent), MeCN or PhCN.

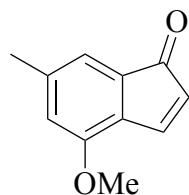
Table B. α,β -Unsaturated Carbonyl Compounds Prepared More Efficiently by Pd-Mediated Oxidative Dehydrogenation of Silyl Enol Ethers Than by Other Methods

α,β -Unsaturated Carbonyl Product	Effective Procedure	Less Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Ref
	C	CS: phenylselenation, oxidative elimination	JDV-14
	A ^C	CS: phenylselenation, oxidative elimination	MMA-97
	A ^S	CS: phenylselenation, oxidative elimination	IZM-01
	A ^S	SS: 2-iodoxybenzoic acid/ 4-methoxypyridine <i>N</i> -oxide/DMSO CS: 2-iodoxybenzoic acid/DMSO	HGC-02
	A ^S	CS: bromination, dehydrobromination and sulfenylation, dehydrosulfenylation	GFB-00
	A ^C	CS: phenylselenation, oxidative elimination, 2-iodoxybenzoic acid/DMSO, 2-iodoxybenzoic acid/ 4-methoxypyridine <i>N</i> -oxide/DMSO, 2-iodoxybenzoic acid/NMO/DMSO, and HIO ₃ /DMSO	CBL-06

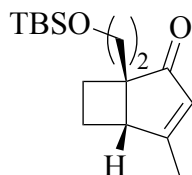
A^S

CS: benzeneseleninic anhydride

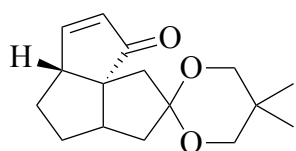
D-99

A^CCS: bromination, ketalisation,
dehydrobromination, deprotection

HZ-96

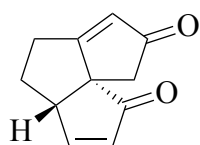
A^SCS: bromination, dehydrobromination
and phenylselenenylation,
oxidative elimination and
2-iodoxybenzoic acid/DMSO

PP-09

A^S

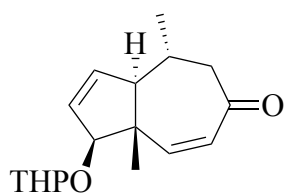
CS: benzeneseleninic anhydride

D-99

A^S

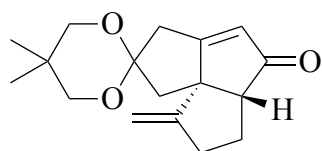
CS: benzeneseleninic anhydride

D-99

A^S

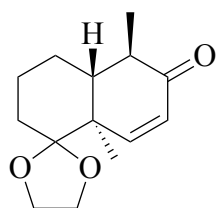
CS: sulfenylation, dehydrosulfenylation

RS-79

A^S

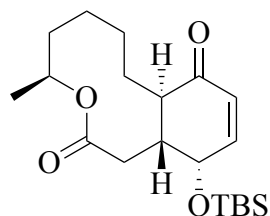
CS: benzeneseleninic anhydride

D-99

A^S

CS: 2-iodoxybenzoic acid/DMSO

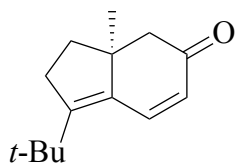
BMO-13



A^S

CS: phenylselenation, oxidative elimination and 2-iodoxybenzoic acid/DMSO

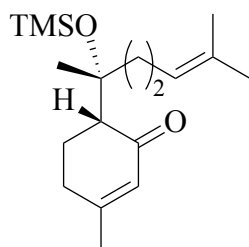
WT-07



A^S

SS: 2-iodoxybenzoic acid

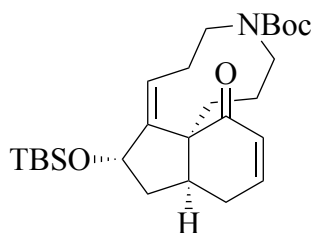
FPK-15



C

SS: 2-iodoxybenzoic acid/
4-methoxypyridine *N*-oxide/DMSO
CS: 2-iodoxybenzoic acid/DMSO

