Asymmetric Epoxidation of Allylic Alcohols: the Katsuki–Sharpless Epoxidation Reaction

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## 1. Introduction

In 1980, Sharpless and Katsuki discovered a system for the asymmetric epoxidation of primary allylic alcohols that utilizes Ti(OPr-i)$_4$, a dialkyl tartrate as a chiral ligand, and *tert*-butyl hydroperoxide as the oxidant. (1) Notably, this reaction exhibits high levels of enantioselectivity (usually > 90% ee). Like other metalcatalyzed epoxidations, this reaction also proceeds under mild conditions with good chemical yield and with high regio- and chemoselectivity. Various aspects of this reaction, including its mechanism, (2) early synthetic applications, (3-6) and further transformations of the epoxy alcohol product, (7) have been reviewed. In the following sections, the full scope and limitations of this reaction, its synthetic applications, and typical experimental conditions are described.

2. Asymmetric Epoxidation with the Titanium(IV)–Tartrate Catalyst

The combination of Ti(OPr-i)$_4$, a dialkyl tartrate, and *tert*-butyl hydroperoxide (hereafter referred to as TBHP) epoxidizes most allylic alcohols in good chemical yield and with predictably high enantiofacial selectivity according to the empirical rule illustrated in scheme 1. When an allylic alcohol (R^4, R^5 = H) is drawn in a plane with the hydroxymethyl group positioned at the lower right, the delivery of oxygen occurs from the bottom side of the olefin to give the (2S)-epoxide if an (R,R)-dialkyl tartrate is used as the chiral auxiliary. Of course, when an (S,S)-dialkyl tartrate is employed, oxygen is delivered from the top side. The enantiofacial selectivity of the reaction is > 90% ee (usually > 95% ee) for substrates without a Z olefinic substituent (R^3 = H). The degree of facial selectivity for a Z allylic alcohol depends on the nature of the Z substituent R^3. The enantioselectivity for substrates with unbranched R^3 substituents ranges from 80 to 94% ee, but that for substrates with a branched substituent is lower. (2) Representative examples of epoxidations of allylic alcohols with diethyl tartrate (DET) as the chiral auxiliary are shown in Eqs. 1–4. (1, 8, 9)


(1)

(77%) 95% ee

(2)

(81%) >95% ee

(3)

(90%) 94% ee

$$\text{(4)}$$

(54%) 66% ee
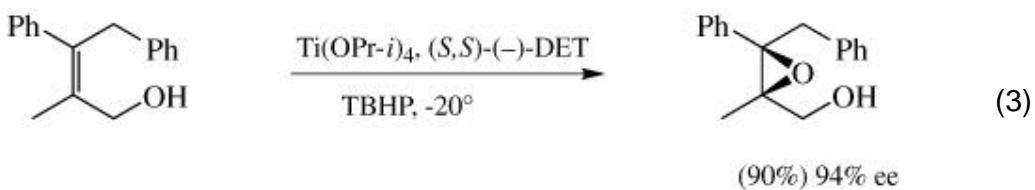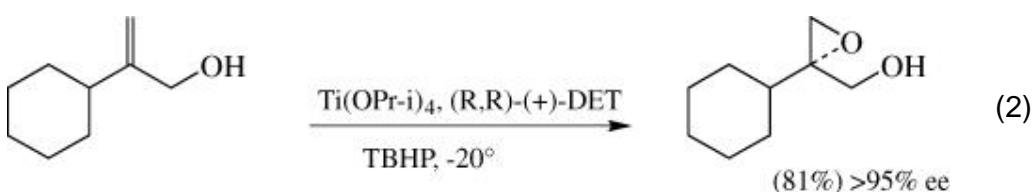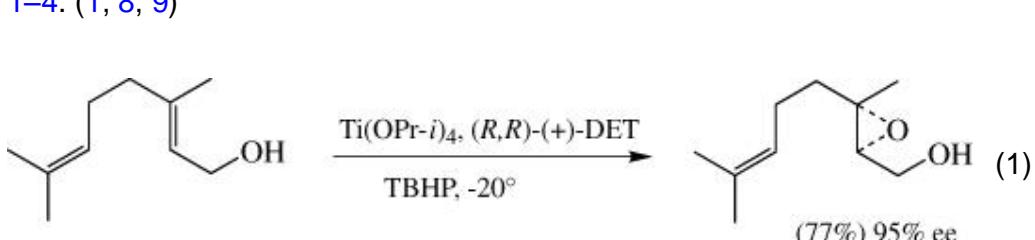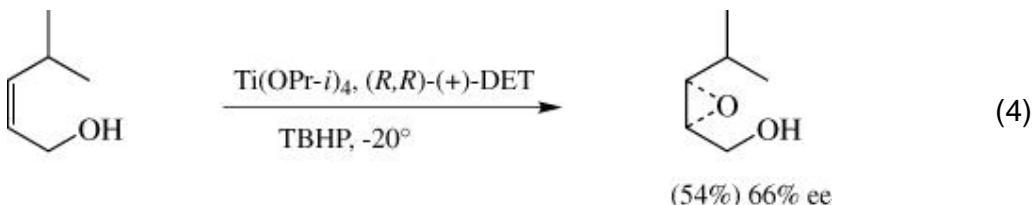
scheme 1.
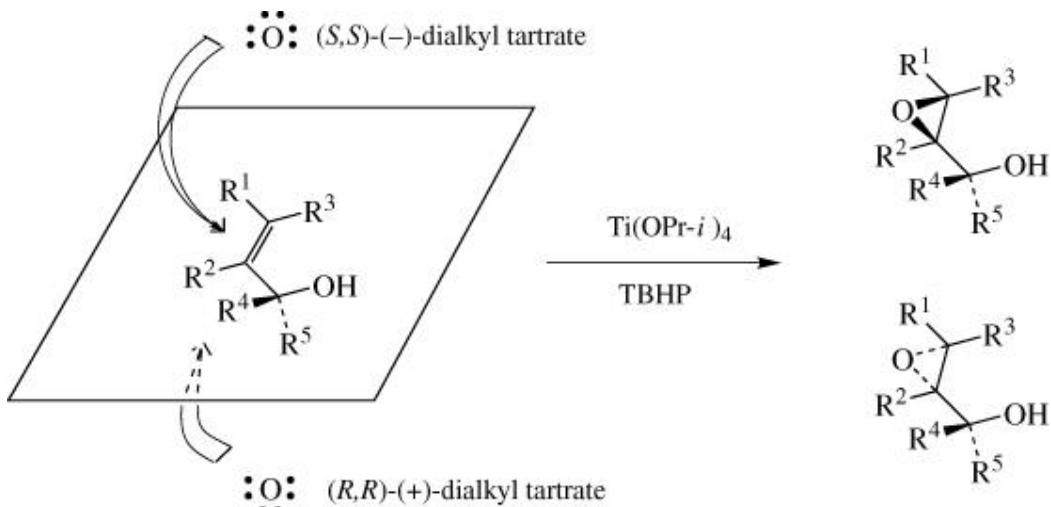
This reagent combination is also effective for the kinetic resolution of racemic secondary allylic alcohols (R^4 = H, R^5 = alkyl and R^4 = alkyl, R^5 = H). When (R,R)-tartrate is used as the chiral auxiliary, the S enantiomer (R^5 = H) of the allylic alcohol reacts faster than the R enantiomer (R^4 = H), and the R enantiomer may be recovered with high enantiomeric purity (Eq. 5). (10) The relative reaction

$$\text{(5)}$$

>96% ee
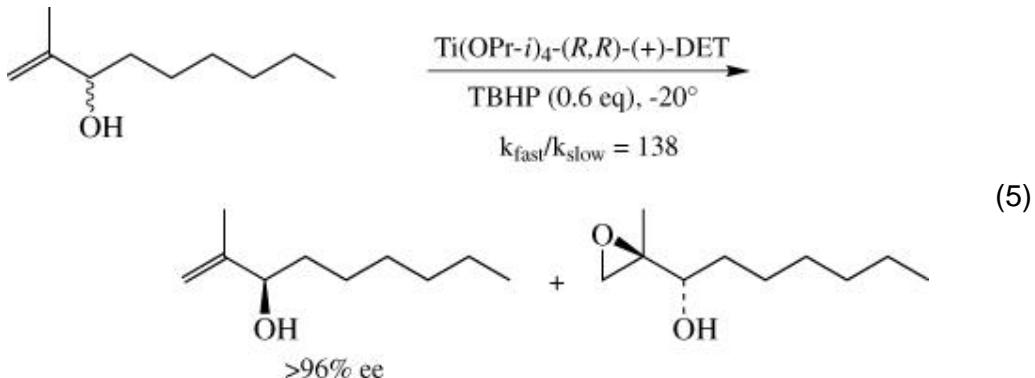
rates (k_{fast}/k_{slow}) for enantiomeric pairs usually range from 15 to 700, (2, 10-16) except for peculiar substrates like allyl-*tert*-butylcarbinol and cyclohexenol. This kinetic resolution is an effective way of obtaining *sec*-allylic alcohols of high optical purity. The relationship between the enantiomeric purity of the unreacted allylic alcohol, the relative reaction rate of a pair of enantiomers, and percent conversion of the starting racemic allylic alcohol is described in the

section on the kinetic resolution of secondary allylic alcohols. This reaction is also effective for preparing epoxy alcohols. The epoxy alcohol derived from the fast-reacting enantiomer, except for substrates with *Z* olefinic substituents, possesses the *erythro* configuration. (10) This is consonant with the empirical rule defining the stereo-chemical outcome of the reaction presented at the beginning of this section.

By adding molecular sieves to the reaction system, the asymmetric epoxidation and kinetic resolution processes can be carried out with a catalytic amount of the titanium—tartrate complex without impairing the enantioselectivity of the reaction. (17-19)

The titanium—tartrate complex and its modified relatives have also been employed for the asymmetric oxidation of heteroatoms like nitrogen, (20, 21) sulfur, (22-25) and selenium. (26)

3. Mechanism

The reaction sequence proposed for the metal-catalyzed epoxidation of allylic alcohols is shown in scheme 2. (27-30)

scheme 2.
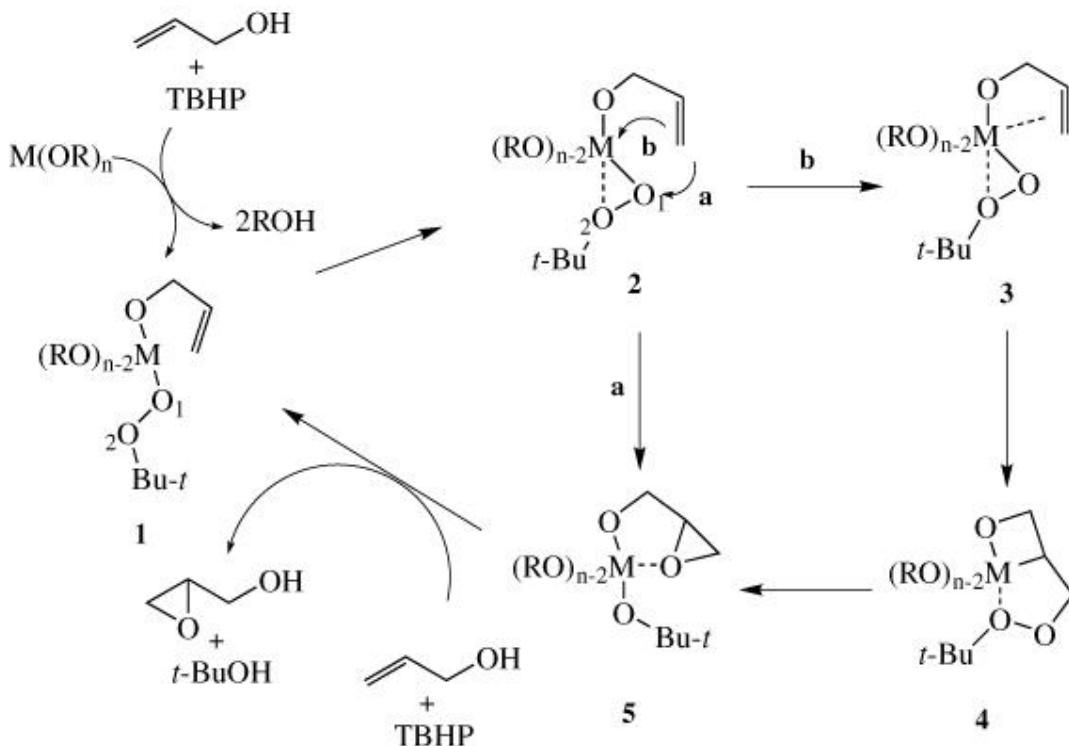
Metal alkoxides generally undergo rapid ligand exchange with alcohols. When a metal alkoxide, an allylic alcohol, and an alkyl hydroperoxide are mixed, ligand exchange occurs to afford a mixture of complexes $M(OR)_{n-x-y}\text{-}(OCH_2CH=CH_2)_x(OOR)_y$. Among them, only species such as **1**, bearing both allylic alkoxide and alkyl hydroperoxide groups, are responsible for the epoxidation. The incorporated alkyl hydroperoxide is thought to be further activated by coordination of the second oxygen atom (O-2) to the metal center (see structures **2** and **3**). That the ensuing transfer of O-1 to the double bond of the allylic alcohol occurs in an intramolecular fashion is supported by comparison of the epoxidation rate of allyl alcohol with that of allyl methyl ether. (31) However, controversy still surrounds the oxygen transfer process (**2** ® **5**). One suggestion is that the double bond first coordinates to the metal center and then inserts into the μ 2-alkyl hydroperoxide ligand to give an epoxide via the peroxometallocycle intermediate **4**. (32-34) An alternative proposal is that the double bond attacks the distal oxygen along the axis of the O - O bond that is broken. (2,30,35–39) Frontier molecular orbital treatment of peroxometal complexes also suggests that *d* transition metal complexes of ROO—exhibit electrophilic behavior. (40) Finally, exchange of *tert*-butoxide and the epoxy

alkoxide so formed with allylic alcohol and alkyl hydroperoxide completes the reaction cycle.

The titanium—tartrate mediated asymmetric epoxidation of allylic alcohols also follows the same basic reaction pathway of scheme 2. Therefore, the remaining mechanistic question is how oxygen is transferred enantioselectively to substrates. To answer this question, structures of titanium—dialkyl tartrate complexes, (37–38,41–45) as well as those prepared from Ti(OPr-i)$_4$ and (R,R)-N,N¢-dibenzyltartramide and from Ti(OEt)$_4$, (R,R)-diethyl tartrate, and PhC(O)-N(OH)Ph were determined. (46-48) Based on the X-ray analysis of these complexes, the structure of the asymmetric epoxidation catalyst has been proposed as **6**.

$E = CO_2R$

6
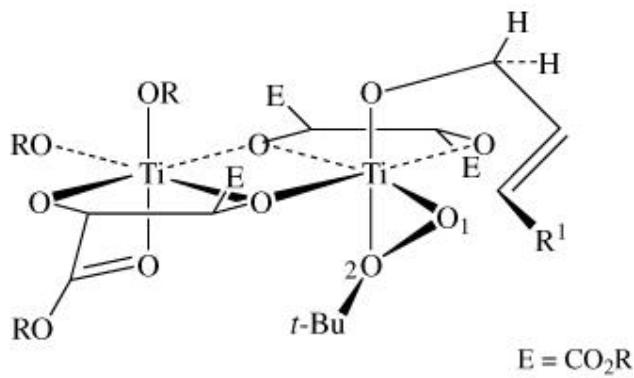
When structure **6** is viewed down the distal peroxide oxygen—titanium bond axis (O^1-Ti), the symmetry of the tartrate "windmill arms" becomes apparent. Within this model, conformer **7**, in which the allylic alcohol

7
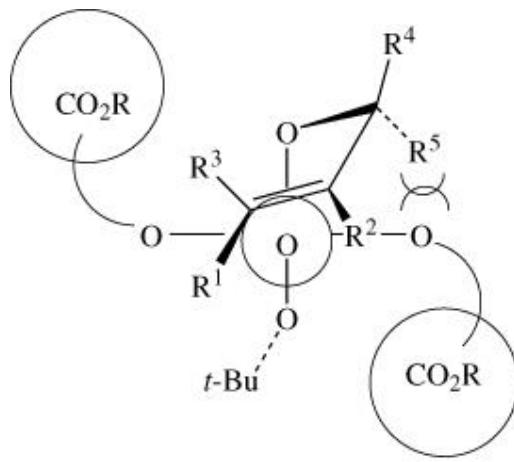
and the TBHP-ligand align meridionally and the TiO - C -C = C dihedral angle is as small as 30°, has been suggested as a transition state. (2)

This conformer experiences severe steric interactions only when $R^5 \neq H$. This explains the high efficiency of kinetic resolution of racemic secondary allylic alcohols where one enantiomer (R^4 = alkyl, R^5 = H) reacts much faster than the other isomer (R^4 = H, R^5 = alkyl). The poor reactivity of tertiary allylic alcohols (R^4 and R^5 = alkyl) is rationalized analogously. (49) We also see that the Z olefinic substituent (R^3) is close to the hydroxymethyl group bound to titanium because of the small O—C—C = C dihedral angle. These interactions destabilize conformer **8** and lower the reactivity of this complex. The C-2 substituent (R^2) in
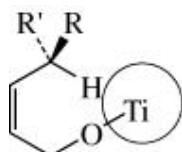
8

7 is also in the vicinity of the titanium complex, and only the E olefinic substituent (R^1) projects toward an open quadrant.

This model explains the following three observations. First, bulky Z olefinic substituents retard epoxidation reactions, and substrates with branched Z substituents exhibit poor reactivity and decreased enantioselectivity. This may be rationalized by the conformational requirement for minimization of allylic strain due to the small C = C—C—OTi dihedral angle. (2) That is, the conformation in which H is in the plane of the olefin (H in-plane conformation) is energetically more accessible than the other two conformations (R and R¢ in-plane conformations). (50) Thus the disposition of an alkyl group (R¢) to the bottom side raises the energy of the transition state depicted as **8** [using (R,R)-tartrate], causing retardation of the reaction and decreased enantioselectivity. When R $\neq$ R¢, each enantiomer of a racemic substrate has different reactivity and treatment of such a racemic mixture with Ti(OPr-i)$_4$-tartrate effects kinetic resolution.

Second, because the C-2 substituent is near the Ti—tartrate moiety, its chirality also affects substrate reactivity. Thus enantiomers of a racemic substrate bearing a chiral C-2 substituent have different reactivities, and in some cases a good level of kinetic resolution is observed.

Third, except for a few examples, the E substituent, which is located in an open quadrant, has little effect on the stereoselectivity of the reaction. Therefore, the epoxidation of chiral E allylic alcohols should proceed with the same high level of enantioselectivity seen with achiral E allylic alcohols. (51)

Although a proposal that the dimeric titanium tartrate complex is in equilibrium

with a monomeric ion pair which catalyzes epoxidation has been presented, (52) kinetic studies of the epoxidation reaction seem to exclude the possibility that the active catalyst species is monomeric. (36)

4. Scope and Limitations

4.1. Asymmetric Epoxidation of Achiral Primary Allylic Alcohols

There are two general procedures for asymmetric epoxidation: stoichiometric and catalytic. These procedures exhibit similar stereo-, chemo-, and regioselectivities. However, the catalytic procedure provides several practical advantages over the stoichiometric one: a) ease of isolating the product, b) extended scope due to use of a catalytic amount of Lewis acidic titanium catalyst, and c) more economical. General features of asymmetric epoxidation are discussed first, and the advantage of the catalytic procedure is described later in this section.

4.1.1. Substrate Reactivity

The reactivity of allylic alcohols changes with the level of olefinic substitution (Table A). (2, 4, 43, 44) Like epoxidation reactions with peracids or other metal-catalyzed epoxidations, the reactivity of the substrates generally rises as the olefinic electron density increases.

Table A. Substrate Reactivity

Entry	Substrate	Relative Reactivity
1		0.048
2		0.600
3		0.220
4		0.420
5		1.00
6		1.20
7		4.39
8		1.48

The reactivity of cinnamyl alcohols changes with the electronic nature of the aromatic substituent. This trend indicates the nucleophilic nature of the olefin (entries 4–7). However, the level of reactivity of the 4-chloro derivative is curious (entry 6).