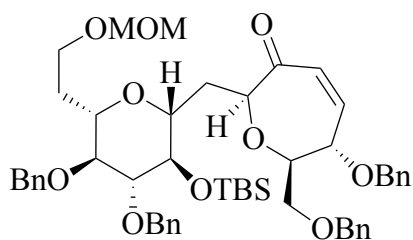
G-08



A^S

CS: iodoxybenzoic acid/NMO/DMSO and 2-iodoxybenzoic acid/DMSO

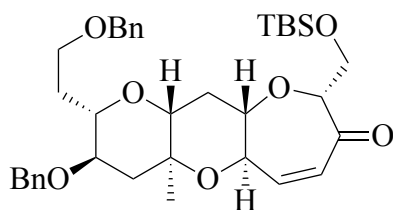
DWJ-14



A^S

CS: phenylselenation, oxidative elimination

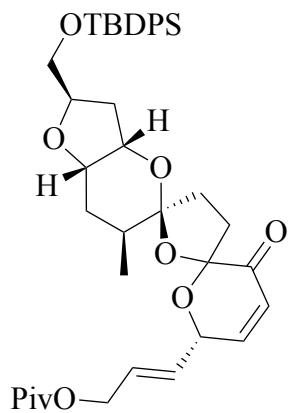
SIF-02



A^S

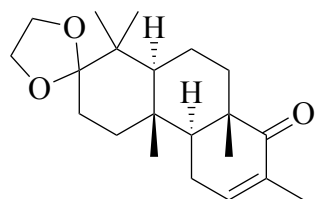
SS: phenylselenation, oxidative elimination
CS: LDA, *N*-*t*-butyl phenylsulfonimidoyl chloride and 2-iodoxybenzoic acid/DMSO

FKT-02



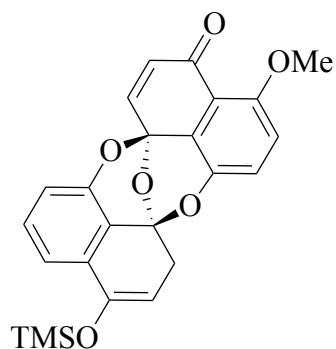
A^S

CS: phenylselenation, oxidative elimination and 2-iodoxybenzoic acid/DMSO NKV-06



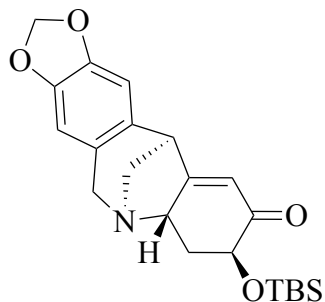
C^a

CS: 2-iodoxybenzoic acid/DMSO YMM-11



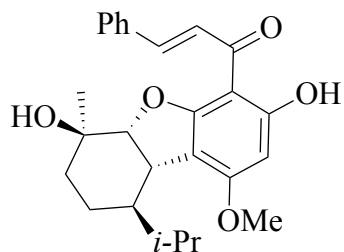
A^S

CS: 2-iodoxybenzoic acid/DMSO and benzeneseleninic anhydride and 2-iodoxybenzoic acid/4-methoxypyridine *N*-oxide/DMSO QST-04 QSR-04



A^S

SS: DDQ/2,6-di-*t*-butyl-4-methylpyridine JW-97b



A^S

CS: 2-iodoxybenzoic acid/DMSO DD-15

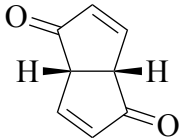
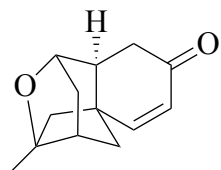
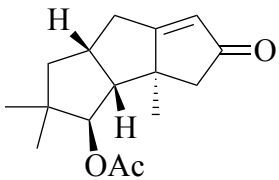
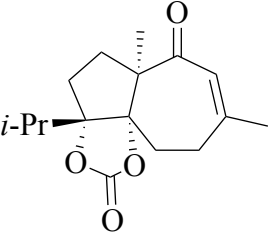
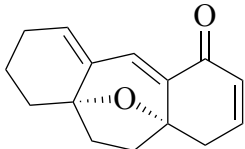
Method A^C: Pd(OAc)₂ (cat.), benzoquinone, MeCN.

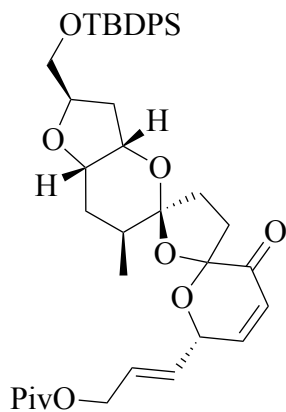
Method A^S: Pd(OAc)₂ (1 equivalent or more), with or without benzoquinone, MeCN.

Method C: Pd(OAc)₂ (cat.), O₂, DMSO.

^a 1.5 equivalents of Pd(OAc)₂ were used.

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

α,β -Unsaturated Carbonyl Product	Seagusa's procedure	Other Effective Method from Silylated (SS) or Carbonyl (CS) Substrate	Ref
	A ^C	CS: 2-iodoxybenzoic acid/DMSO or HIO ₃ /DMSO	CBL-06
	A ^S	SS: 2-iodoxybenzoic acid/4-methoxypyridine <i>N</i> -oxide/DMSO	NPT-08
	A ^S	CS: 2-iodoxybenzoic acid/DMSO, TsOH	BBW-13
	A ^S	SS: 2-iodoxybenzoic acid/DMSO	FTF-05
	A ^C	SS: 2-iodoxybenzoic acid/4-methoxypyridine <i>N</i> -oxide/DMSO	NPS-09



A^S

CS: LDA, *N*-*t*-butyl phenylsulfonimidoyl chloride or phenylselenation, oxidative elimination