A *Z*-olefinic substituent decreases substrate reactivity (Eqs. 6, 7), (18) especially when it is branched at C-4 (see section on mechanism).

$$n\text{-}C_8H_{17} \diagdown \diagup OH \xrightarrow[\text{TBHP, 4 Å MS, -10°, 1.5 h}]{\text{Ti(OPr-}i)_4 \text{ (0.05 eq), (}R,R\text{)-(+)-DET (0.06 eq)}} n\text{-}C_8H_{17} \diagdown \diagup OH \quad (6)$$

(78%) 94% ee

$$n\text{-}C_8H_{17} \diagdown \diagup OH \xrightarrow[\text{TBHP, 4 Å MS, -12°, 42 h}]{\text{Ti(OPr-}i)_4 \text{ (0.05 eq), (}R,R\text{)-(+)-DET (0.06 eq)}} n\text{-}C_8H_{17} \diagdown \diagup OH \quad (7)$$

(63%) >83% ee
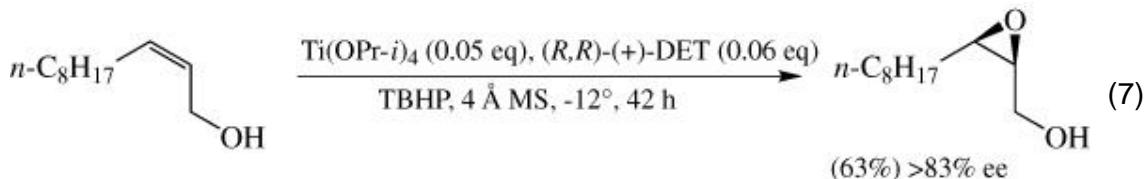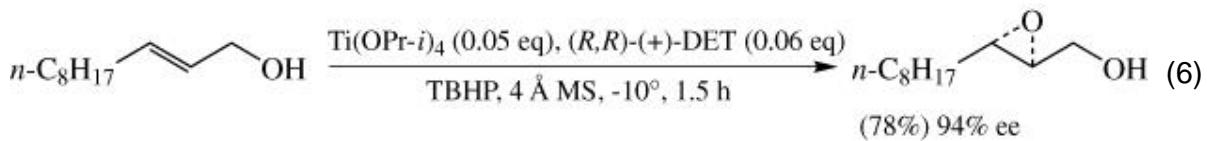
Epoxidations of tertiary allylic alcohols are usually sluggish, though (*E*)-2,5-dihydroxy-2,5-dimethylhex-3-ene is epoxidized smoothly to give the corresponding epoxide with moderate enantioselectivity (Eq. 8). (53)

$$\xrightarrow[\text{TBHP, 4 Å MS, -20°}]{\text{Ti(OPr-}i)_4, \text{ (}R,R\text{)-(+)-DIPT}} \quad (96\%) \text{ 70\% ee} \quad (8)$$
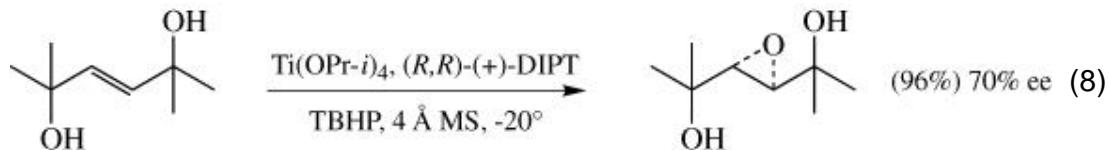
However, the epoxidation of dimethyl(2-phenylvinyl)silanol (**9**) proceeds with high enantioselectivity (85–95% ee), whereas that of diphenyl(2-phenylvinyl)silanol (**10**) exhibits an enantioselectivity of only 20%. (54)

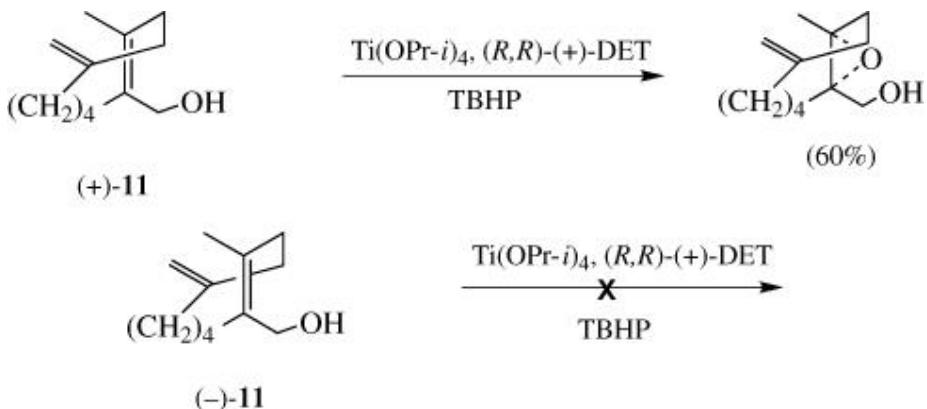9 R = Me
10 R = Ph

(71%) 85-95% ee
(70%) 20% ee
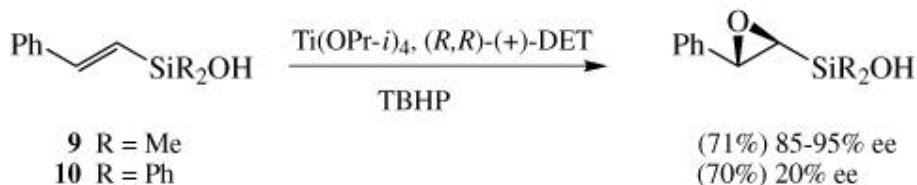
The presence of a coordinating functional group adjacent to the allylic hydroxy group sometimes decreases the reactivity of the allylic alcohol below useful levels (Eq. 9). (55)


(9)
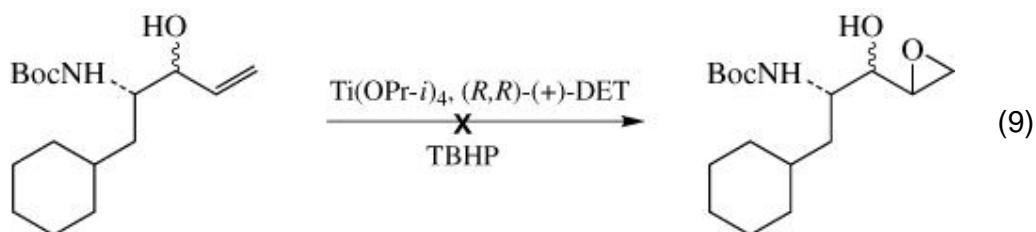
4.1.2. Stereoselectivity

The stereochemistry of this reaction can be predicted by the empirical rule shown in scheme 1, except for a few substrates bearing bulky chiral substituents near the site of epoxidation. There have been no exceptions for achiral substrates to date. Thus the reaction has been used to assign or verify absolute configuration. For example, the (–)-(*E*)-cycloalkenemethanol **11** was assigned the *S* configuration by chemical correlation to a substance whose stereochemistry had been determined on the basis of an ORD curve. However, the (–)-enantiomer [(–)-**11**] did not react under the titanium-mediated epoxidation conditions using (*R*,*R*)-diethyl tartrate, although the (+)-enantiomer [(+)-**11**)] reacted smoothly. The empirical rule therefore indicates that (–)-**11**

Ti(OPr-i)$_4$, (R,R)-(+)-DET
TBHP

(CH$_2$)$_4$ —OH

(+)-**11**

(CH$_2$)$_4$ —OH

(60%)

Ti(OPr-i)$_4$, (R,R)-(+)-DET
✗
TBHP

(CH$_2$)$_4$ —OH

(−)-**11**

should have the R, not the S, configuration. In fact, a different and unambiguous chemical correlation later established that the conclusion based on the empirical rule was correct. (56)

The following examples illustrate the effect of allylic alcohol substitution on stereoselectivity. The asymmetric epoxidation of a substrate with an E *tert*-butyl group exhibits normal enantioselectivity (Eq. 10). (57) This confirms that E allylic

OH

Ti(OPr-i)$_4$, (R,R)-(+)-DET
TBHP

O
OH (10)

(52%) >95% ee
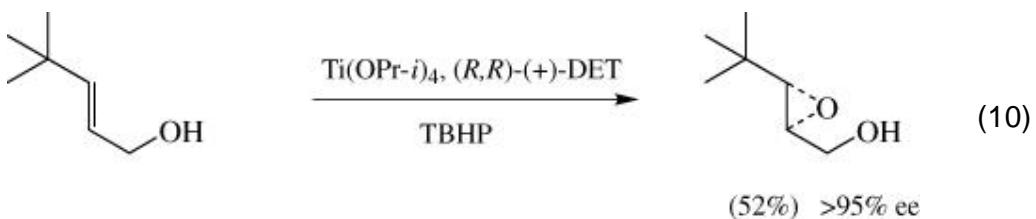
alcohols are good substrates for this titanium-mediated asymmetric epoxidation, and there are many such examples (Eq. 11).

n-C$_{15}$H$_{31}$ OH

Ti(OPr-i)$_4$, (S,S)-(−)-DET
TBHP

n-C$_{15}$H$_{31}$ O
OH (11)

(88%) >95% ee
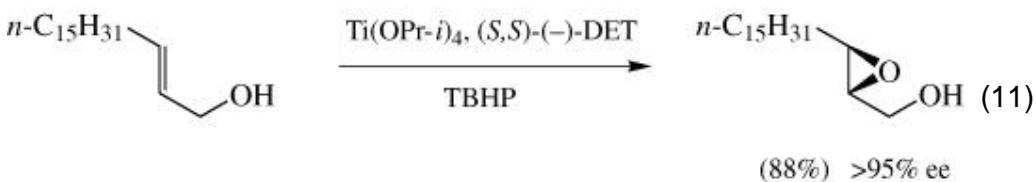
The reaction with 2-*tert*-butylallyl alcohol gives lower enantioselectivity (Eq. 12). However, the optical purity (85% ee) determined for the product is

$$(42\%) \quad 85\% \text{ ee} \qquad (12)$$
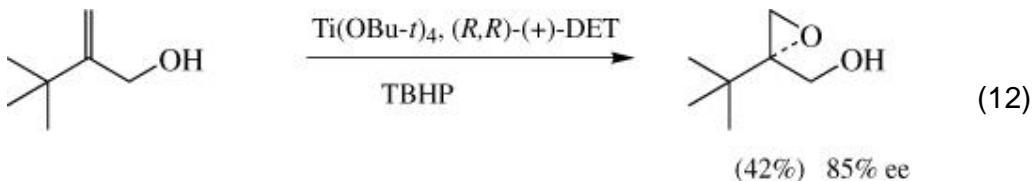
probably the lower limit, since the major enantiomer of the alcohol is preferentially attacked and consumed by an alcoholic nucleophile under the influence of the chiral titanium catalyst. (57)

The propensity for large C-2 substituents to erode enantioselectivity is also illustrated by the epoxidation of compound **12**. (58) This reaction shows diminished
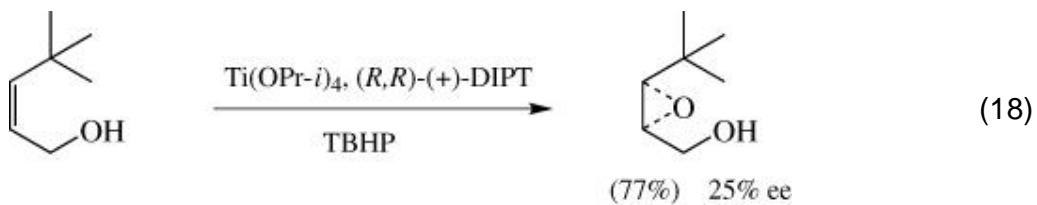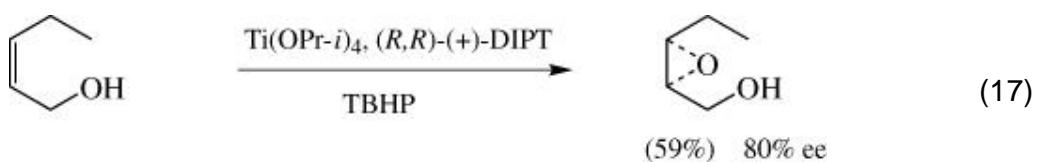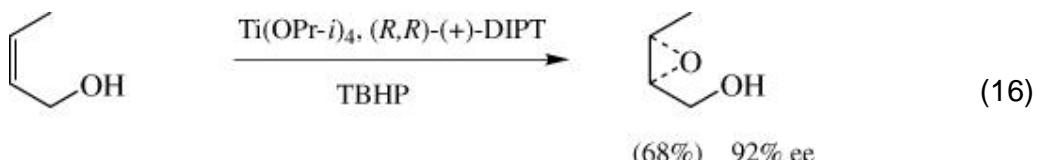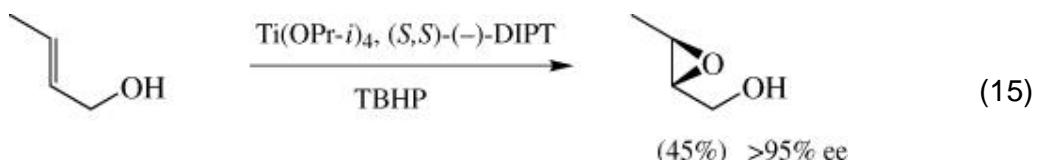

$$(80\%) \quad 70\% \text{ ee}$$
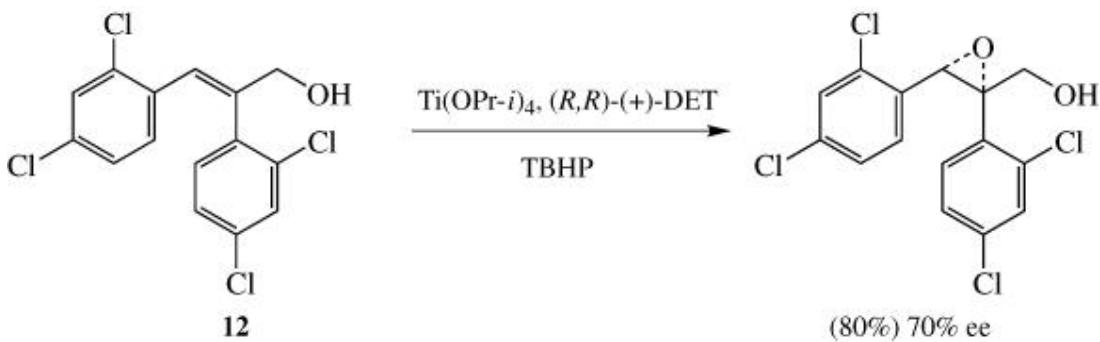
enantioselectivity (70% ee), though that of the parent 2-phenylcinnamyl alcohol exhibits high enantioselectivity (>95% ee). Although these examples are consonant with the mechanistic view that places the C-2 substituent in the vicinity of the titanium—tartrate complex, the effect of an achiral C-2 substituent on enantioselectivity is usually small. Consequently, the epoxidation of most C-2 substituted allylic alcohols proceeds with high enantioselectivity (>90% ee) (Eqs. 13, 14).

$$(91\%) \quad >96\% \text{ ee} \qquad (13)$$

$$\text{(14)}$$

$$\text{(86\%)} \quad \text{>95\% ee}$$
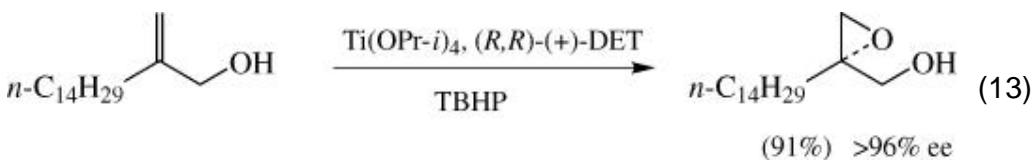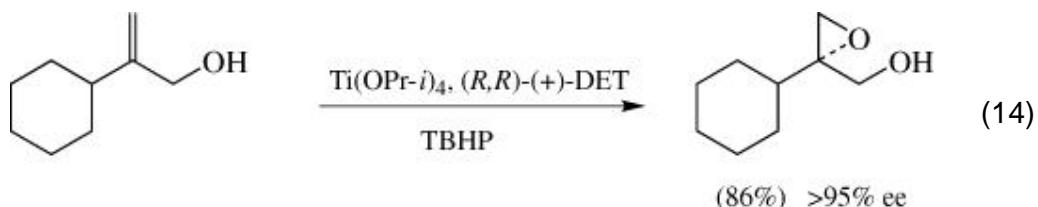
In spite of the high enantioselectivity of the titanium—tartrate complex, substandard stereoselectivity is observed for some sterically crowded allylic alcohols. The enantioselectivity of the epoxidation of Z-olefinic substrates with C-4 branched substituents decreases as the substituent become larger (Eqs. 4, 15, 16, 17, 18). (8,57,59–61) A substrate with a Z tert-butyl group undergoes epoxidation with very poor asymmetric induction, although face selection for this substrate is still in the normal direction (Eq. 18). (57)

$$\text{(15)}$$

$$\text{(45\%)} \quad \text{>95\% ee}$$

$$\text{(16)}$$

$$\text{(68\%)} \quad \text{92\% ee}$$

$$\text{(17)}$$

$$\text{(59\%)} \quad \text{80\% ee}$$

$$\text{(18)}$$

$$\text{(77\%)} \quad \text{25\% ee}$$

Asymmetric epoxidation of some allylic alcohols proceeds with diminished enantioselectivity. In many cases, however, the product epoxy alcohols are crystalline compounds that can be recrystallized to optical purity. As an example, alcohol **13** produces epoxy alcohol **14** in 86% ee, and recrystallization of **14** affords
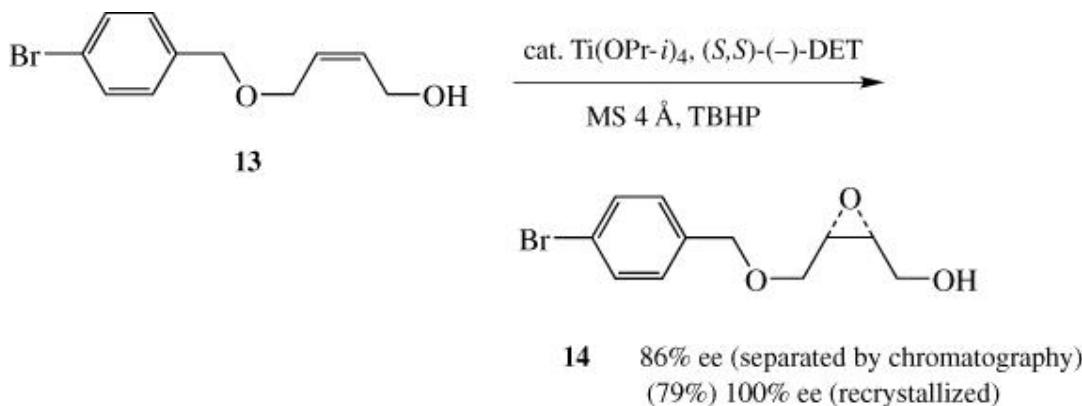
only a single enantiomer in 79% yield. (62) Noncrystalline epoxy alcohols can often be converted to crystalline derivatives such as **15**, (18) **16**, (63, 64) and **17**, (65) which also
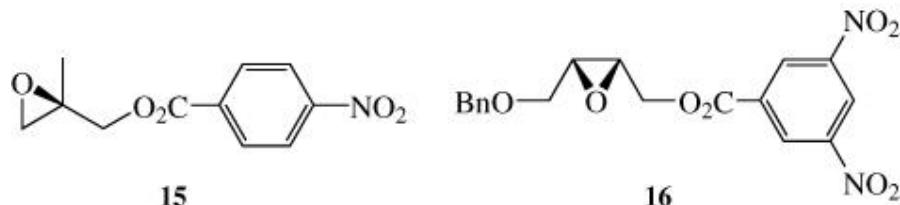
allow enhancement of enantiomeric purity through recrystallization. These derivatives can be obtained by catalytic asymmetric epoxidation and subsequent in situ derivatization (vide infra). (18, 66, 67) Unfortunately, increases in enantiomeric purity by recrystallization are not universal. Some compounds like **18** decrease in enantiomeric purity upon repeated recrystallization. (67)

Epoxidation of bisallylic alcohols possessing C_s symmetry provides diepoxy products of high enantiomeric purity together with a small amount of *meso*

isomer. (68-72) For example, if epoxidation of each allylic alcohol group in compound **19** proceeded with the usual enantioselectivity (95% ee), the product should be a mixture of (2*S*,3*S*,10*S*,11*S*)-**20**, (2*R*,3*R*,10*R*,11*R*)-**20**, and *meso*-**21** isomers in the
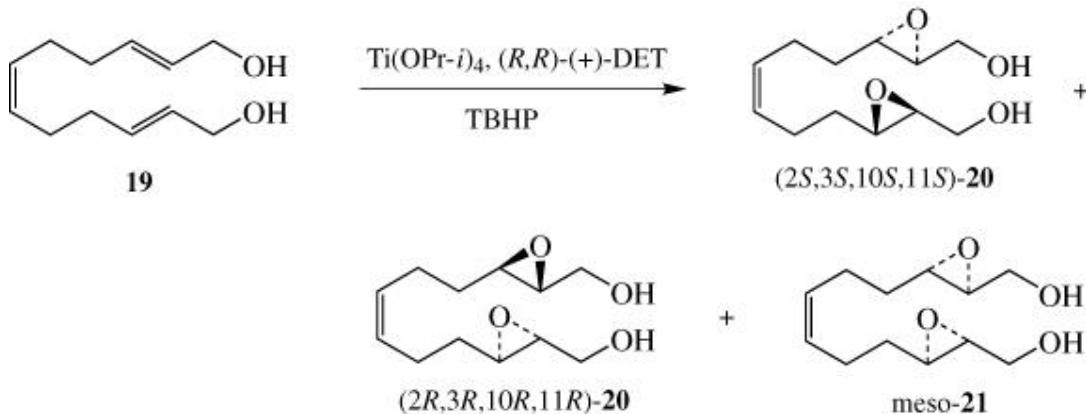
ratio 361:1:38. Actually, the reaction of **19** gives a mixture of **20** and **21** in a ratio of 9:1, though the enantiomeric purity of **20** has not been determined. (68)

4.1.3. Chemoselectivity

One of the important features of this metal-catalyzed epoxidation is its high chemoselectivity. Allylic alcohols bearing other functional groups such as ether **(22)**, (73, 74) epoxide **(23)**, (75-78) acetal [e.g., acetonide **(22)**, (73) tetrahydropyranyl (THP) ether **(24)**, (79) 1,3-dioxane **(25)**, (80) and ethoxyethyl (EE) ether **(26)** (81)], silyloxy **(23)**, (77, 78, 82-89) carbonyl **(27)**, (90) enone **(23)**, (77, 78) ester **(28)** (1, 91) α , β -unsaturated ester **(29)**, (92, 93) carbonate **(30)**, (94) urethane **(31)**, (95-97) toluenesulfonamide **(32)**, (98) acetylene **(33)**, (99-104) 4,5-diphenyloxazole **(34)**, (105) nitrile **(35)**, (106-108) nonfunctionalized olefin **(36)**, (1, 109, 110) vinylsilane **(37)**, (111) trialkylsilyl-acetylene **(38)**, (112) allylsilane **(29)**, (93) *tert*-allylic alcohol **(39)**, (113) furan **(40)** (114) (except for furfuryl alcohol) (114), and lactim ether **(41)** (115) units, as exemplified by the structures in Fig. 1, can be successfully epoxidized without interference from the other resident functional group. However, when a carbonyl group (116) (including ester (117) and amide carbonyls), a 4,5-diphenyloxazole, or a hydroxy group (117-119) is located in an appropriate position for intramolecular attack on the epoxide that is formed, a subsequent epoxide-opening reaction often occurs in situ or during workup to give a cyclic product (Eq. 19) (116) or a mixture of unidentified products other than the desired epoxide (Eq. 20). (105)
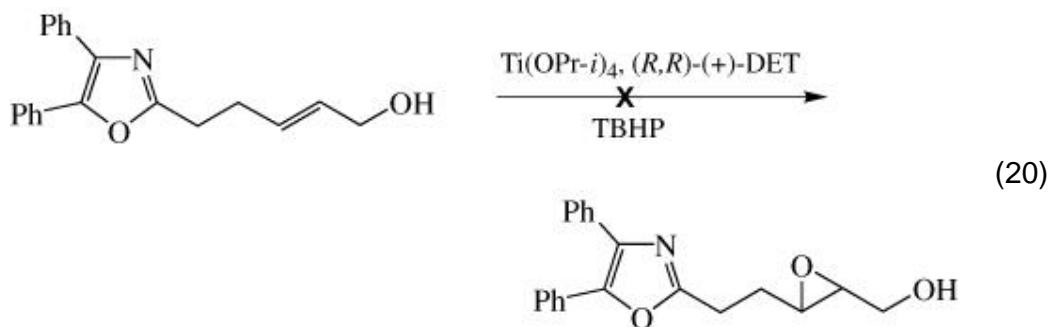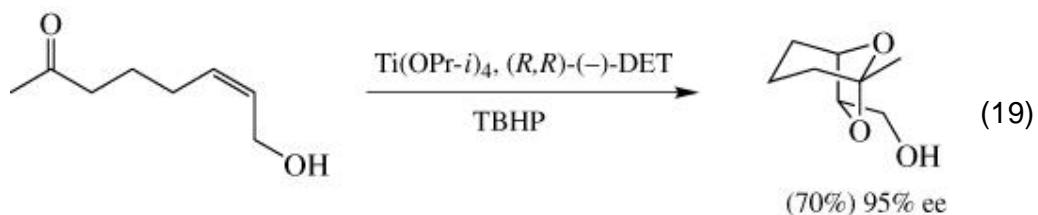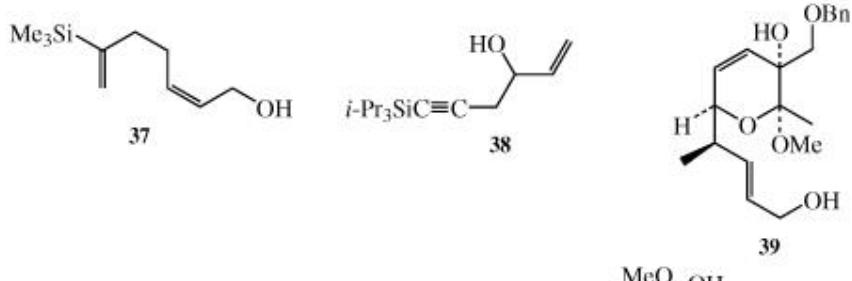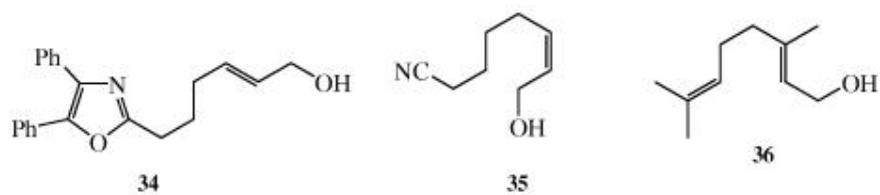
(19)

(70%) 95% ee

(20)

fig 1.

22

BnO

OH

23

O

OTBDMS

OH

24

THPO

OH

25

O O

OH

26

OEE

OH

27

O

H O

OH

28

MeO₂C

HO

OH

29

OTBDMS

HO

CO₂Et

SiMe₃

30

O O

O

OH

OH

31

NHCO₂Bn

OH

32

OBn

TsN

Bn OBn

OH

33

C₅H₁₁C≡C

OH

34

Ph

N

Ph O

OH

35

NC

OH

36

OH

37

Me₃Si

OH

38

HO

i-Pr₃SiC≡C

39

HO OBn

H O

OMe

OH

MeO OH
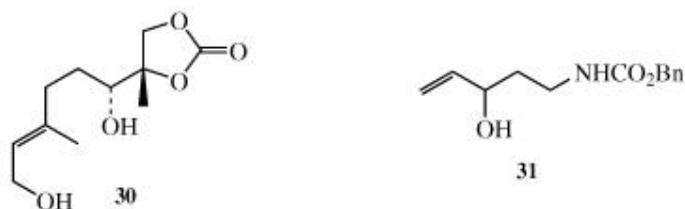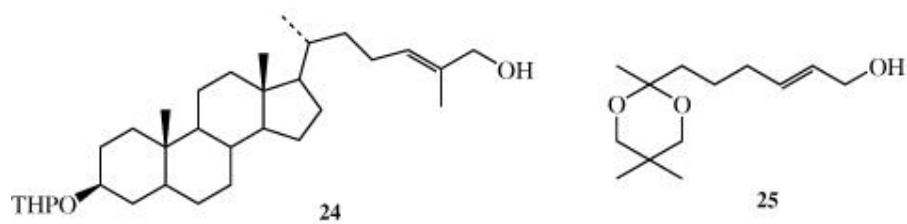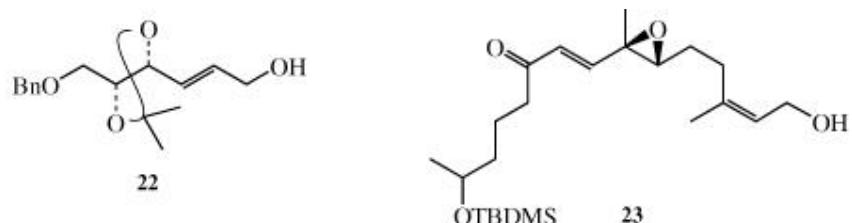
Asymmetric epoxidation of phenol **42** proceeds with diminished enantioselectivity (53% ee), possibly because of the strong coordination of phenols to titanium(IV). (120, 121) The epoxidation of compound **43**, in which the phenolic hydroxy groups are protected, proceeds with high enantioselectivity. (122)
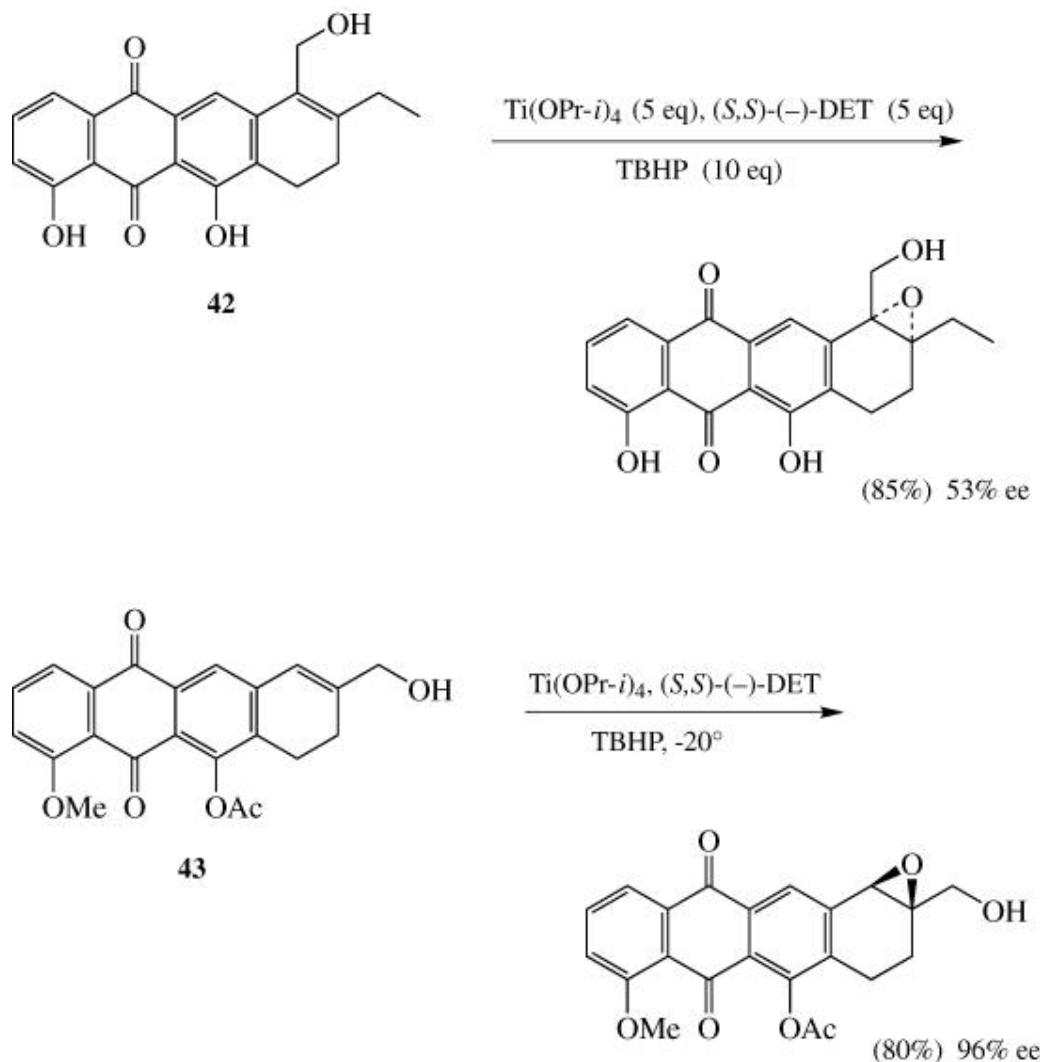
Certain functional groups in the vicinity of the reacting site may affect the stereoselectivity. For example, asymmetric epoxidation of ether **44** using (*R,R*)-and (*S,S*)-diethyl tartrate gives 3:1 and 1:3 mixtures of **45** and **46**, respectively. (123)
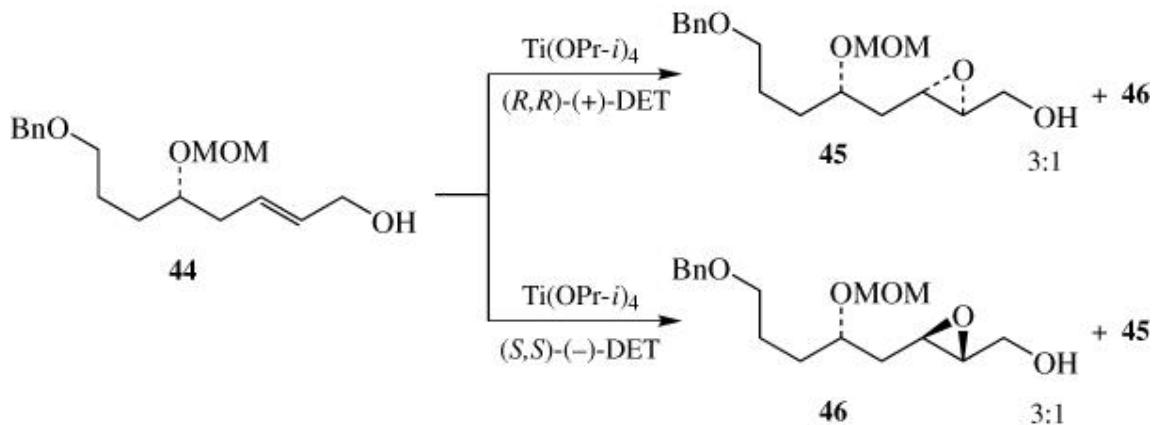
The asymmetric epoxidation of alcohol **47**, however, proceeds with high selectivity. (124)

(63%) 95% de
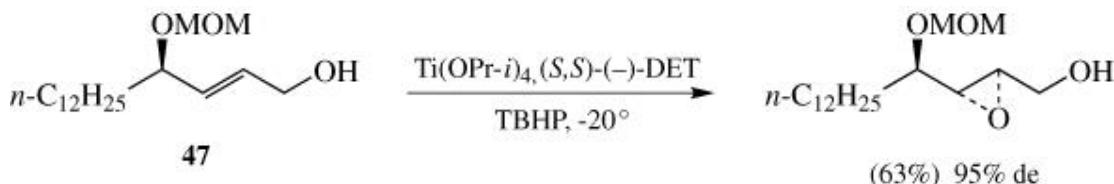
4.1.4. Regioselectivity

In metal-catalyzed epoxidation reactions, the reactivity of allylic alcohols is superior to that of homoallylic alcohols when both substrates have the same substitution pattern. (125) Although there is no detailed study on the regioselectivity of titanium(IV)-tartrate epoxidation, the above trend in regioselectivity probably holds in this reaction. However, when the degree of substitution of a homoallylic alcohol is greater than that of an allylic alcohol, the homoallylic alcohol (e.g., **48**) can be epoxidized preferentially. (126) Olefins without coordinating

(35%)

(26%) 10% ee
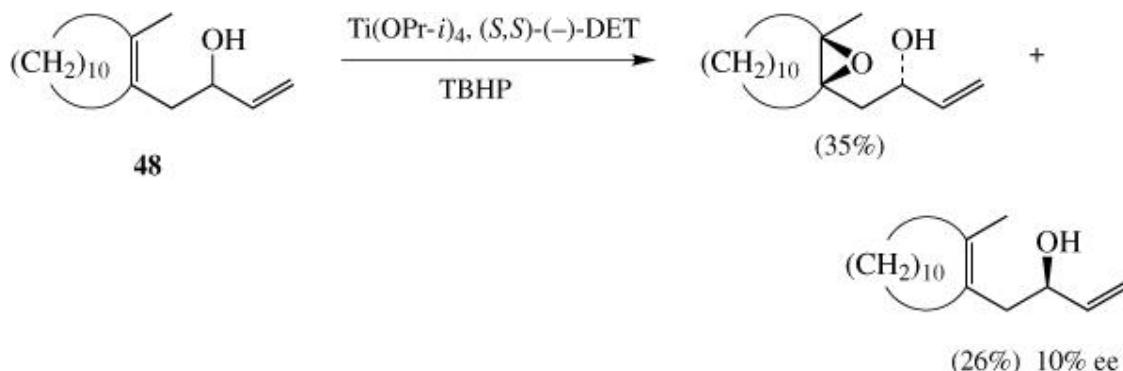
functional groups are inert to the titanium(IV) mediated asymmetric epoxidation reaction conditions.

4.1.5. Product Stability

The epoxy alcohol product is usually stable to the reaction conditions for titanium-mediated asymmetric epoxidation. However, the stoichiometric titanium-mediated asymmetric epoxidation (1) has some limitations. For example, the unsubstituted conjugated dienol **49** reacts slowly but the desired
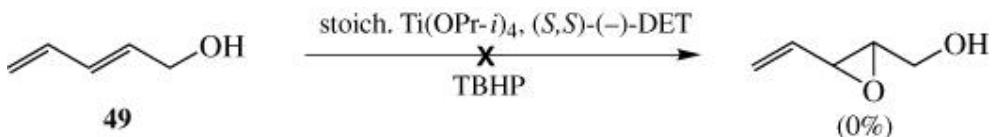
epoxide is not obtained because of its instability. (2, 19, 102) However, the C2-substituted dienol **50** (4) gives the desired epoxide in good yields. A related secondary
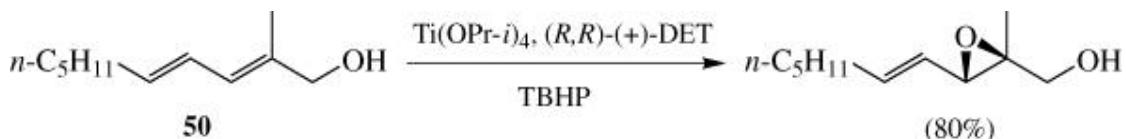
dienol **51** (127) also gives the desired epoxides **52** with an *erythro:threo* ratio (>13:1), though product yields are not given.
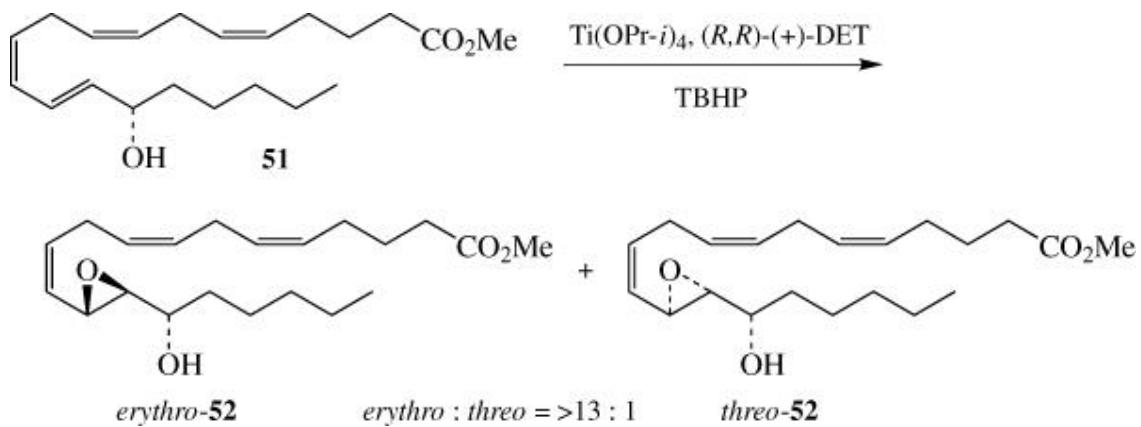

Epoxidation of *p*-methoxycinnamyl alcohol also does not give the desired epoxide because of product instability due to the presence of the *p*-methoxy group (Eq. 21), (2, 128) though *meta*-substituted compound **53** is a good

substrate (Eq. 22). (129) Product instability due to the presence of a neighboring nucleophilic

(21)

53

(82%) 97% ee

(22)
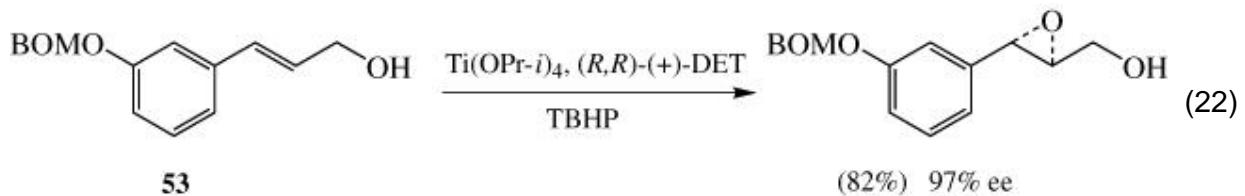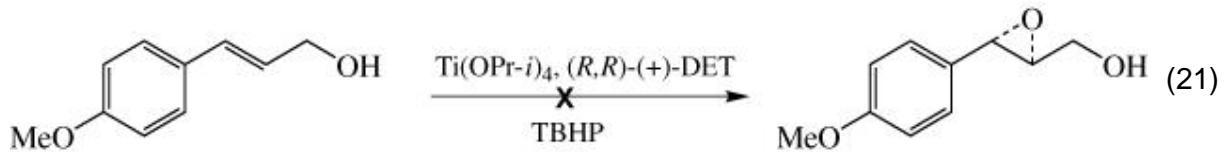
functional group has already been discussed (Eqs. 19 and 20). In addition, epoxy alcohols lacking substituents at C-3 are sensitive to nucleophilic opening, (17, 18) and this sensitivity is enhanced by complexation to a metal ion. For example, the reaction of 2-*tert*-butylallyl alcohol **54** with Ti(OPr-*i*)$_4$-tartrate gives predominantly


54

(15%)

(51%)
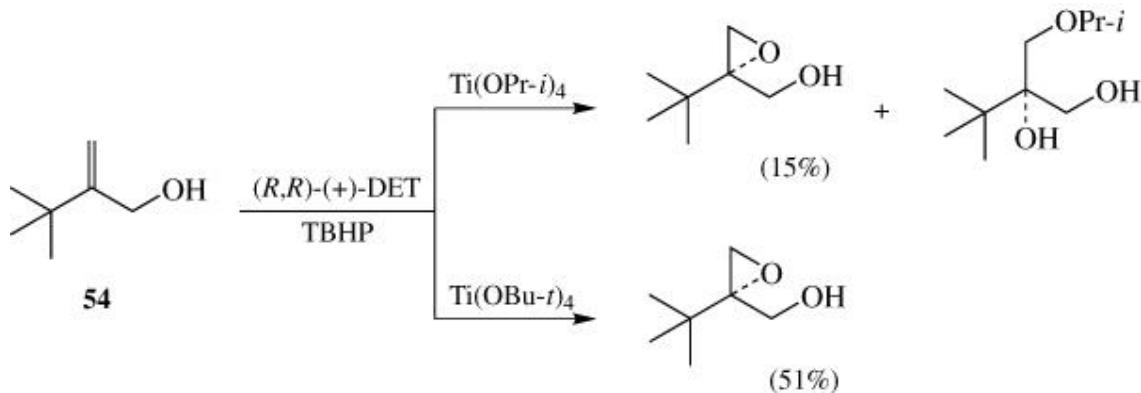
the isopropanol substitution product. (130-132) Use of Ti(OBu-*t*)$_4$ instead of Ti(OPr-*i*)$_4$, however, improves the yield of the epoxy alcohol. Epoxidation of 2-alkyl-2-cyclopropylidenethanols provides 2-alkyl-2-hydroxymethylcyclobutanones, probably via a labile epoxy alcohol (Eq. 23). (133, 134)

(23)
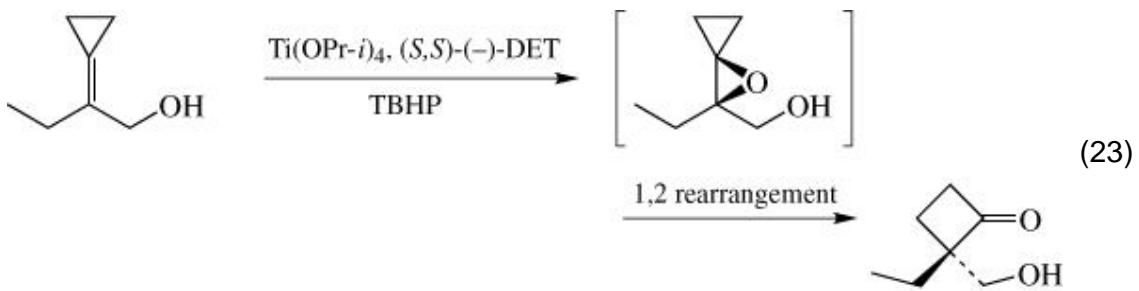
4.1.6. Catalytic Asymmetric Epoxidation

Since the principal difficulties (isolation of unstable and/or water-soluble epoxy alcohols) with the stoichiometric reaction are mainly attributed to the mild Lewis acidity of titanium alkoxide and the aqueous workup required for hydrolysis of the stoichiometric catalyst, it is not surprising that these problems are minimized when the reaction is conducted in a catalytic manner. In 1986, it was discovered that addition of molecular sieves to the reaction mixture allows epoxidation to proceed to completion in the presence of only 5–10% of the Ti(IV)—tartrate complex. (17, 18) A catalyst with 5 mol% Ti(OPr-i)$_4$ and 6 mol% tartrate has been recommended as the most widely applicable system for asymmetric epoxidation. Below the 5 mol% level, the enantioselectivity of the reaction decreases remarkably. The amount of tartrate ester must be carefully controlled, because a large excess of tartrate (>100% excess) decreases the reaction rate [the titanium—tartrate (1:2) complex is inactive], while with too little tartrate (<10% excess) the enantioselectivity may suffer.

By using the catalytic procedure, the unstable and water-soluble glycidol (Eq. 24) and low molecular weight 2-substituted glycidols are obtained in moderate


(24)

(65%) 91% ee
stoich: (17%) 87% ee
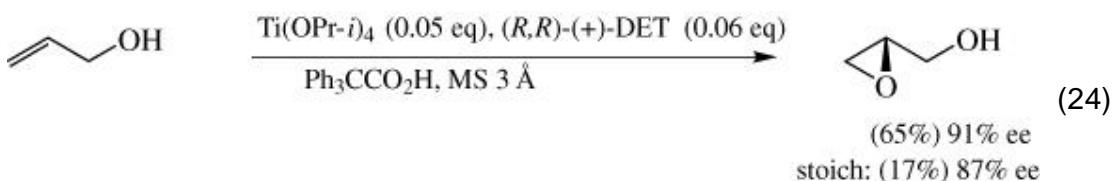
to good yields. (19, 131, 132) Other unstable epoxy alcohols like 3-arylglycidols and 3-vinylglycidols (Eq. 25), which decompose under stoichiometric conditions, are

$$(25)$$

(45%) 95% ee
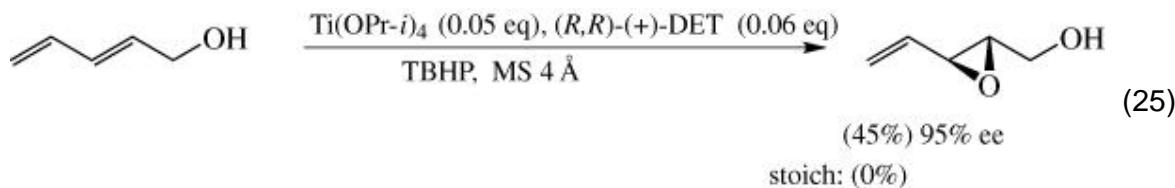
stoich: (0%)

also isolated in acceptable yields via the catalytic procedure. (19) These examples demonstrate several advantages of the catalytic procedure (economy, mildness of conditions, ease of product isolation, and increased yield) over the stoichiometric procedure, though enantioselectivity is often reduced by 1–5% relative to stoichiometric reactions.