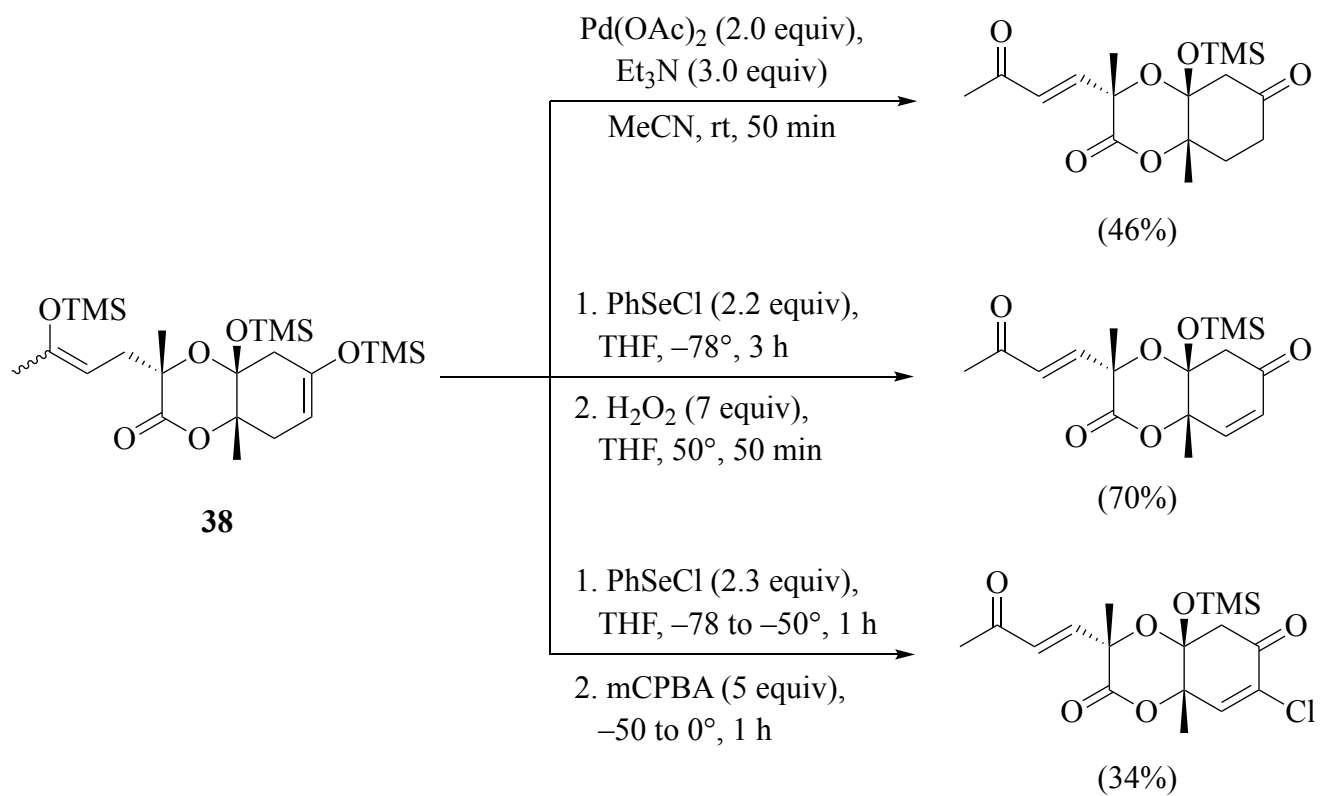
NKV-06

Method A^C: Pd(OAc)₂ (cat.), benzoquinone, MeCN.

Method A^S: Pd(OAc)₂ (1 equivalent or more), with or without benzoquinone, MeCN.

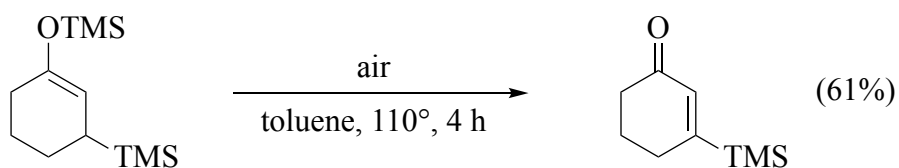
Method C: Pd(OAc)₂ (cat.), O₂, DMSO.