Furthermore, epoxy alcohols produced by the catalytic procedure can be converted in situ into *p*-nitrobenzoates or *p*-toluenesulfonates, which are more easily isolated than the parent epoxy alcohols and can serve as versatile intermediates for further transformations (Eq. 26). (18, 135-137) The combination of asymmetric

$$(26)$$

(65%) >98% ee; after recrystallization
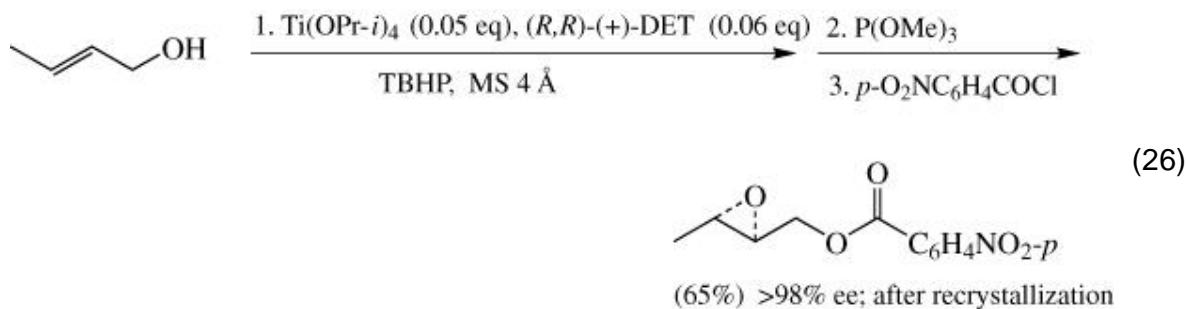
epoxidation and in situ titanium-mediated epoxide-opening reactions also provides access to diol derivatives without isolating unstable and/or water-soluble epoxy alcohols. For example, allyl alcohol can be converted to (2*S*)-propranolol **55** without isolating the glycidol. (135, 136)
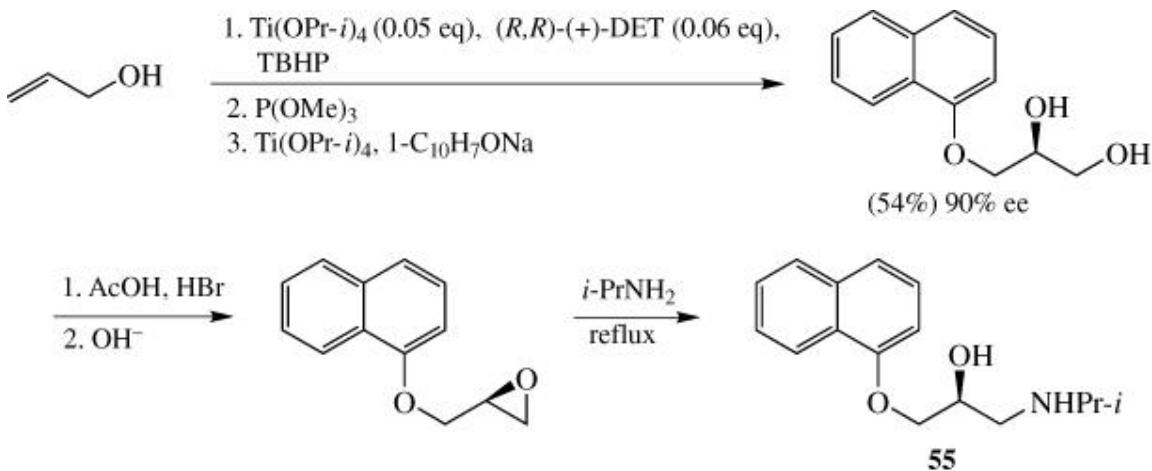
Another advantage of the catalytic process is high substrate concentration. In the stoichiometric reaction, the substrate concentration must be kept low (0.1–0.3 M) to avoid undesired side reactions like epoxide opening, while the catalytic process can be performed at concentrations up to 0.5–1.0 M. Even with the catalytic procedure, the epoxidation of a sensitive substrate like cinnamyl alcohol should be carried out at around 0.1 M concentration.

A heterogeneous catalyst prepared from montmorillonite pillared by Ti(OPr-i)$_4$ and dialkyl tartrate promotes asymmetric epoxidation of allylic alcohols with high enantiomeric selectivity in a catalytic manner (Eq. 27). (138) This procedure provides easy separation of epoxy alcohols by simple filtration without tedious workup.
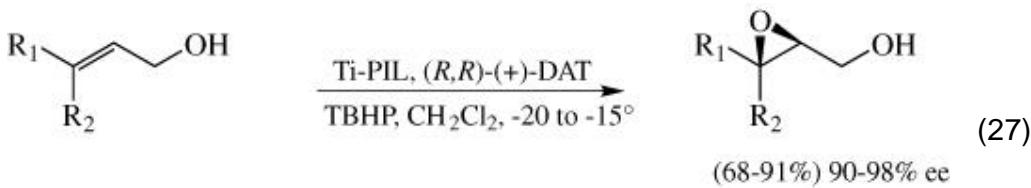
Ti-PIL = montmorillonite pillared with Ti(OPr-i)$_4$

4.1.7. Modification of the Titanium–Tartrate Complex

In the standard asymmetric epoxidation, the complex with 2:2 Ti:tartrate stoichiometry is the active catalyst. [Despite the 2:2 stoichiometry, it is strongly recommended that at least 1.2 equivalents of tartrate to Ti(OPr-i)$_4$ be used in both the catalytic and stoichiometric epoxidation of allylic alcohols. See "Experimental Conditions."] (18) Modifications of the 2:2 catalyst by varying the

chiral auxiliary or the titanium-to-auxiliary stoichiometry lead to new catalyst systems with different enantioselectivity. (2, 130) When tartramide **56** is used as a chiral auxiliary, the catalyst with 2:1 [Ti(OPr-*i*)₄:**56**] stoichiometry exhibits reversed enantiofacial selection from the standard 2:2 asymmetric epoxidation catalyst, though the enantioselectivity decreases to some extent (Eq. 28).
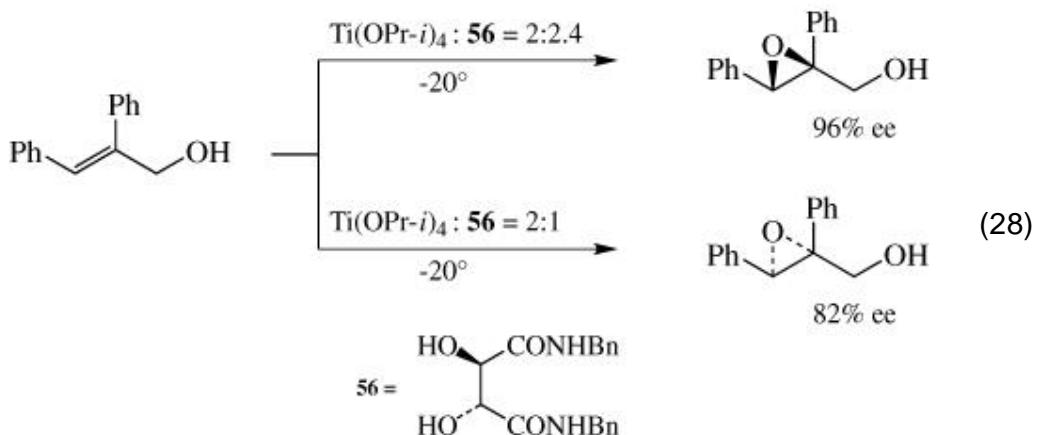

Reversed facial selection is also observed when a TiCl₂(OPr-*i*)₂ and diisopropyl tartrate (2:1) system is used. In this reaction, chloro diol **57** is obtained instead of epoxy alcohol **58**, but **57** is readily cyclized to **58** on alkaline treatment.
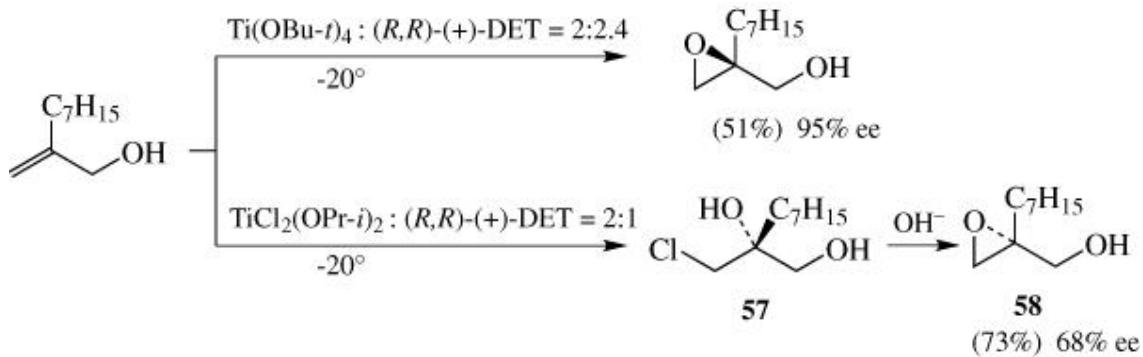
Catalysts with other than 2:2 stoichiometry also show high efficiency for the oxidation of heteroatoms such as nitrogen (20, 21, 139) and sulfur, (22-25) as described in the section on asymmetric oxidations of sulfides, selenides, and amines.

Addition of catalytic amounts of CaH_2 and silica gel to the reaction mixture also enhances the epoxidation rate without affecting the enantioselectivity, though use of a stoichiometric amount of catalyst is required. (140-142) Tertiary allylic alcohols can be epoxidized under these conditions (Eq. 29).

$$\text{(29)}$$

(70%) 100% de
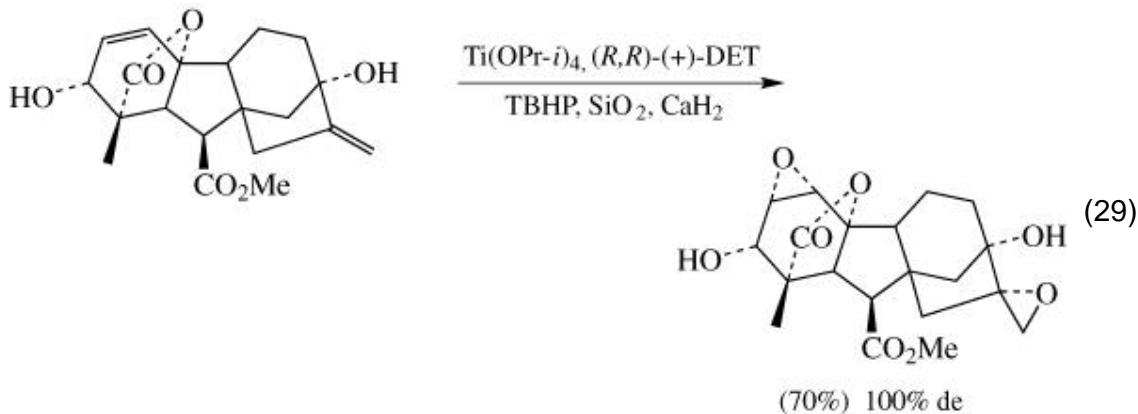
Combinations of Ti(OPr-i)$_4$ and vicinal diols other than tartaric acid derivatives usually provide poor enantioselectivity. (3-6) However, use of (1S,2S)-1,2-di(o-methoxyphenyl)ethylene glycol **59** as a chiral auxiliary gives high enantioselectivity. (143)

(78%) 95% ee
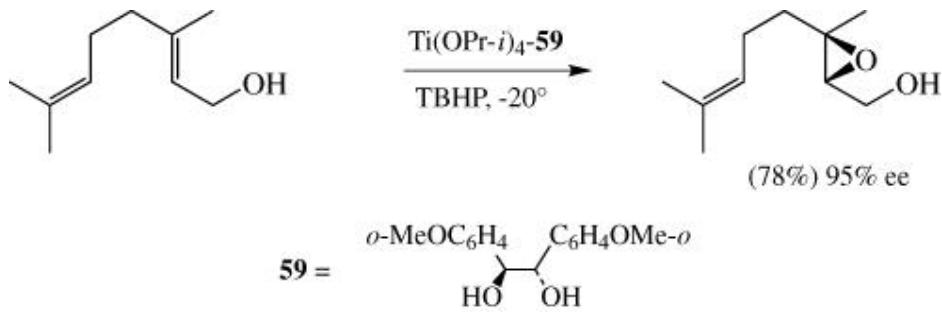
Tartrate esters linked to 1% cross-linked polystyrene resin can be used as chiral auxiliaries, but are less effective than dialkyl tartrate in inducing asymmetry. (144)

4.2. Asymmetric Epoxidation of Chiral Primary Allylic Alcohols

While the sense of facial selectivity for asymmetric epoxidation of a chiral allylic alcohol is determined by the chirality of the tartrate, the magnitude is affected by the substrate chirality. The level of influence depends on the location of the stereocenter and on the bulkiness and polarity of its

substituents. (51) The reactions of (+)-**11** and (–)-**11** described in the previous section are examples of double asymmetric epoxidations where one side of the olefin is blocked by a methylene chain. The (+) isomer makes a matched pair with the Ti-(R,R)-diethyl tartrate system, while the (–) isomer constitutes a mismatched pair. In the following sections, examples of asymmetric epoxidation of chiral substrates are described. Except for a few isolated cases, the results follow the empirical face-selection rule presented in scheme 1.

4.2.1. Chiral z Allylic Alcohols

The C-4 stereogenic center in this type of allylic alcohol strongly influences the stereochemistry of the reaction. For example, effective kinetic resolution of racemic (Z)-4-phenyl-2-penten-1-ol is observed when it is treated with Ti(OPr-i)$_4$/(R,R)-(+)-diethyl tartrate/TBHP (Eq. 30). (145, 146) The mismatched double asymmetric epoxidation of compound **60**

(30)
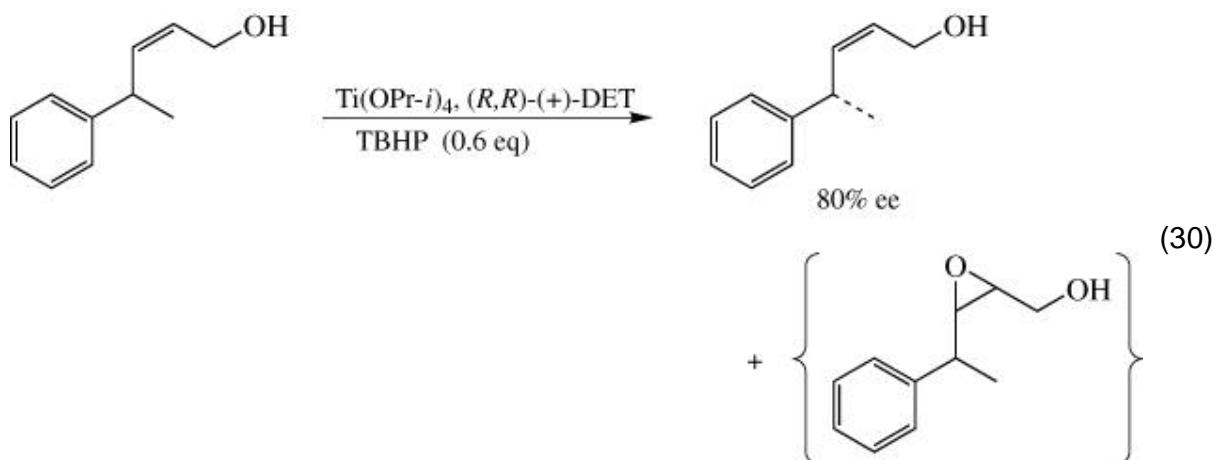
with the titanium-(S,S)-tartrate catalyst is very slow, and the desired epoxy alcohol **61** is not produced, while epoxidation of the same substrate with (R,R)-tartrate as a chiral source (matched pair) proceeds with high stereoselectivity (30:1). (73) A bulky and highly oxygenated Z olefinic substituent sometimes retards epoxidation using either enantiomer of the dialkyl tartrate auxiliary (Eq. 31). (147-149)


60

61

(R,R)-(+)-DET   (55%) 30:1
(S,S)-(–)-DET   Products were not isolated

(31)
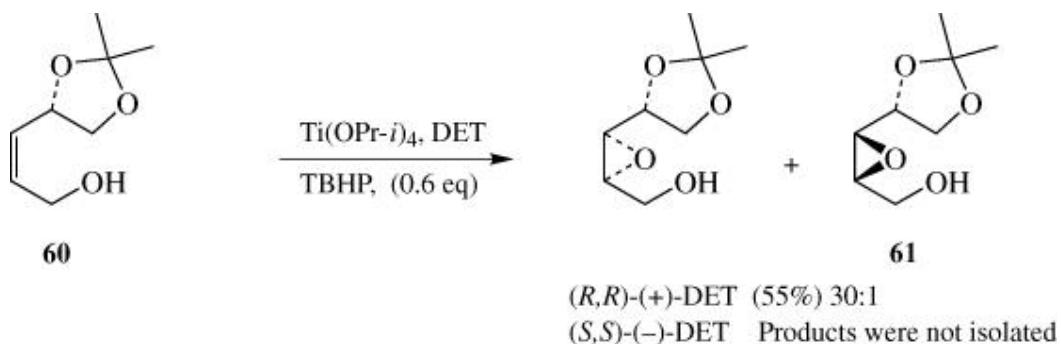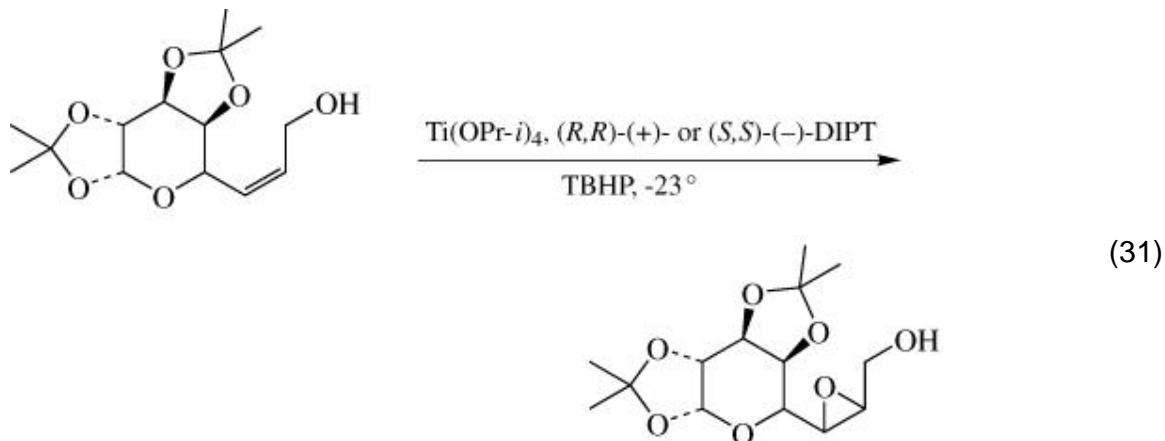
Both reactions are slow and no yield was reported.
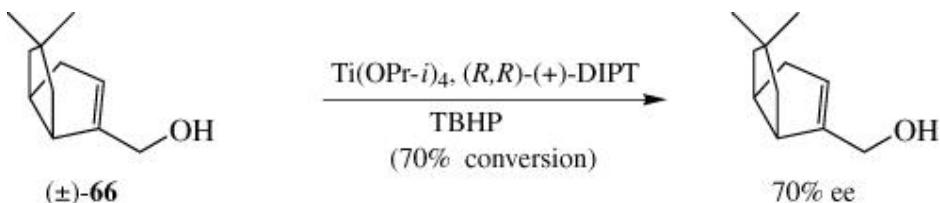
4.2.2. Chiral 2-substituted Allylic Alcohols

Racemic 2-(1-phenylethyl)allyl alcohol (62) can be effectively resolved. (145) Epoxidation of chiral, nonracemic allylic alcohol 63 with (R,R)-(+)-diisopropyl tartrate provides epoxides 64 and 65
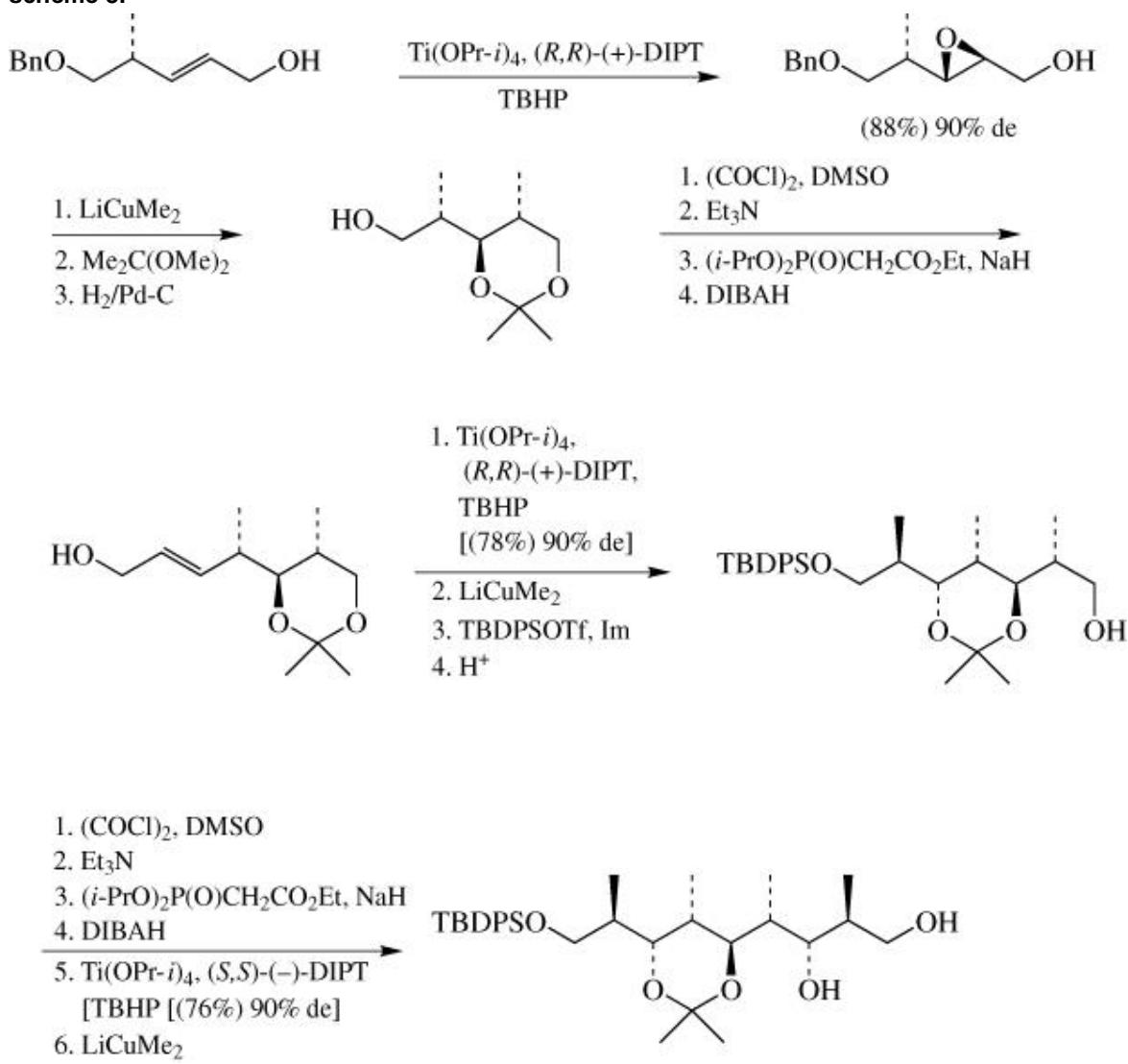
63

(R,R)-(+)-DIPT

Ti(OPr-*i*)₄
cumene hydroperoxide

(S,S)-(−)-DIPT

64 (81%) 92% de

65 (69%) 50% de
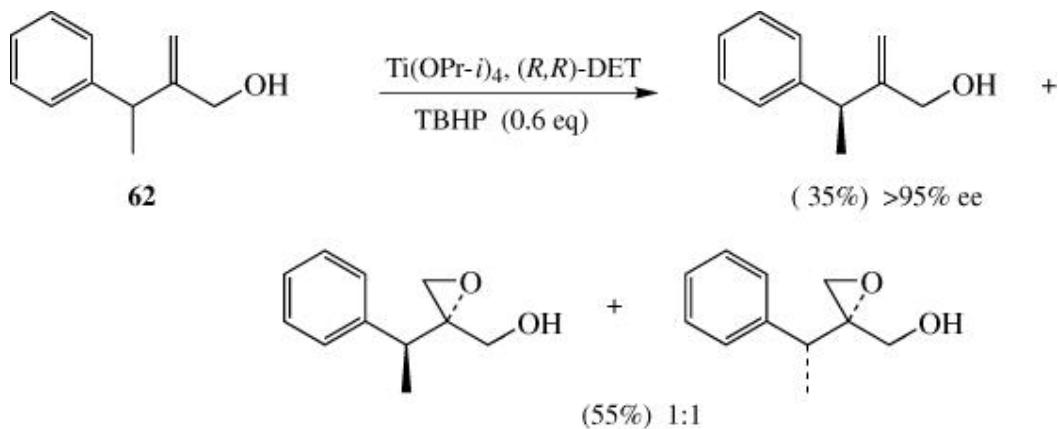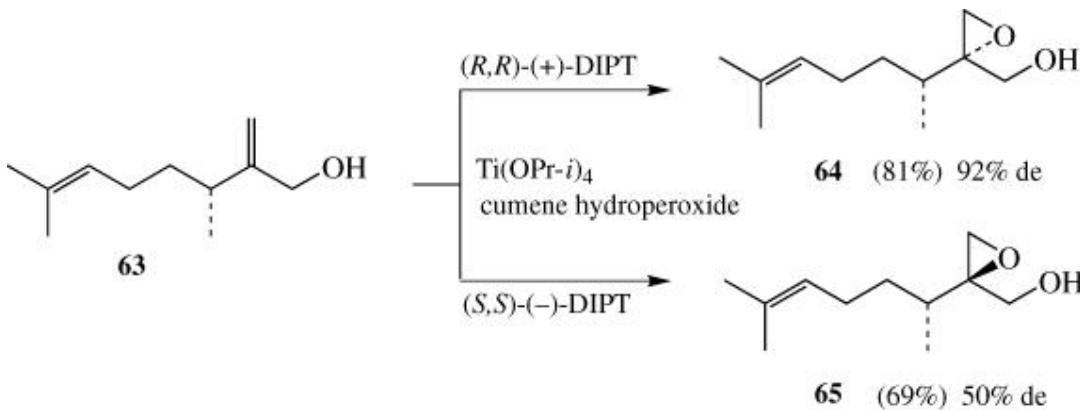
in a 96:4 ratio, whereas a 25:75 mixture of **64** and **65** is obtained with (−)-diisopropyl tartrate. (150-152) However, kinetic resolution of racemic cyclic allylic alcohol **66** is not very efficient. The enantiomeric purity of recovered allylic alcohol is only 70% ee, even after 70% conversion of **66**. (153)
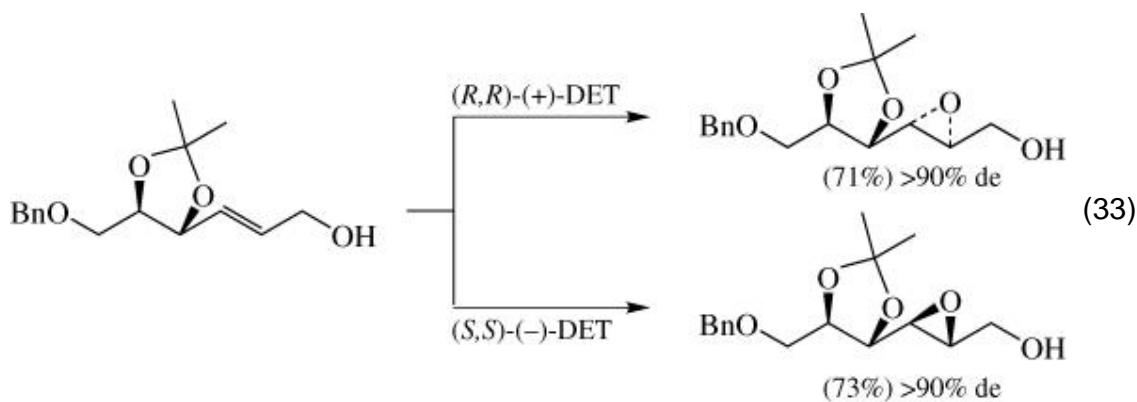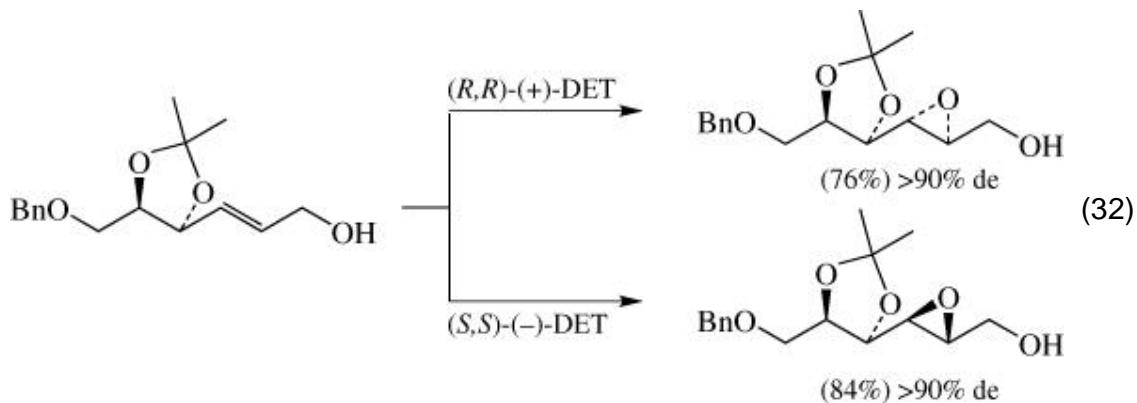

(±)-**66**

Ti(OPr-*i*)₄, (R,R)-(+)-DIPT

TBHP
(70% conversion)

70% ee

4.2.3. Chiral E Allylic Alcohols

A stereogenic center in the 3*E* substituent is expected to have little influence on the facial selectivity of asymmetric epoxidation. Indeed, the kinetic resolution of racemic (*E*)-4-phenyl-2-penten-1-ol is very poor. Therefore, the high facial selectivity observed for achiral *E* allylic alcohols can also be expected for the epoxidation of chiral *E* allylic alcohols, (51) and many successful examples of the epoxidation of substrates of this type are known. (154-160) For example, the stereoselective construction of the ansa chain of rifamycin, *S*, where the methyl and hydroxy groups are arranged consecutively in an alternating pattern, has been achieved by using asymmetric epoxidation for the key steps (scheme 3). (154) Other examples are found in sugar synthesis. A combination of titanium-mediated asymmetric epoxidation and regioselective opening of the resulting epoxy alcohols allows the stereoselective construction of consecutively polyhydroxylated compounds. (73, 160-162) High asymmetric induction in the expected direction has been attained in all epoxidations whether they are matched or mismatched combinations (Eqs. 32, 33). This carbohydrate chain-extension method has also been applied successfully to syntheses of various segments of palytoxin, a large complex organic molecule. (163-166)

scheme 3.

BnO⌣⌣⌣OH

Ti(OPr-i)$_4$, (R,R)-(+)-DIPT
—————————————→
TBHP

BnO⌣⌣epoxide⌣OH

(88%) 90% de

1. LiCuMe$_2$
—————————→
2. Me$_2$C(OMe)$_2$
3. H$_2$/Pd-C

HO⌣⌣⌣ (dioxane ring structure)

1. (COCl)$_2$, DMSO
2. Et$_3$N
—————————————————→
3. (i-PrO)$_2$P(O)CH$_2$CO$_2$Et, NaH
4. DIBAH

HO⌣⌣=⌣ (dioxane ring structure)

1. Ti(OPr-i)$_4$,
   (R,R)-(+)-DIPT,
   TBHP
   [(78%) 90% de]
—————————————→
2. LiCuMe$_2$
3. TBDPSOTf, Im
4. H$^+$

TBDPSO⌣⌣ (dioxane ring structure) ⌣OH

1. (COCl)$_2$, DMSO
2. Et$_3$N
3. (i-PrO)$_2$P(O)CH$_2$CO$_2$Et, NaH
4. DIBAH
—————————————————→
5. Ti(OPr-i)$_4$, (S,S)-(−)-DIPT
   [TBHP [(76%) 90% de]
6. LiCuMe$_2$

TBDPSO⌣⌣ (dioxane ring structure) ⌣OH

Even in the case of *E* allylic alcohols, a bulky and highly oxygenated *E* olefinic substituent affects enantiofacial selectivity of the reaction. Epoxidation of **67** with (R,R)-diisopropyl tartrate gives the single epoxy alcohol **68**, while epoxidation with (S,S)-diisopropyl tartrate gives a mixture of **68** and its

(R,R)-(+)-DET

BnO

(76%) >90% de

(S,S)-(–)-DET

BnO

(84%) >90% de

(32)

(R,R)-(+)-DET

BnO

(71%) >90% de

(S,S)-(–)-DET

BnO

(73%) >90% de

(33)

OH

67

Ti(OPr-*i*)₄, DIPT

TBHP, -23°

OH

68

OH

69

+

(R,R)-(+)-DIPT   (66%)

(0%)

(S,S)-(–)-DIPT   A mixture containing a slight excess of **68**.
(The reaction is very slow and yields are not given).
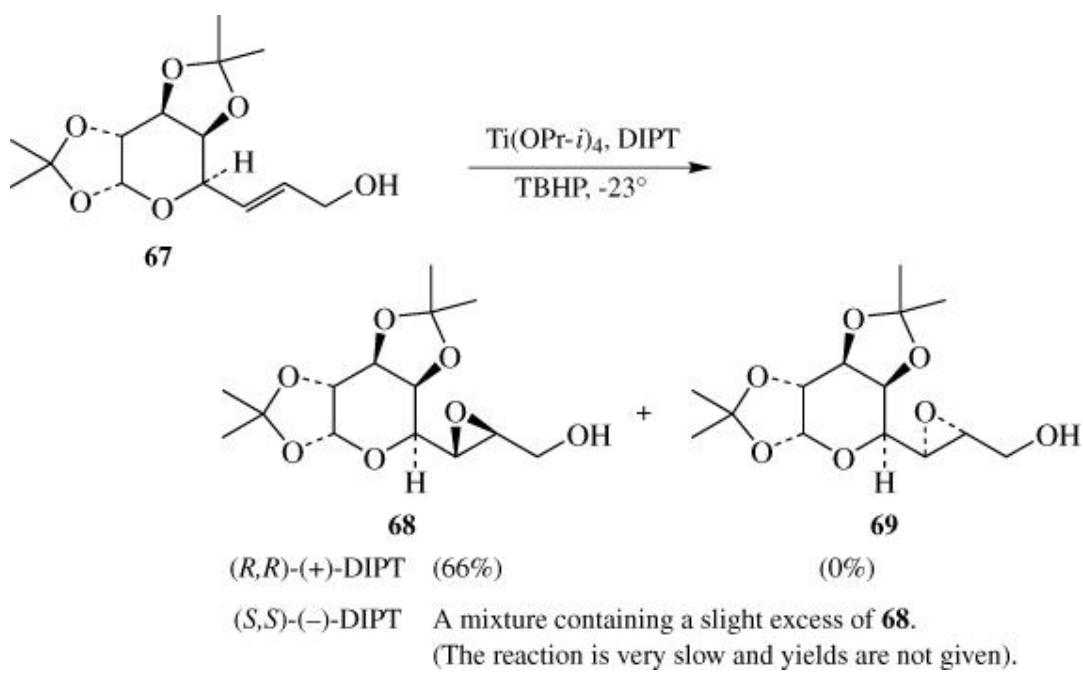
diastereomer **69**. (147, 148) Epoxidation of **70** with both (*R,R*)- and (*S,S*)-diisopropyl tartrates proceeds with only moderate diastereofacial selectivity. (149)

When a substrate has a bulky and polar *E* substituent, substantial kinetic resolution has also been observed (Eq. 34). (167)

(*R,R*)-(+)-DIPT (63%) 5:1
(*S,S*)-(–)-DIPT (—)   1:4

(34)
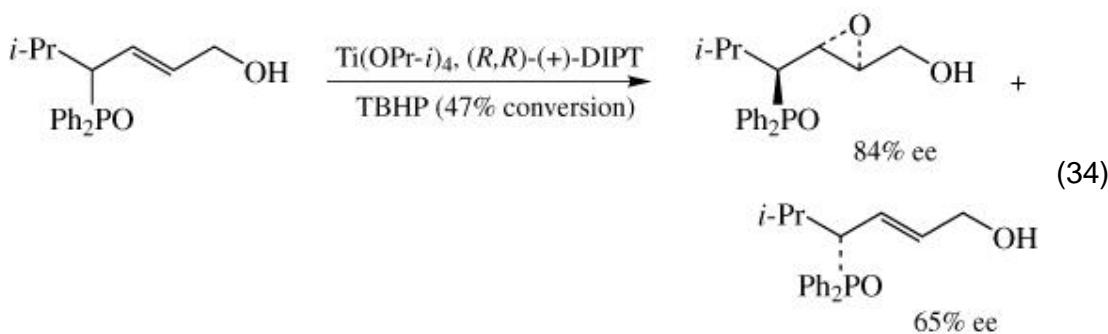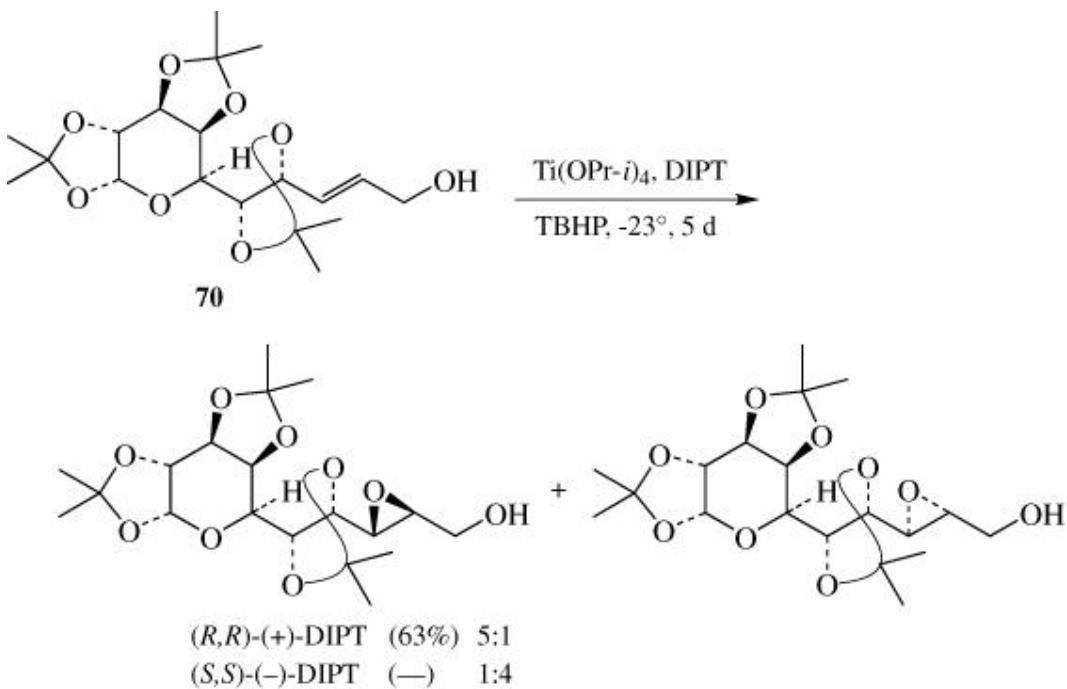
With C-2 substituted *E* allylic alcohols, the stereogenic center at C-4 has considerable influence on the facial selectivity. (168-172) On treatment with Ti-(*R,R*)-(+)-diethyl tartrate, racemic allylic alcohol **71** affords two enantiomeric epoxides **72** and **73** having the (2*S*,3*S*,4*S*) and (2*R*,3*R*,4*R*) configurations; no

(±)-71

R= CH₂C(OMe)₂CH(OMe)CH₂OAc

72 29%

73 (19%)

(4R)-71 (10%) >95% ee
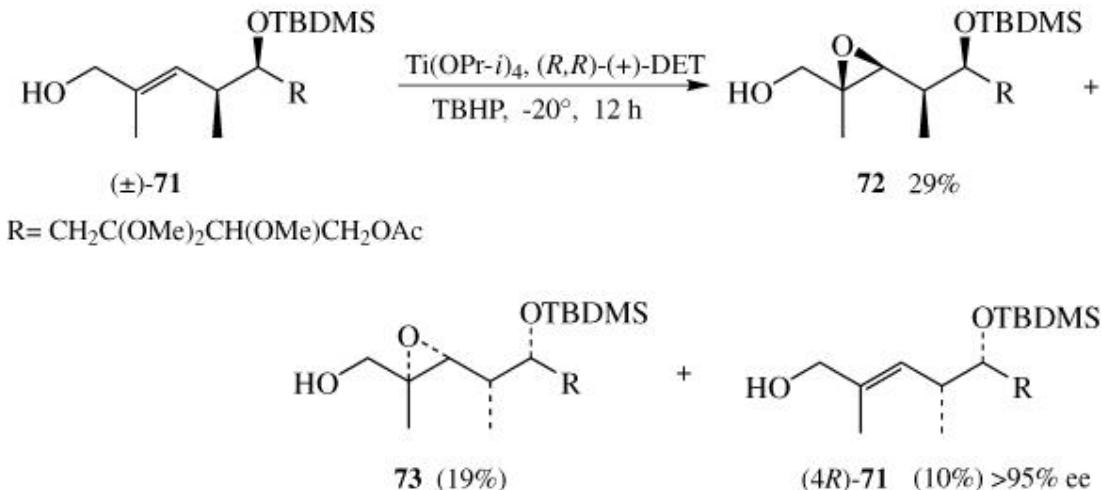
(2S,3S,4R) isomer is obtained. The enantiomeric purity of recovered (4R)-**71** is > 95% ee. This very strong diastereofacial control by the C-4 stereogenic center is attributed to the forced in-plane conformation of the C-4 hydrogen by the C-2 substituent. (168, 169) However, less highly substituted chiral *E* allylic alcohols can be epoxidized with high selectivity [e.g., 99% de using the Ti-(*R,R*)-(+)-diethyl tartrate catalyst (Eq. 35)]. (173-175) In this example, the C-4 stereogenic center and the

(93%) 99% ee

(35)
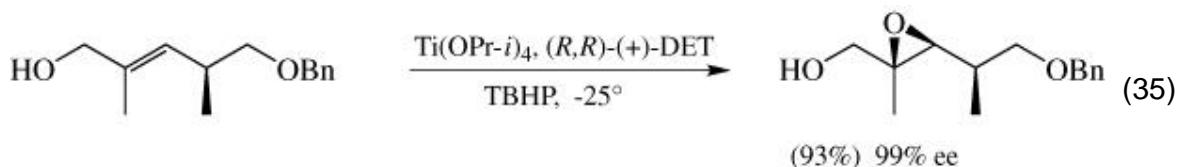
titanium-(*R,R*)-tartrate catalyst may constitute a matched pair in terms of double diastereoselection, although epoxidation of the same substrate with titanium (*S,S*)-tartrate has not been examined.

4.2.4. Miscellaneous Chiral Substrates

Other types of racemic substrates, including compounds **74** and **75**, possessing axial chirality can also be resolved. The resulting stereoselectivity can be explained by the empirical rule. (145, 146)

(±)-74

(32%) 70% ee

$n\text{-}C_7H_{15}$ —C= —OH (±)-**75**

Ti(OPr-*i*)$_4$, (*R*,*R*)-(+)-DET
TBHP, (0.6 eq)

$n\text{-}C_7H_{15}$ —C= —OH, H, H (35%) 40% ee
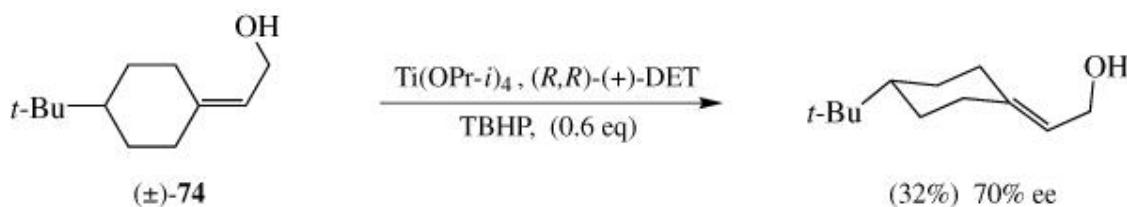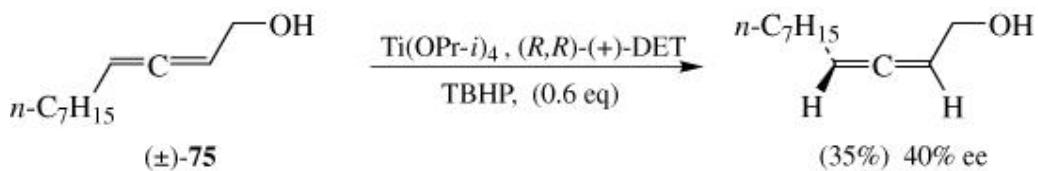
4.3. Asymmetric Epoxidation of Homo-, Bishomo-, Trishomoallylic Alcohols and Unfunctionalized Olefins

The Ti(OPr-*i*)$_4$, dialkyl tartrate, and *tert*-butyl hydroperoxide system has been applied to asymmetric epoxidation of homoallylic alcohols with limited success. (176) The reaction is fairly slow and shows rather low enantioselectivities ranging from 23 to 55% ee. The sense of asymmetric induction with homoallylic alcohols is opposite to that with allylic alcohols. That is, epoxidation of homoallylic alcohols with (*R*,*R*)-(+)-diethyl tartrate gives products enriched in the 3*R* enantiomer, while epoxidation of allylic alcohols with the same chiral source gives the 2*S* isomer with high enantioselectivity (scheme 4).

scheme 4.
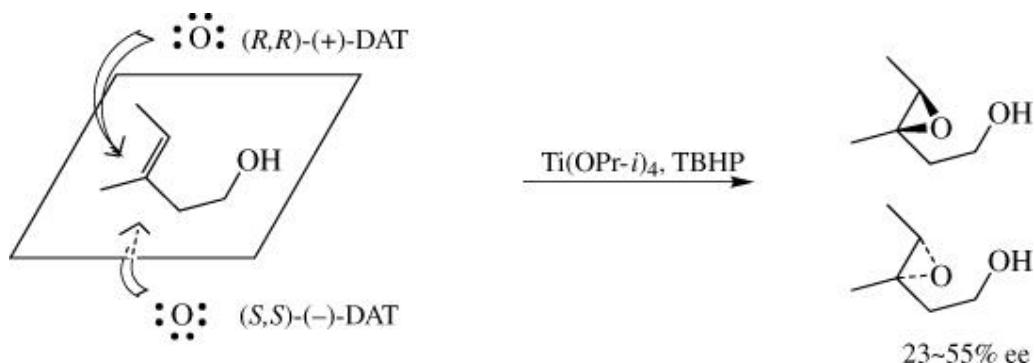
Treatment of chiral homoallylic alcohol **76** with a Ti(OPr-*i*)$_4$, (*R*,*R*)-(+)-dimethyl tartrate, *tert*-butyl hydroperoxide system provides a 3:1 mixture of diastereomeric tetrahydrofuran derivatives via attack of the intermediate epoxide by the neighboring hydroxy group. (76)
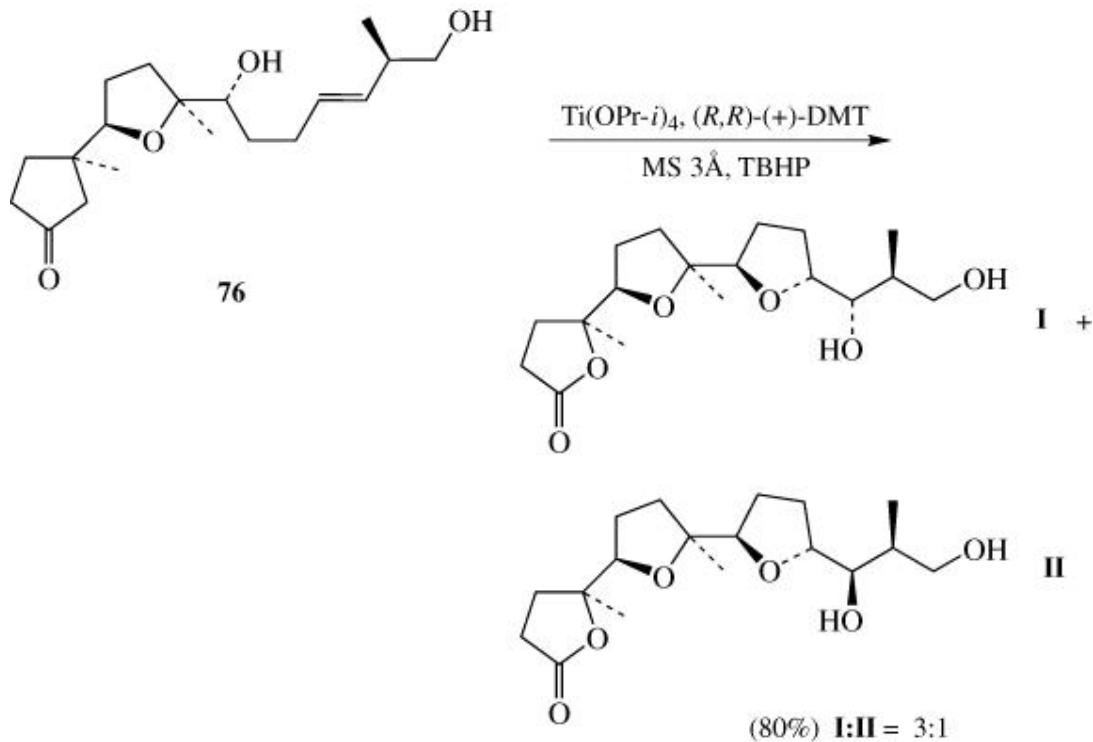
Epoxidation of alkenylethylene glycols which have hydroxy groups at both allylic and homoallylic carbons shows high but reversed diastereofacial selection to that expected for secondary allylic alcohols (vide infra) (Eq. 36). (177) A Zr(OPr-n)$_4$, dicyclohexyltartramide, and *tert*-butyl hydroperoxide system shows slightly better asymmetric induction for the epoxidation of Z homoallylic alcohols, (178) though the chemical yield is only modest (Eq. 37).