55



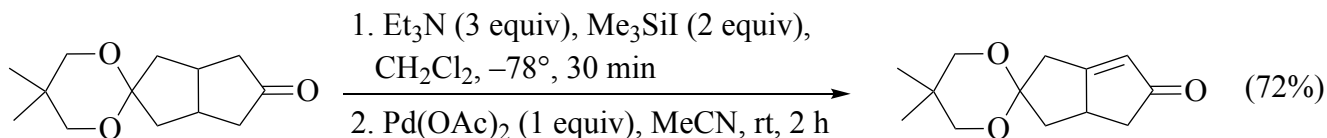
Scheme 48

56

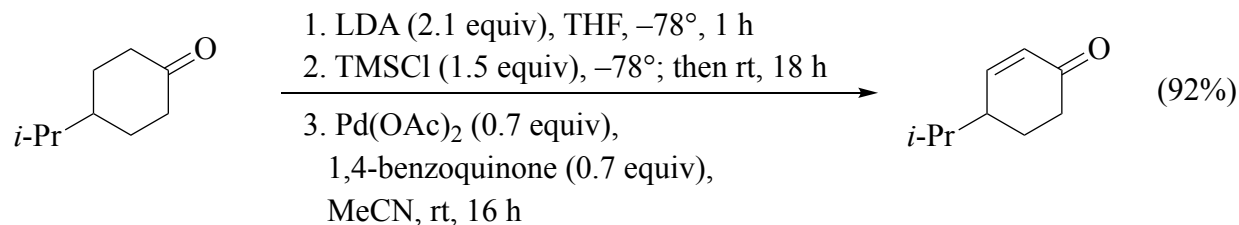


Scheme 49

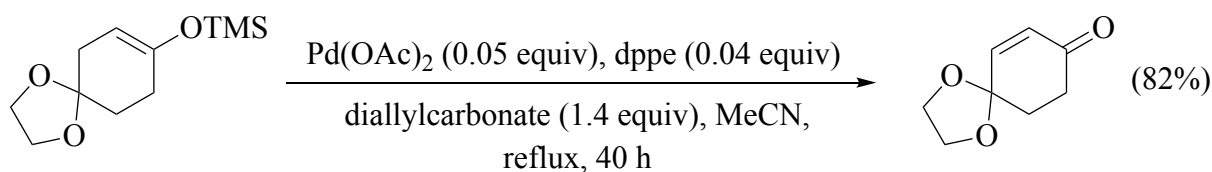
57



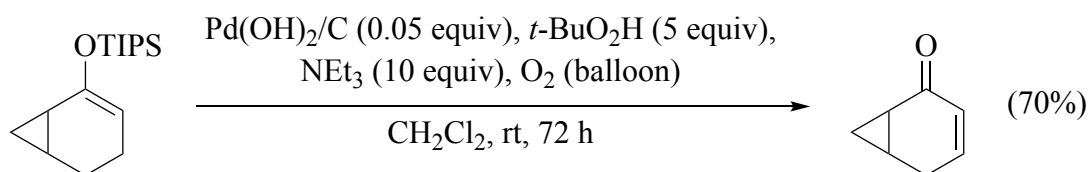
58



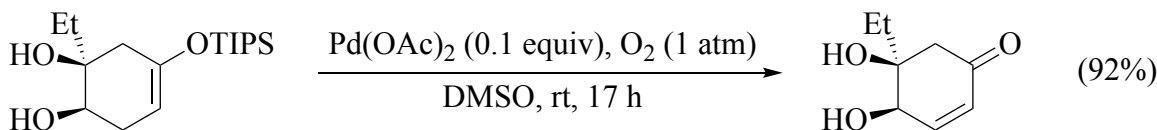
59



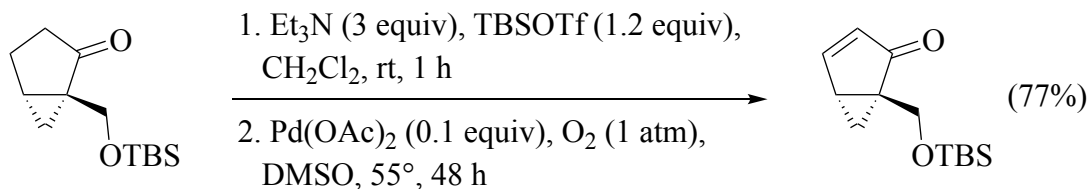