(36)

$$R = \text{Me, Et, } n\text{-C}_5\text{H}_{11} \qquad\qquad (23\text{-}28\%)\ 50\text{-}74\%\ ee \qquad (37)$$
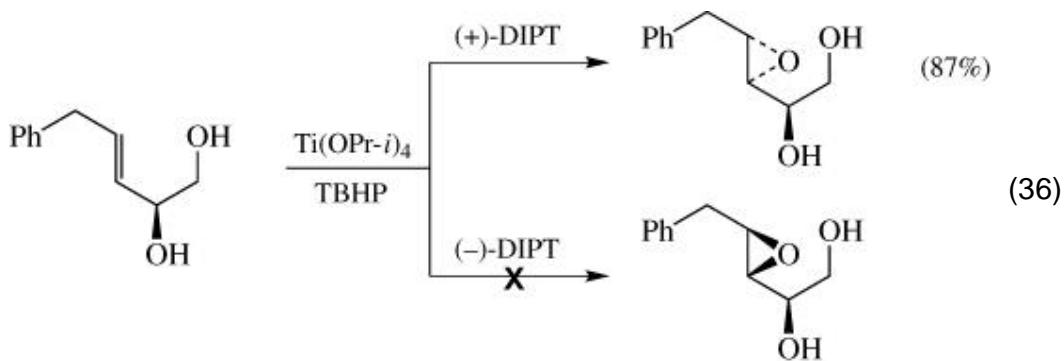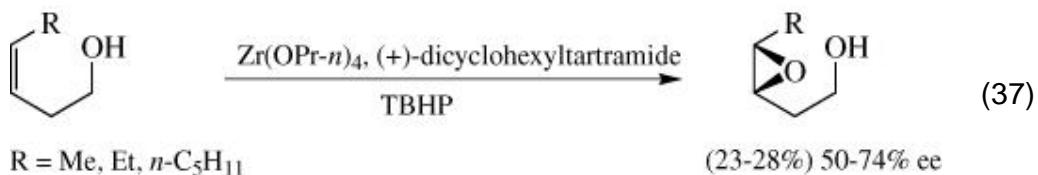
Epoxidation of trishomoallylic alcohol **77** with (*S,S*)-(–)-diethyl tartrate as a chiral source provides epoxide **78** preferentially and does not produce an appreciable amount of its diastereomer when trityl hydroperoxide is used instead of *tert*-butyl hydroperoxide. (179) No diastereoselectivity is observed when TBHP is used as an oxidant. On the other hand, epoxidation of **77** with (*R,R*)-(+)-diethyl tartrate provides a 3:4 mixture of **78** and its diastereomer.
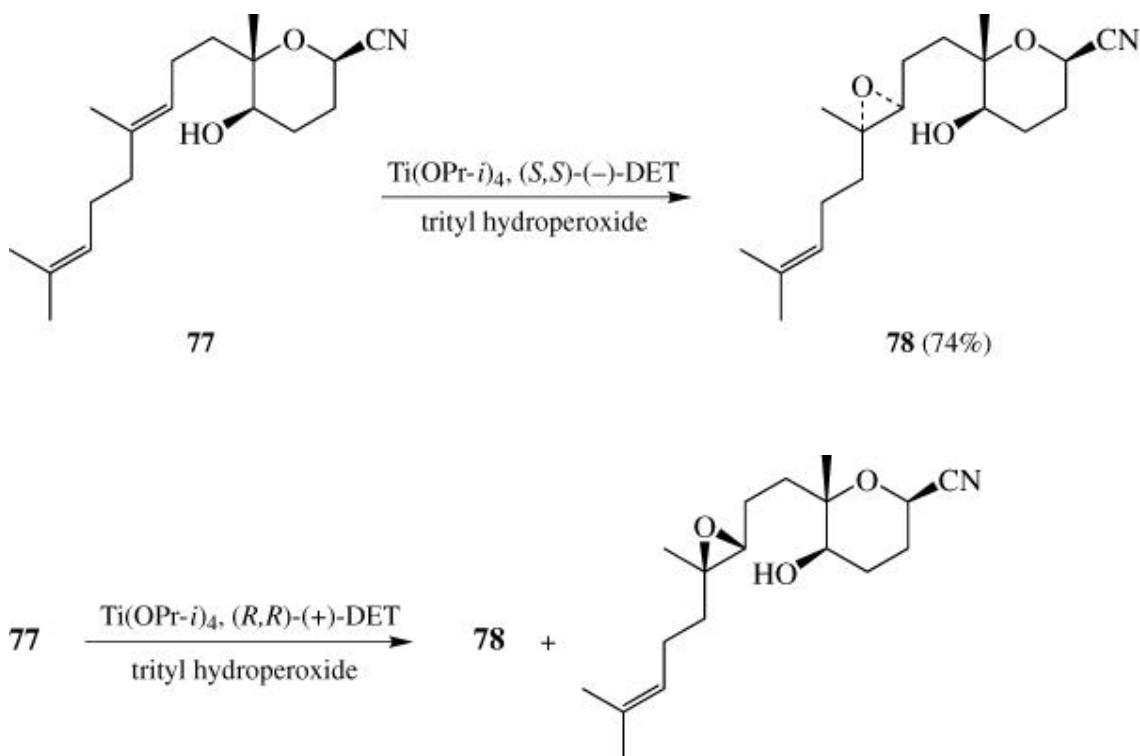
Olefins that have no neighboring hydroxy group are not epoxidized by the present reaction. However, oxidation of olefins with singlet oxygen in the presence of Ti(OBu-*t*)$_4$ and (*R,R*)-(+)-diethyl tartrate provides optically active epoxy alcohols. The allylic hydroperoxides produced by the ene reaction are converted to allylic alcohols and further epoxidized enantioselectively by the titanium—tartrate catalyst (Eq. 38). (180-182)

$$^3O_2, \text{TPP}, h\nu$$
$$\overline{\text{Ti(OBu-}t)_4, (R,R)\text{-(+)-DET}}$$

(79%) 72% ee

(38)
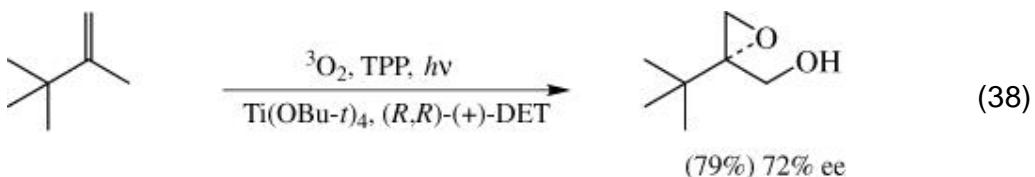
4.4. Kinetic Resolution of Secondary Allylic Alcohols

The kinetic resolution of secondary allylic alcohols was first reported in 1981 (scheme 5), (10) wherein some examples were performed with as little as 13–25% catalyst. Although this catalytic procedure has been used by other researchers, (183-186) only recently has there been reported a way to accomplish kinetic resolution in a truly catalytic manner with selectivity only slightly lower (0–4%) than that achieved in the stoichiometric reaction. (18) The key feature of this catalytic procedure is the use of molecular sieves (zeolites).

scheme 5.
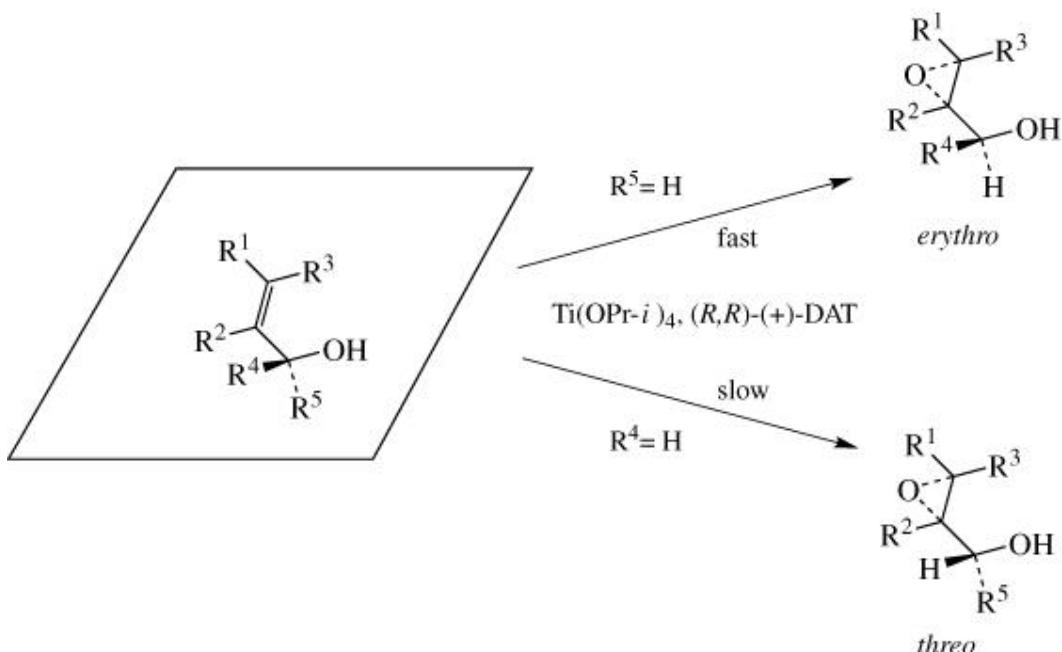
With cyclohexyl (E)-1-propenyl carbinol as the model
($R^1 = CH_3, R^2 = R^3 = R^4 = H, R^5 = C_6H_{11}$, and
$R^1 = CH_3, R^2 = R^3 = R^5 = H, R^4 = C_6H_{11}$ in scheme 5), it was found that the S enantiomer reacts 74 times faster than the R enantiomer at 0° when (R,R)-(+)-diisopropyl tartrate is used as the chiral auxiliary. (43) As in the epoxidation of primary allylic alcohols, (1) the stereochemical course of the kinetic resolution processes has been highly predictable. When the secondary allylic alcohol is drawn so that the hydroxy group lies in the lower right corner

of the plane (scheme 5), the enantiomer that reacts rapidly with
(R,R)-(+)-dialkyl tartrates is the one in which the substituent (R^4) on C-1 is
located above the plane. Epoxidation occurs from the underside to give the
usual 2S epoxide (*erythro* selectivity, 98:2). The slow-reacting enantiomer is
the one in which the C-1 substituent (R^5) is located on the underside,
interfering with the "normal" delivery of the oxygen atom. This interference
reduces the expected *threo* selectivity for the slow-reacting enantiomer (38
erythro:62 *threo*, scheme 6). This enantioselection rule has consistently been
observed for all secondary allylic alcohols except for those with bulky Z
substituents and 1,2-divinylethylene glycols. Kinetic resolution is very poor for
allylic alcohols with bulky Z substituents, (10) and reversed but high
enantioselectivity is observed in the kinetic resolutions of 1,2-divinylethylene
glycols (Eq. 39). (187, 188)

scheme 6.

erythro   98:2   *threo*

erythro   38:62   *threo*
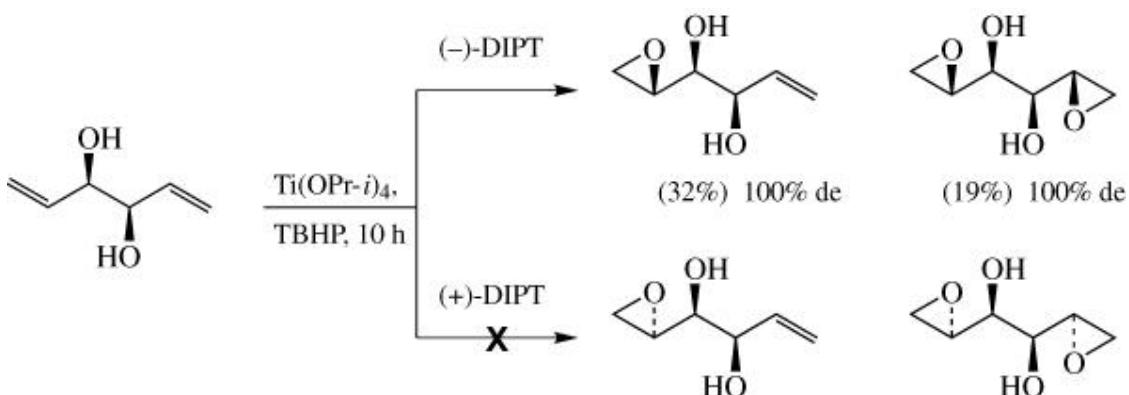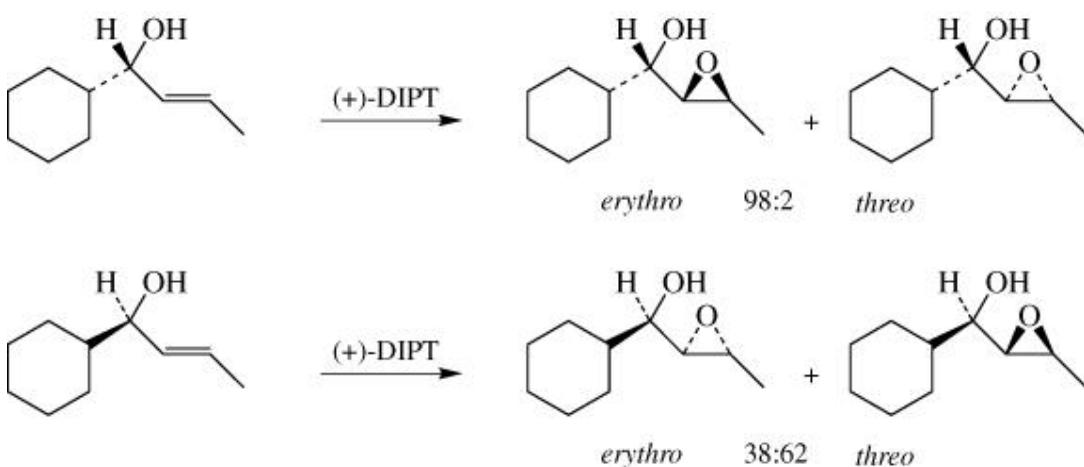
The most important parameters in kinetic resolution are the relative rates of
reaction of the two allylic alcohol enantiomers. The graph in Fig. 2, which
represents solutions of Eq. 40, (189) enables the relative rate difference to be
related to the percent ee of unreacted allylic alcohol. Three variables influence
solutions to Eq. 40: the percent ee of the remaining substrate, the percent
conversion of the racemic material, and the relative rate (k_{rel}) of reaction of the

two enantiomers. Knowledge of any two allows specification of the third. The maximum effectiveness of a kinetic resolution procedure is, of course, when $k_{rel} = $, but a value of 50–100 is almost as effective. Actual values are in the range 15 to 700. (10,12,190–198)

Fig 2.

$$K_{rel} = \frac{k_f}{k_s} = \frac{\ln(F/F°)}{\ln(S/S°)} = \frac{\ln(1-c)(1-ee)}{\ln(1-c)(1+ee)} \qquad \text{(Eq. 40)}$$

k_f = rate constant of fast reacting isomer
k_s = rate constant of slow reacting isomer
c = Fraction of consumption of racemate
ee = % ee/100
F = Concentration of the fast reacting isomer
S = Concentration of the slow reacting isomer
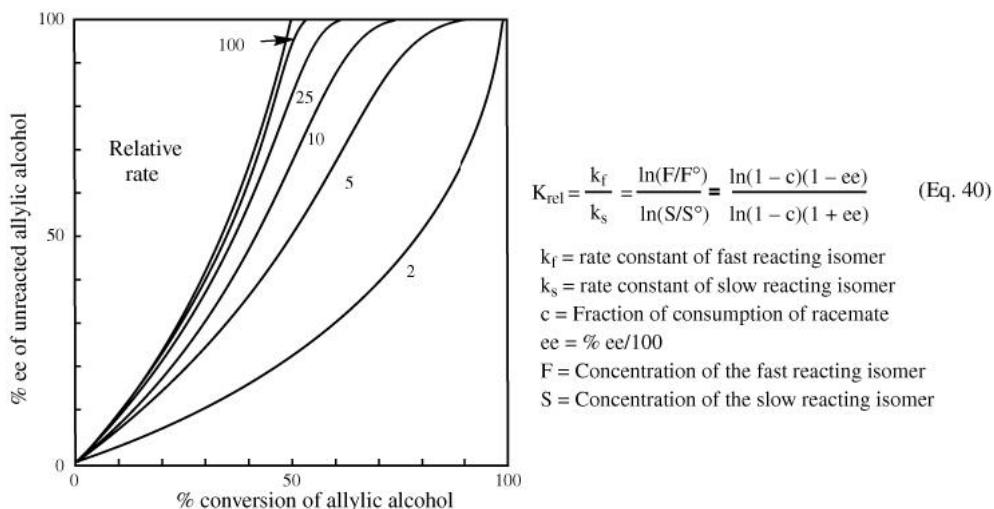
The kinetic resolution of racemic secondary allylic alcohols has almost the same substituent effects as the normal asymmetric epoxidation of primary allylic alcohols excepting, of course, the substituents labeled R^4 (or R^5) in **5**. (10) Bulky R^1 groups (scheme 5) increase the rate of epoxidation of the fast-reacting enantiomer and decrease the rate of the slow-reacting enantiomer, thus increasing k_{rel}. It should be recalled that *E*-substituted primary allylic alcohols, even with very bulky groups, are the best substrates for asymmetric epoxidation in terms of rate, yield, and enantioselectivity. The most efficiently resolved substrates to date are those in which the *E* substituent R^1 is trimethylsilyl, iodo, or tri-*n*-butylstannyl; at 50% conversion of the racemic substrate, both the recovered allylic alcohol and the *erythro*-epoxy alcohol have more than 99% ee. (12, 190-195) A careful measurement of k_{rel} for (*E*)-1-trimethylsilyl-1-octen-3-ol shows a value of k_{rel} = 700. (16) Optical purities, k_{rel}, and conversion are in complete agreement with Eq. 40 and the graph in Fig. 2.

Bulky *Z* substituents (R^3) are especially deleterious for achieving good kinetic resolution. A few examples where stereochemistry of the epoxidation does not follow the empirical rule belong to this class. (10) For example, the kinetic resolution of (*Z*)-2-cyclohexylethenyl cyclohexyl carbinol is inefficient, and the configuration of the recovered allylic alcohol is opposite to that expected from the empirical rule (Eq. 41). In contrast, resolution of the corresponding *E* isomer proceeds with high enantioselectivity to leave the expected *R* allylic alcohol (Eq. 42).

$$(41)$$

(38%) ≈10% ee

$$(42)$$

(32%) >96% ee
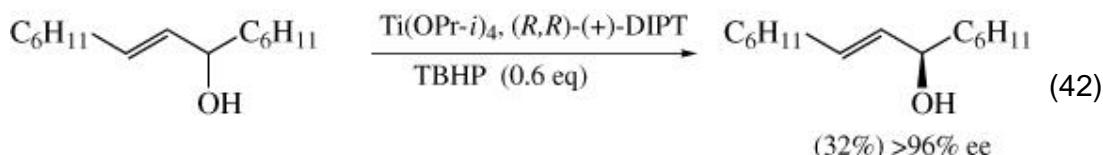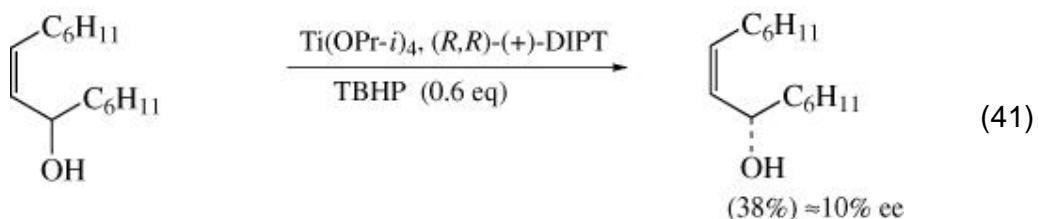
Kinetic resolution proceeds smoothly when R^2 is an unbranched alkyl group. The effect of very bulky groups has been tested by introducing sterically demanding *tert*-butyl substituents in all positions labeled R^1 - R^5 (scheme 5). (57) The results observed are consistent with examples in which $R^1 = R^3 = $ *tert*-butyl. When $R^2 = $ *tert*-butyl, at 60% conversion the recovered allylic alcohol had only 30% ee (k_{rel} 2) (Eq. 43), although the epoxy alcohol consisted largely (ca.40:1)

$$(43)$$

≈30% ee
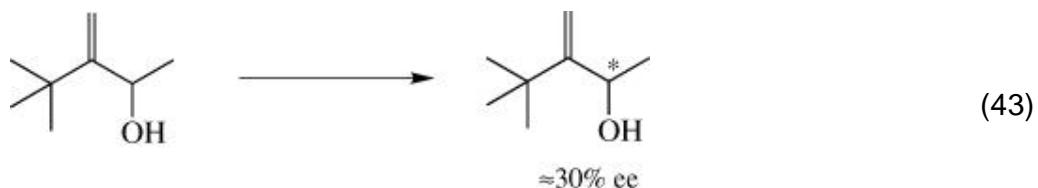
of one of the two possible diastereoisomers (the absolute configurations of both the remaining allylic alcohol and the epoxy alcohol have not been determined). This is one substitution pattern where there is not complete correlation between normal asymmetric epoxidation of the primary allylic alcohol and effective kinetic resolution of the corresponding secondary allylic alcohol [the epoxidation of the primary allylic alcohol with the same alkene substituents is achieved with 85% ee. (Eq. 12)].