60



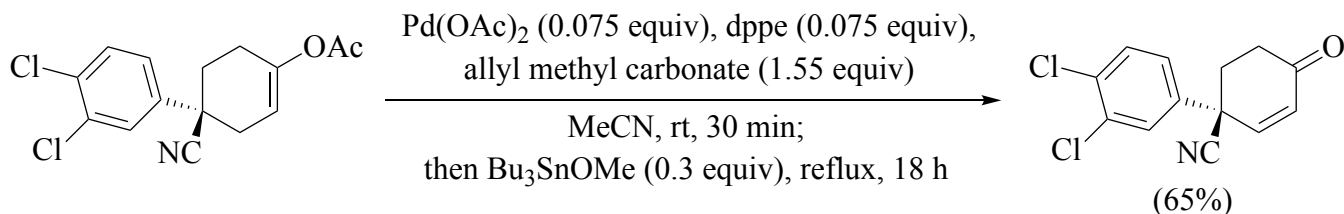
61



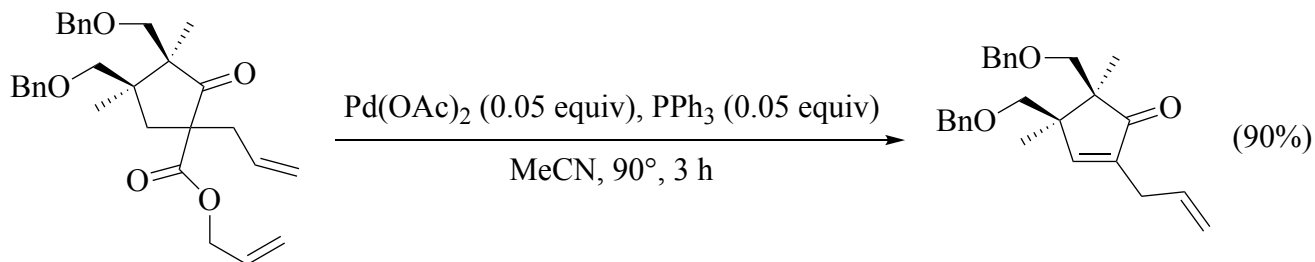
62



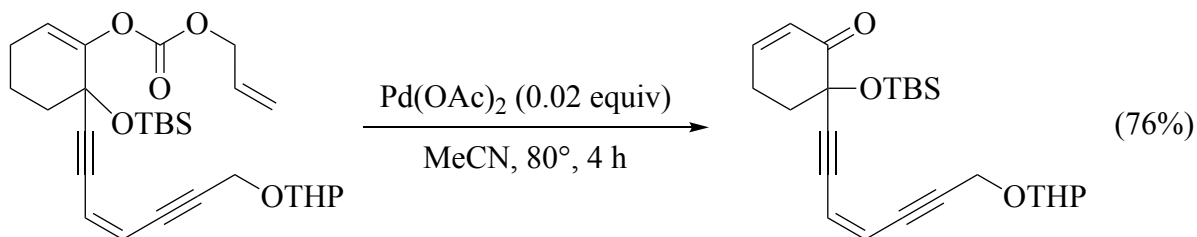
63



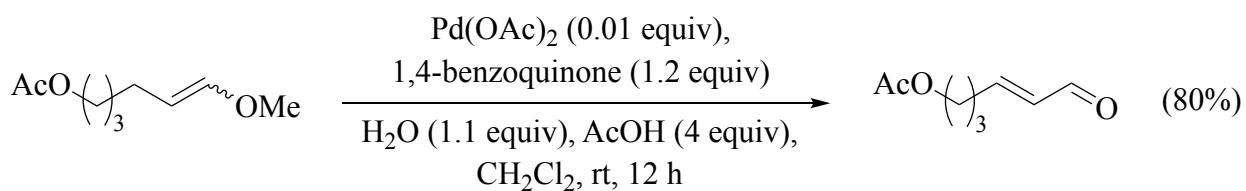
64



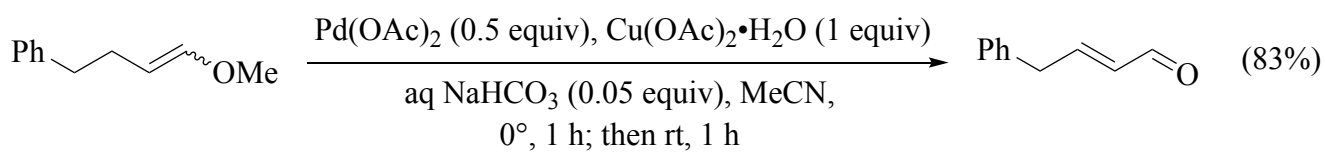
65



66



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