Finally, when R^4(or R^5) = *tert*-butyl, the substrate is not useful for kinetic resolution, a surprising result considering that branched (aryl and secondary) substituents are among the best substrates [e.g., cyclohexyl propenyl carbinol (scheme 6)]. Kinetic resolution is not effective in these cases, probably because of steric difficulties associated with the formation and/or reaction of the allylic alkoxide complex. (57)

Another important feature of kinetic resolution is that k_{rel} increases as the temperature is lowered, as is seen by comparing the k_{rel} for cyclohexyl propenyl carbinol with (R,R)-diisopropyl tartrate at 0°(k_{rel} = 74) and – 20°(k_{rel} = 104). The immediate conclusion is that kinetic resolution should be performed at – 20° or lower, depending on the reactivity of the substrate. For convenience, most kinetic resolutions are run by storing the reaction mixture in a freezer. Both the reaction rate and the enantiomeric excess improve with stirring. (17, 18) Hence, when possible, the resolution should be carried out with constant stirring and appropriate temperature control.

The efficiency of a kinetic resolution decreases when titanium tetra-*tert*-butoxide is used to generate titanium—tartrate complex. (38)

When the epoxy alcohol is the desired product of a kinetic resolution, care should be taken to avoid extending the reaction time unnecessarily. For example, when a 4:6 mixture of (±)-*erythro*- and (±)-*threo*-1,2-epoxynonan-3-ol is exposed to the standard conditions of kinetic resolution, preferential decomposition of the *threo* diastereomer is observed. After several days at 0°(conversion   70%), the remaining epoxide has an *erythro: threo* ratio of 8:2. The remaining *threo*-epoxy alcohol has 90% ee of the 3S enantiomer; the remaining *erythro*-epoxy alcohol has 12% ee of the 3R enantiomer (Eq. 44). Because of its

n-C$_6$H$_{13}$ ⟶ Ti(OPr-i)$_4$, (R,R)-(+)-DET, TBHP, 0° (conversion = 70%)

(±)-*erythro*:(±)-*threo* = 4:6

n-C$_6$H$_{13}$ + n-C$_6$H$_{13}$ (44)

erythro 12% ee   threo 90% ee

erythro:threo = 8:2
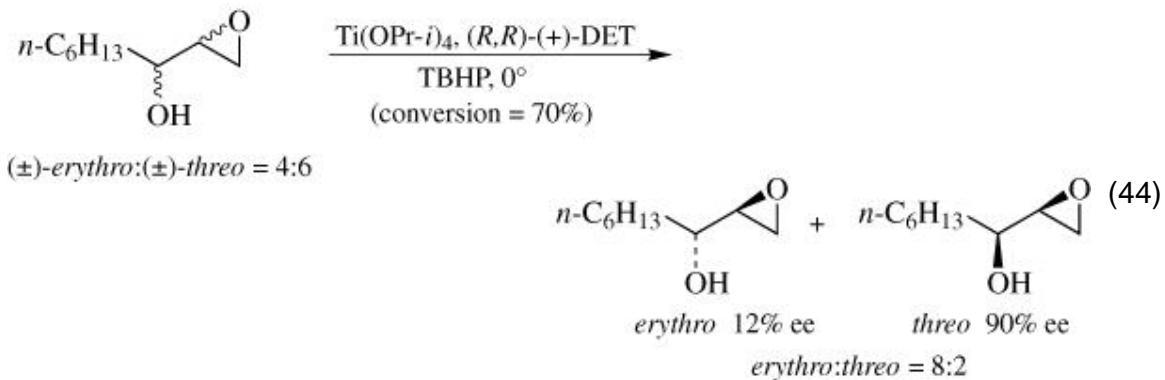
Lewis acidity, the titanium—tartrate system acts here as a catalyst for the ring opening reaction, promoting attack of some alcohols in the reaction mixture (isopropanol, allylic alcohol, epoxy alcohol, or TBHP). The resulting diol ethers are potent inhibitors of kinetic resolution because of their capacity to chelate strongly with the titanium atom, thereby reducing access of TBHP and the allylic alcohol to the metal. Although such ring-opening processes are attenuated at – 20°, they retain the potential (above all with slowly reacting substrates) to degrade both the diastereomeric ratio and the enantiomeric

purity. To minimize such problems, monitoring of the reaction mixture (GLC with an internal standard) is recommended.

Like all resolutions, this kinetic resolution is limited to a theoretical yield of 50% of one enantiomer from the racemic mixture. If an epoxy alcohol is converted to an allylic alcohol of the same absolute configuration as the unreacted enantiomer, a racemic allylic alcohol is converted to a single enantiomer with theoretically 100% yield. This conversion is effected by a combination of methanesulfonation and telluride reduction, though substrates are limited to terminal epoxides (Eq. 45). (199) The actual combined yields of allylic alcohol from both the kinetic resolution and telluride steps range from 75 to 88%.

(45)
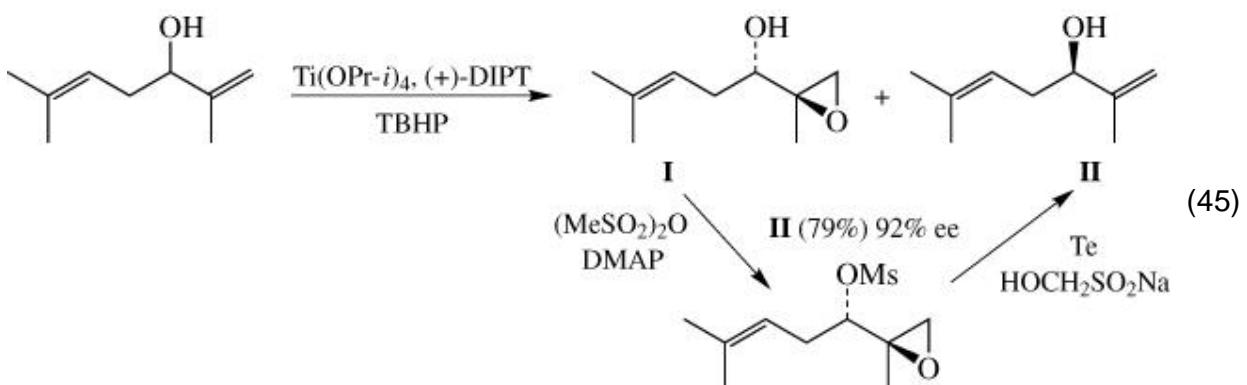
Kinetic resolution can be extended to other secondary carbinol systems in which a suitably oxidizable group is located in the allylic position. Thus 2-furyl and 2-thienyl carbinols can be resolved efficiently in both the stoichiometric and catalytic manner. (14, 15) The expected epoxy alcohol **79** is the precursor of the isolated oxidized materials **80**.
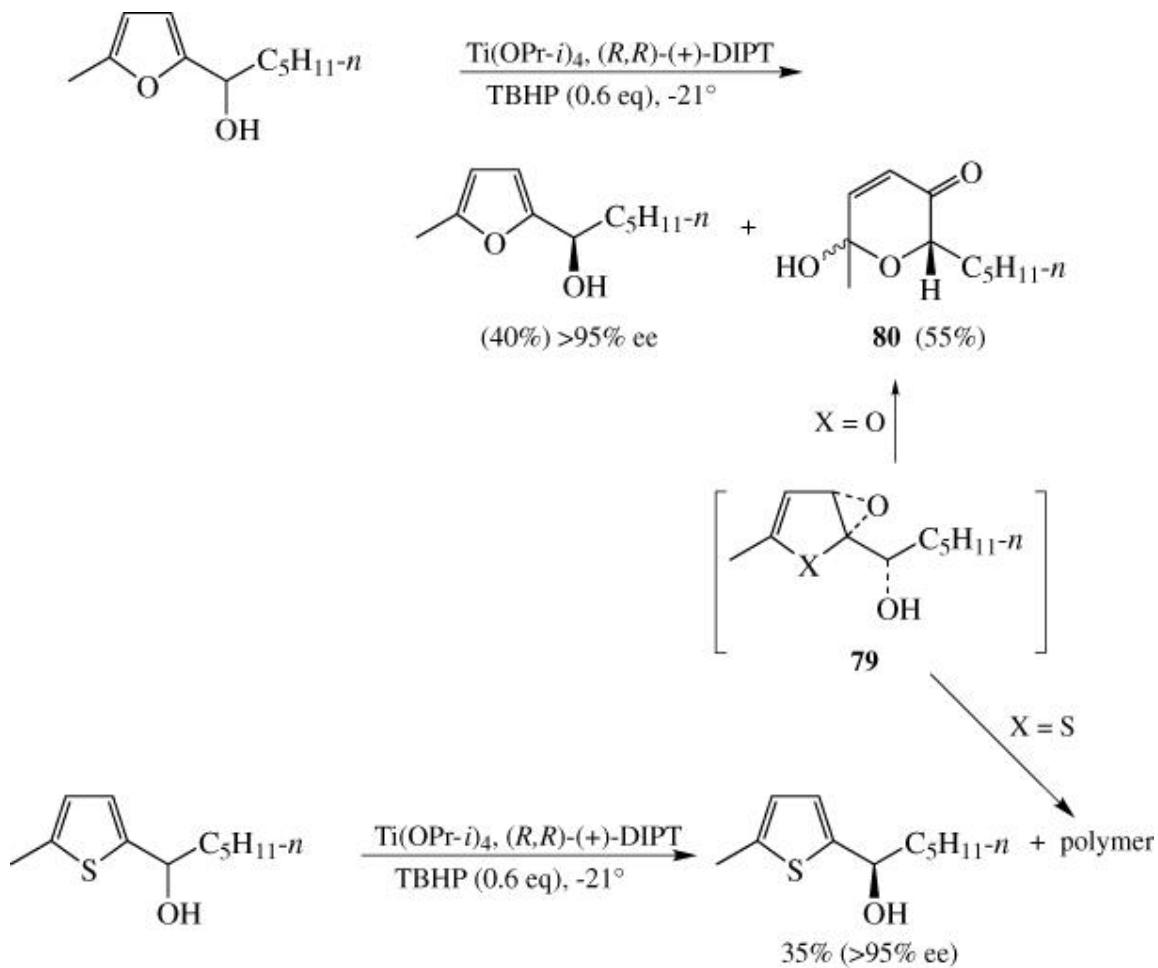
α -Furfuryl toluenesulfonamide is also resolved efficiently by using modified reaction conditions (Eq. 46), (200) although the stereochemistry is opposite to the empirical rule.

(46)
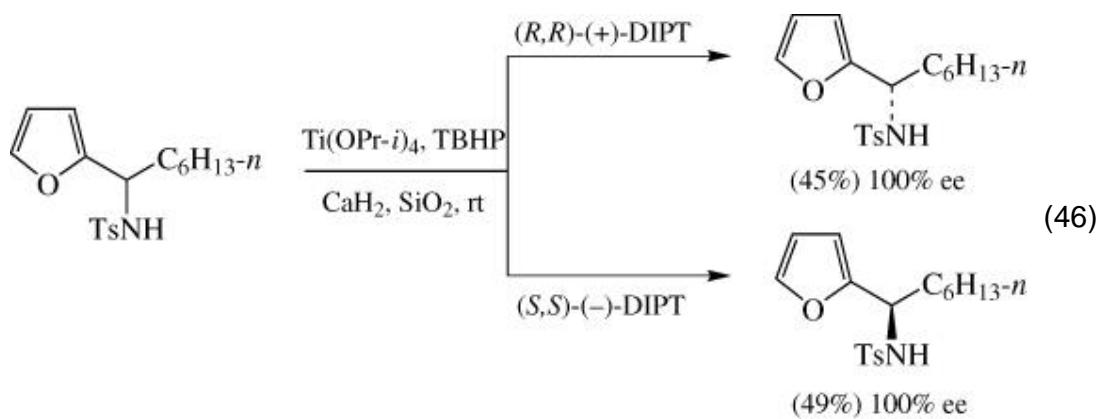
4.5. Asymmetric Oxidation of Sulfides, Selenides, and Amines

Titanium—tartrate complexes are also applicable to asymmetric oxidation of heteroatoms. Two procedures have been reported for oxidation of sulfides. (22-25) When methyl *p*-tolyl sulfide is used as a substrate, the standard procedure using Ti(OPr-*i*)$_4$, dialkyl tartrate, and TBHP (1:1:2) leads to a mixture of the racemic sulfoxide and the sulfone (Eq. 47). (22) Although increasing the tartrate/titanium tetraisopropoxide
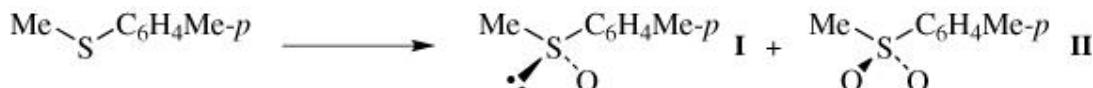
$$Ti(OPr\text{-}i)_4 : (R,R)\text{-}(+)\text{-}DIPT : TBHP = 1:1:2, \ \textbf{I} \ (41\%) \ 0\% \ ee \ + \ \textbf{II} \ (17\%)$$

$$Ti(OPr\text{-}i)_4 : (R,R)\text{-}(+)\text{-}DIPT : TBHP = 1:4:2, \ \textbf{I} \ (60\%) \ 88\% \ ee$$

$$Ti(OPr\text{-}i)_4 : (R,R)\text{-}(+)\text{-}DIPT : H_2O : TBHP = 1:2:1:1, \ \textbf{I} \ (90\%) \ 90\% \ ee$$

$$Ti(OPr\text{-}i)_4 : (R,R)\text{-}(+)\text{-}DET : H_2O : CHP = 1:2:1:1, \ \textbf{I} \ (90\%) \ 93\% \ ee$$

(47)

ratio improves the enantioselectivity, (24) a combination of titanium tetraisopropoxide/tartrate/water/hydroperoxide (1:2:1:1) further enhances both the chemical yield and enantioselectivity. (22, 23) Use of cumene hydroperoxide (CHP) instead of TBHP improves enantioselectivity. (25) Reaction enantioselectivity is also temperature dependent, and an optimal ee is obtained around – 21°. Functional groups such as allylic alcohols, isolated double bonds, amines, phenols, and alcohols are compatible with this reaction. (201-207) Although the role of water is not completely understood, it has been suggested that the water hydrolyzes a Ti-OPr-*i* bond with formation of a new μ -oxo bridge (Ti-O-Ti) between two dimeric species. (23)

Simple chiral selenoxides readily racemize through a tetracoordinated achiral hydrate. However, some selenides bearing bulky substituents are enantiomerically stable. Oxidation of selenide **81** with a modified titanium—tartrate system (2:4) system proceeds with moderate enantioselectivity. (26)
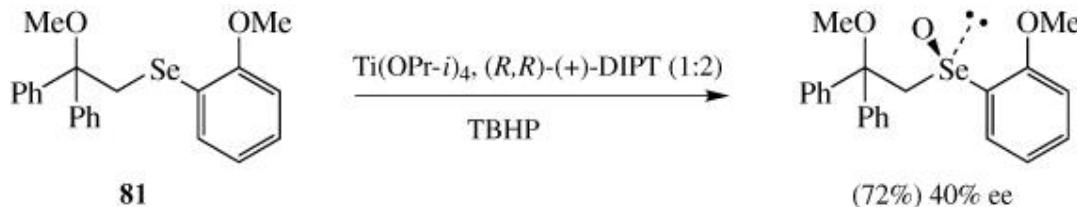
Racemic β -amino alcohols are efficiently resolved by using the complex with 2:1 [Ti(OPr-i)$_4$:tartrate] stoichiometry as a catalyst (Eq. 48), and the standard 2:2 catalyst is less effective. (20, 21, 139)

$$\text{(48)}$$

(37%) 95% ee   (59%) 63% ee
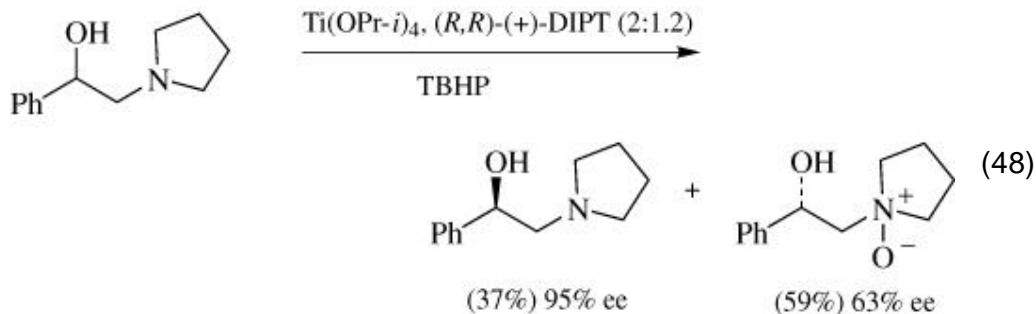
4.6. Synthetic Applications: Transformations of Epoxy Alcohols into Other Functional Units

The great utility of the titanium-mediated asymmetric epoxidation in organic synthesis is attributable to its enantioselectivity and to the numerous applications of epoxy alcohols as precursors to diversely functionalized compounds. However, since epoxy alcohols have three reactive sites (scheme 7), regio- and stereoselective reactions are essential for their use, and many studies have been directed toward developing regioselective transformations of epoxy alcohols. For convenience, these reactions are classified into three categories: (1) direct substitution reactions and other transformations of the hydroxy group at C-1; (2) rearrangement of 2,3-epoxy alcohols into 1,2-epoxy alcohols (Payne rearrangement) which undergo regioselective substitution at C-1; and (3) epoxide ring opening at C-2 or C-3.

scheme 7.
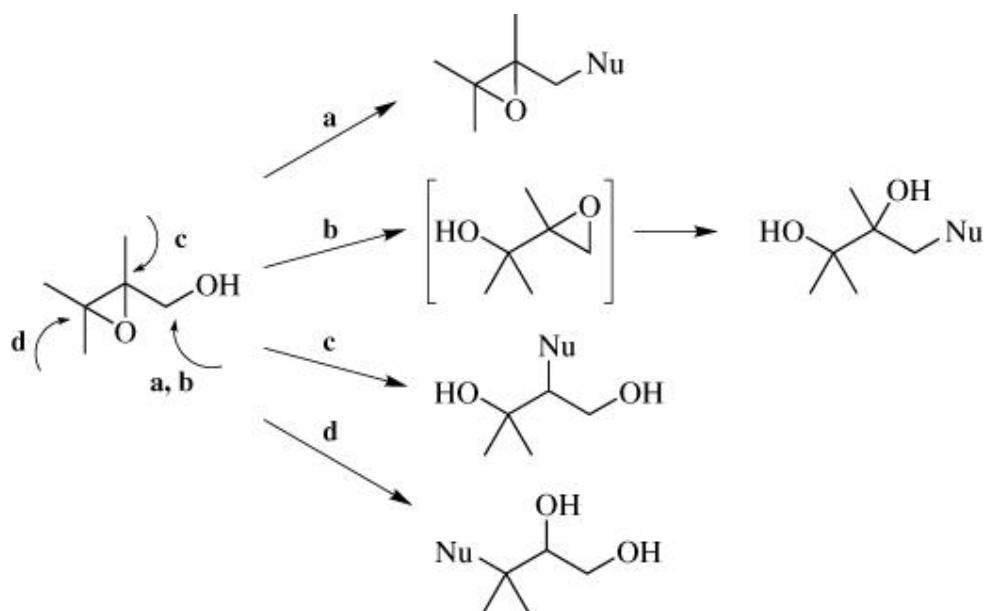
4.6.1. Transformations of the Hydroxy Group at C-1

Epoxy alcohols can be converted directly into the corresponding epoxy ethers by using Mitsunobu procedures. (208, 209) Activation of the hydroxy group as the corresponding mesylate or tosylate also provides a useful means of replacing it with various nucleophiles like organolithium and organocopper reagents (109, 110) and hydride sources. (1) For example, insect pheromones bearing an isolated epoxide, such as disparlure **83** and the saltmarsh caterpillar moth pheromone **85**, have been prepared enantiospecifically by the alkylation of epoxy tosylates **82** and **84**. (109, 110)

Alkynyl epoxides can be obtained by treatment of epoxy triflates with alkynyllithiums (Eq. 49). (210)

Treatment of epoxy tosylates with a telluride reagent gives allylic alcohols (Eq. 50). (211)

Reduction of epoxy tosylates with dibutylaluminum hydride provides 2-alkanols directly with high regioselectivity (>99:1) (Eq. 51). (212)

1. Ti(OPr-*i*)₄, (*R,R*)-(+)-DET,
   TBHP
2. DNBCl, C₅H₅N

3. K₂CO₃, MeOH
4. TsCl

82 (55%) 100% ee
(the intermediate dinitrobenzoate
was recrystallized.)

(*n*-C₉H₁₉)₂CuLi/ether

83

1. Ti(OPr-*i*)₄, (*R,R*)-(+)-DET,
   TBHP
2. DNBCl, C₅H₅N

3. K₂CO₃, MeOH
4. TsCl

84 (36%) 100% ee
(the intermediate dinitrobenzoate
was recrystallized.)

(*n*-C₁₀H₂₁)₂CuLi/ether

85

1. Tf₂O

2. MeCH(OLi)C≡CLi

(49)

Te, HOCH₂SO₂Na

NaOH

(66%)

(50)

1. Ti(OPr-i)$_4$, (R,R)-(+)-DET,
   TBHP
2. DNBCl, C$_5$H$_5$N

3. K$_2$CO$_3$, MeOH
4. TsCl

82 (55%) 100% ee
(the intermediate dinitrobenzoate
was recrystallized.)

OTs

(*n*-C$_9$H$_{19}$)$_2$CuLi/ether

83

1. Ti(OPr-i)$_4$, (R,R)-(+)-DET,
   TBHP
2. DNBCl, C$_5$H$_5$N

3. K$_2$CO$_3$, MeOH
4. TsCl

84 (36%) 100% ee
(the intermediate dinitrobenzoate
was recrystallized.)

OTs

(*n*-C$_{10}$H$_{21}$)$_2$CuLi/ether

85

OH

1. Tf$_2$O

2. MeCH(OLi)C≡CLi

C≡C

OH

(49)

OTs

Te, HOCH$_2$SO$_2$Na

NaOH

OH

(66%)

(50)

$$n\text{-}C_{10}H_{21}\text{—}\overset{O}{\triangle}\text{—OTs} \quad \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{DIBAH, }0°} \quad n\text{-}C_{10}H_{21}\overset{\ \ \ }{\underset{\text{OH}}{\bigvee}} \quad (98\%) \quad (51)$$

Epoxy mesylates and tosylates can be converted further into epoxy halides, (1, 213, 214) which also undergo several useful reactions. (215-217) For example, treatment of epoxy bromide **86** with (diisopropoxymethylsilyl)methyl-magnesium chloride

1. Ti(OPr-i)$_4$, (R,R)-(+)-DET, TBHP
2. MsCl
3. NaBr

86

1. (i-PrO)$_2$SiCH$_2$MgCl (Me)
2. H$_2$O$_2$

87 (38%)
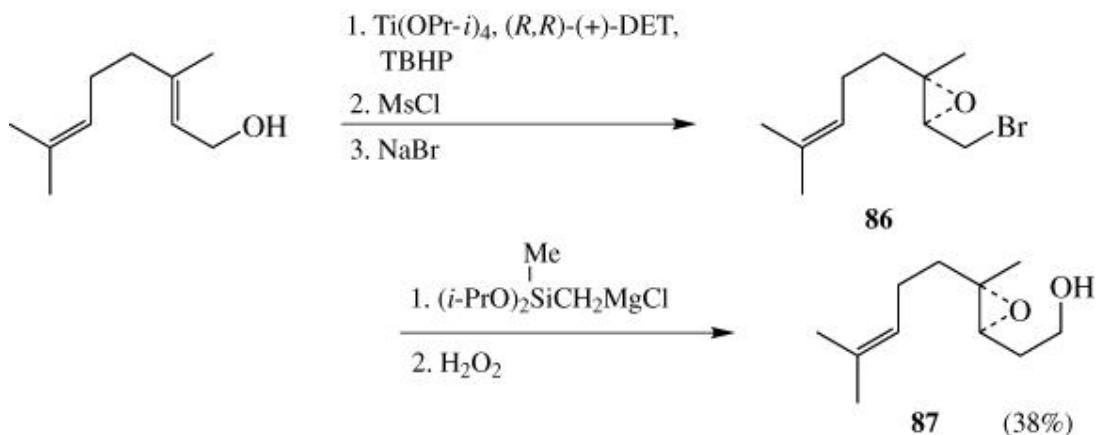
followed by hydrogen peroxide oxidation gives the 3,4-epoxy alcohol **87**. (218) This sequence is a useful alternative to asymmetric epoxidation of the corresponding homoallylic alcohol because only moderate enantioselectivity is usually observed in asymmetric epoxidations of homoallylic alcohols. (176) Epoxy iodides can also be extended by two carbons by treatment with the lithium enolate of *tert*-butyl acetate to give the γ , δ -epoxy esters (Eq. 52). (76)

1. TsCl, C$_5$H$_5$N
2. NaI
3. $\overset{\text{OLi}}{\underset{\text{OBu-}t}{=}}$

(52)
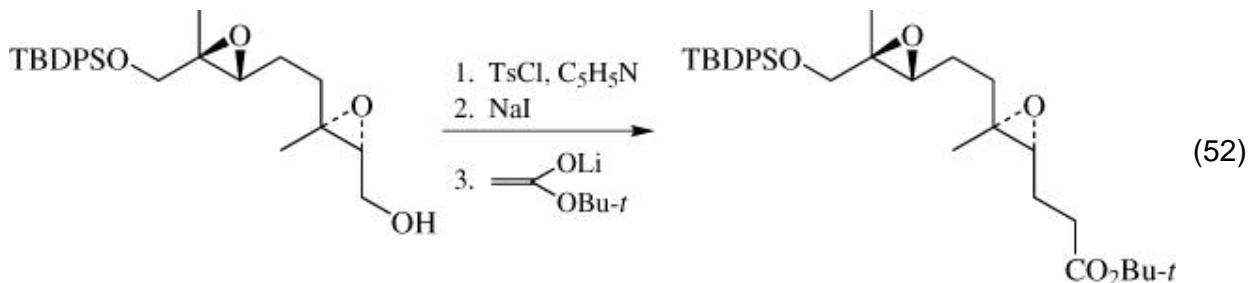
The reactions of epoxy iodides with vinylmagnesium bromide—cuprous iodide provide allylic alcohols, but ordinary substitution products can be obtained when vinylmagnesium bromide is added to a solution of an epoxy iodide in the presence of hexamethylphosphoric triamide (Eq. 53). (219, 220) Treatment of epoxy iodides with *tert*-butyllithium also gives allylic alcohols. (221)

(53)
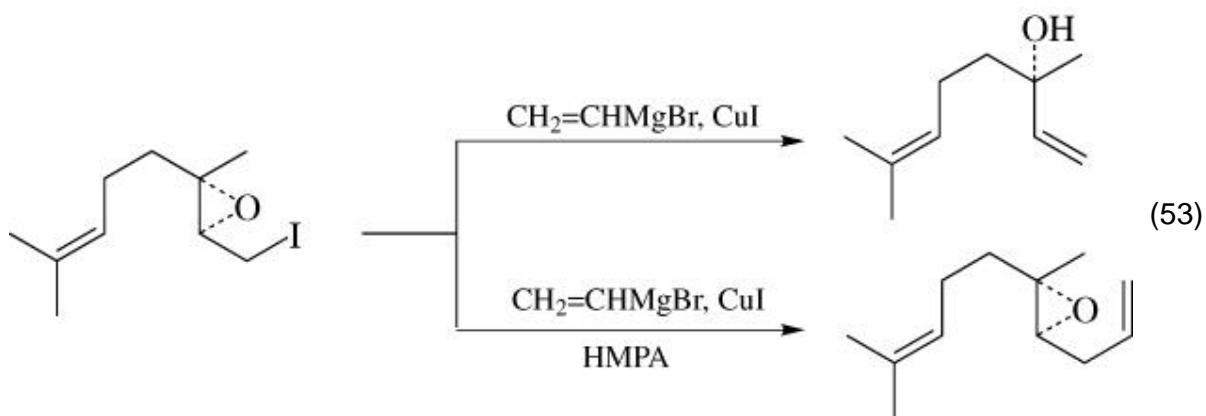
Transformations of epoxy halides to allylic alcohols can also be effected by treatment with zinc—acetic acid or $Bu_3SnAlEt_2$ (Eq. 54). (213, 214, 222)

(54)

(−)-nerolidol
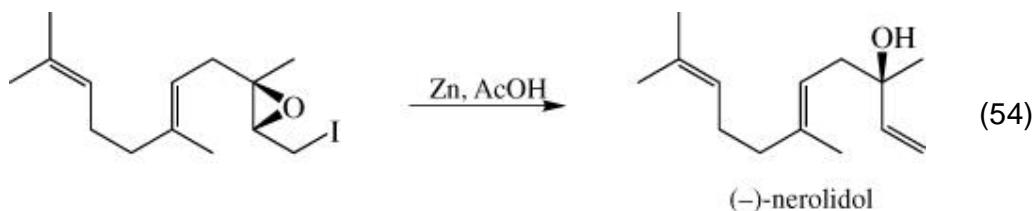
Direct transformation of epoxy alcohols to allylic alcohols is effected by treatment with bis(cyclopentadienyl)titanium chloride (Eq. 55). (223)

(88%) (55)
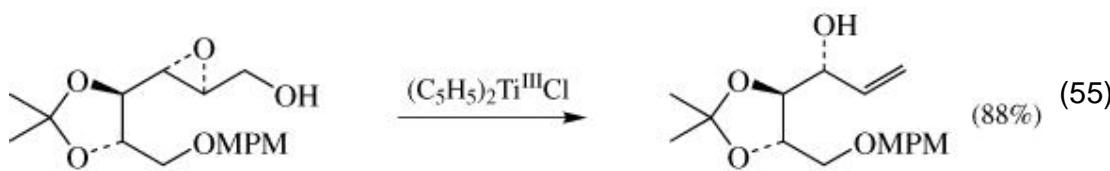
Treatment of epoxy alcohols with triphenylphosphine—carbon tetrachloride gives epoxy chlorides, which are converted into propargylic alcohols by further treatment with 3 equivalents of an alkyllithium or lithium diisopropylamide (Eq. 56). (224, 225) On the other hand, treatment with 1 equivalent of lithium amide or

(56)
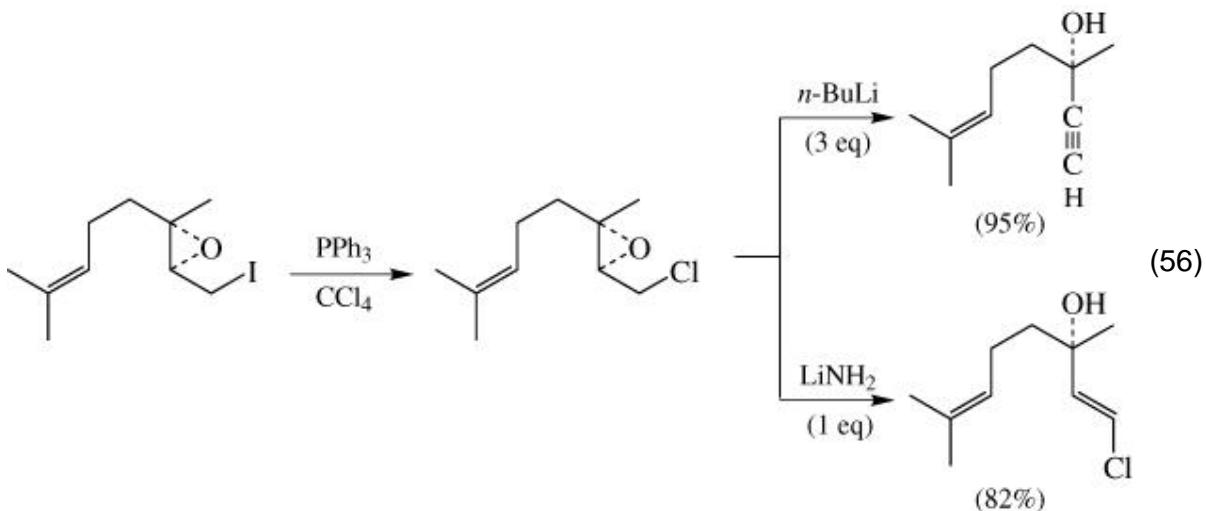
lithium diisopropylamide gives vinyl chlorides. However, use of 1 equivalent of an alkyllithium instead of lithium amide gives a mixture of propargylic alcohol and vinyl chloride. (226-228)

Epoxy alcohols can be oxidized without epimerization to epoxy aldehydes by various procedures such as Swern, Collins, and Mukaiyama oxidations. (229-232) Epoxy aldehydes can be further converted to vinyl epoxides by Wittig olefination. (233) For example, oxidation of epoxy alcohols **88** with Collins reagent followed by Wittig olefination provides vinyl epoxide **89**, hydrogenation of which gives (–)-disparlure **83**. (59)
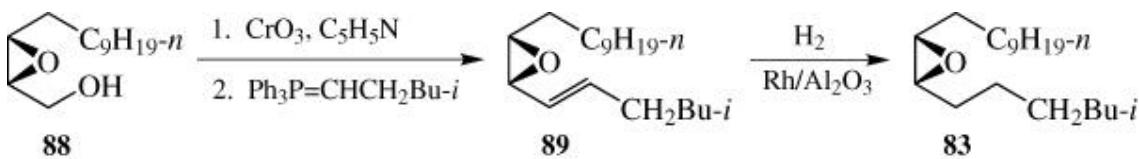
Addition of LiCuMe$_2$ to epoxy allyl alcohol **90** proceeds in an *anti* S$_{N2'}$ manner to give an *E* allylic alcohol predominantly. (234-238)

90

R = Me₂C=CH(CH₂)₂
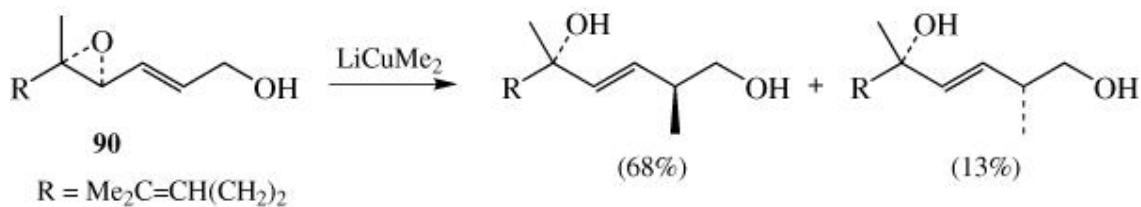
Wittig product **91** is reduced regioselectively by diisobutylaluminum hydride, (85-87) samarium iodide, (239) or [tris(dibenzylideneacetone)-chloroform]-dipalladium-PBu₃-HCO₂H (240) to give the δ -hydroxy allylic alcohol, δ -hydroxy- β , γ -unsaturated ester, and δ -hydroxy- α, β -unsaturated ester, respectively.
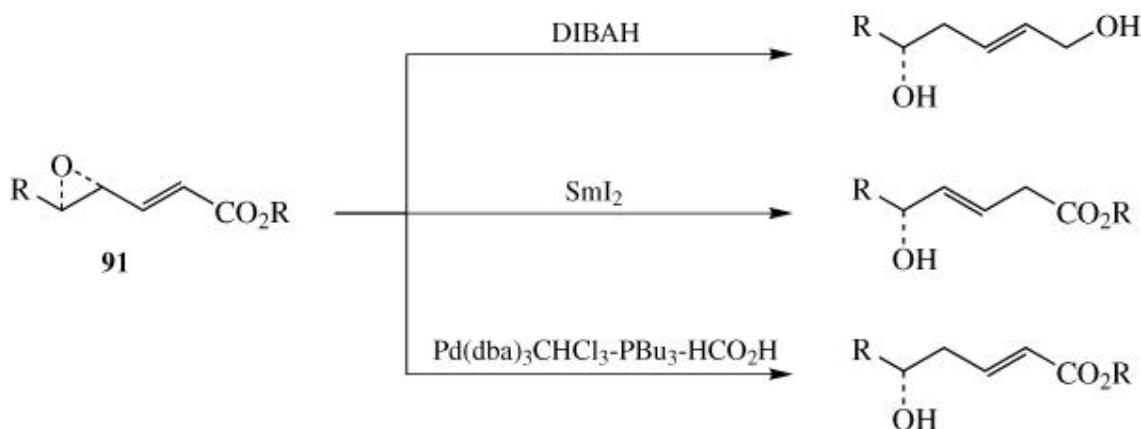
Repetition of a sequence of asymmetric epoxidation, oxidation, Wittig olefination, and DIBAH reduction provides easy access to 1,3,5-polyols (scheme 8). (85)

scheme 8.
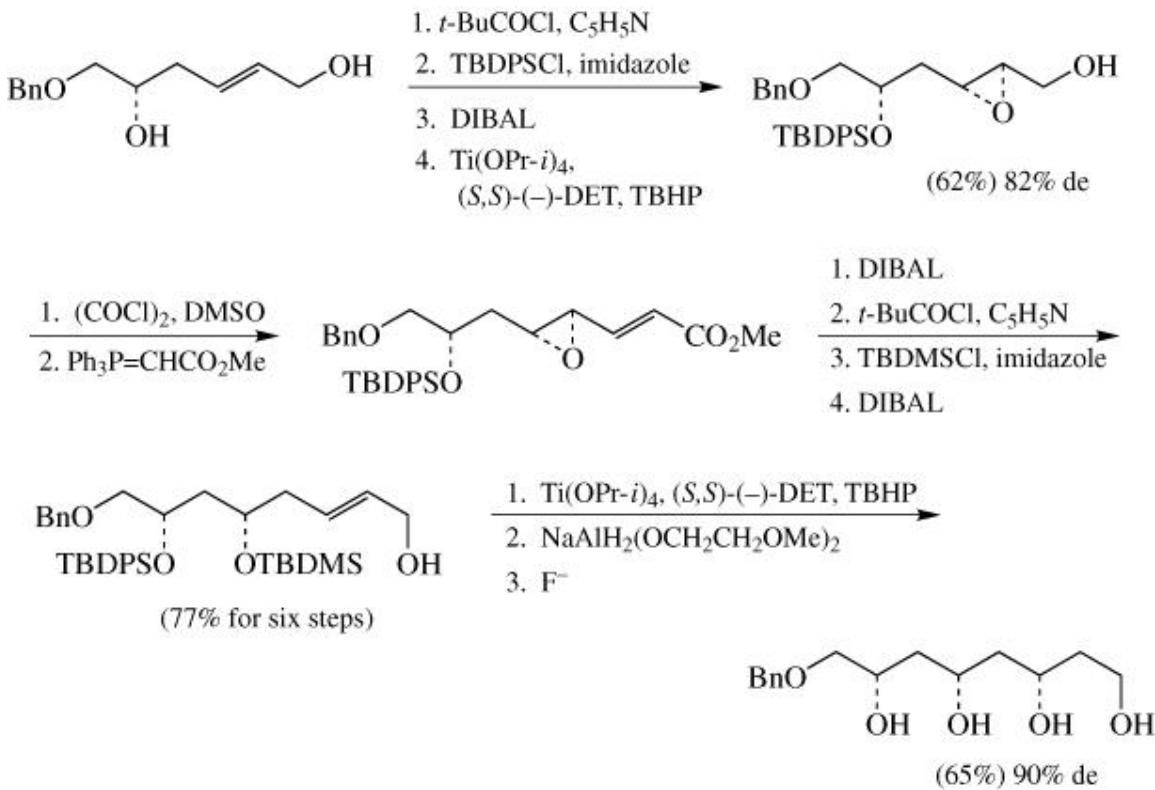
On the other hand, unsaturated epoxide **92** is converted into carbonate **93** or carbamate **94** with retention of epoxide configuration by respective treatment with carbon dioxide or phenyl isocyanate in the presence of a Pd(0) catalyst. (241-243)

Both *endo*- and *exo*-brevicomins can be synthesized from the same epoxy tosylate **95** by the choice of appropriate epoxide-opening methodology. (244)

The [3 + 3] annulation reaction of epoxy aldehydes with 3-iodo-2-[(trimethylsilyl)methyl]propene in the presence of tin(II) fluoride provides cyclohexanediols in a single step with high stereoselectivity (Eq. 57). (245)
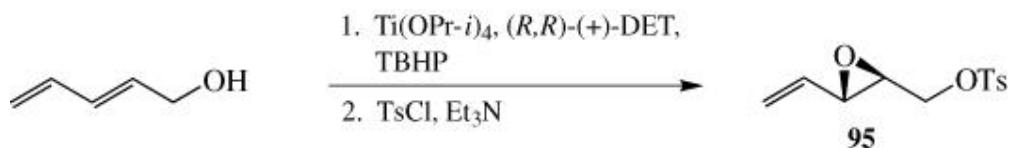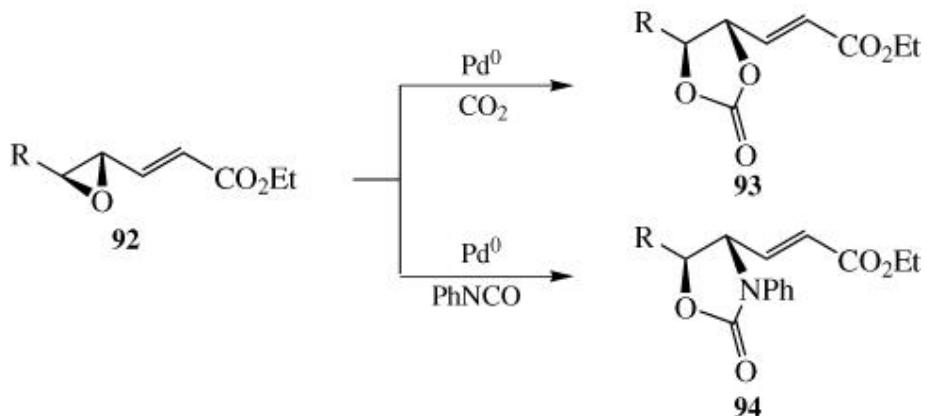
Reaction of Grignard reagents with β -trimethylsilyl- α , β -epoxyketones, which are readily available by kinetic resolution of *dl*- β -trimethylsilylvinyl carbinol and subsequent Swern oxidation, gives γ -trimethylsilyl- β , γ -epoxy alcohols with high diastereoselectivity (Eq. 58). (246) The asymmetric allylboration of (*R,R*)-epoxy

AlCl₃, acetone →

95

OTs

PhSO₂ (ketone structure)

PPA

PhSO₂ OTs

1. NaH
2. Na/Hg

endo-brevicomin

1. Pd⁰, CO₂
2. MeOH, HCl
3. Me₂C(OMe)₂

OTs

PhSO₂ (dioxolane structure)

NaH

PhSO₂

1. Na/Hg
2. H₃O⁺

exo-brevicomin

(epoxide)CHO + (I—CH₂—C(=CH₂)—CH₂—SiMe₃)

SnF₂

OH
OH

(57)

TMS / Bu-*n* / OH

Ti(OPr-*i*)₄
(*R,R*)-(+)-DIPT

TMS (epoxide) Bu-*n* OH

DMSO
(COCl)₂

(58)

TMS (epoxide) Bu-*n* O

EtMgBr

TMS (epoxide) Bu-*n* OH
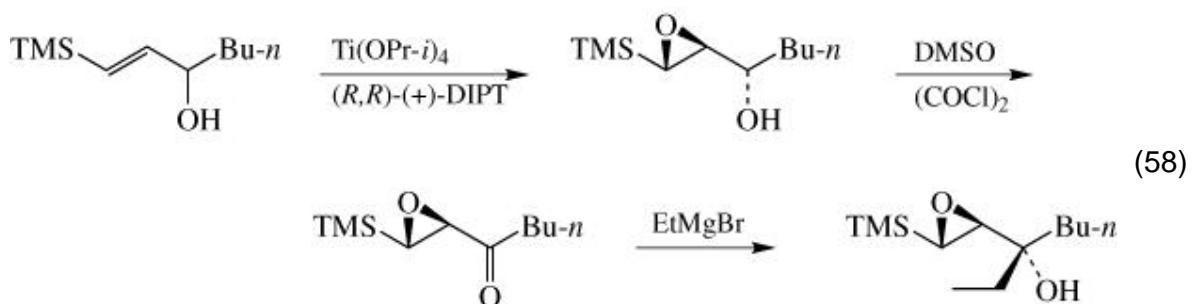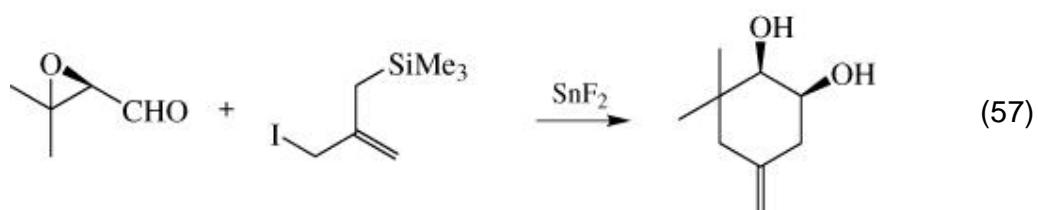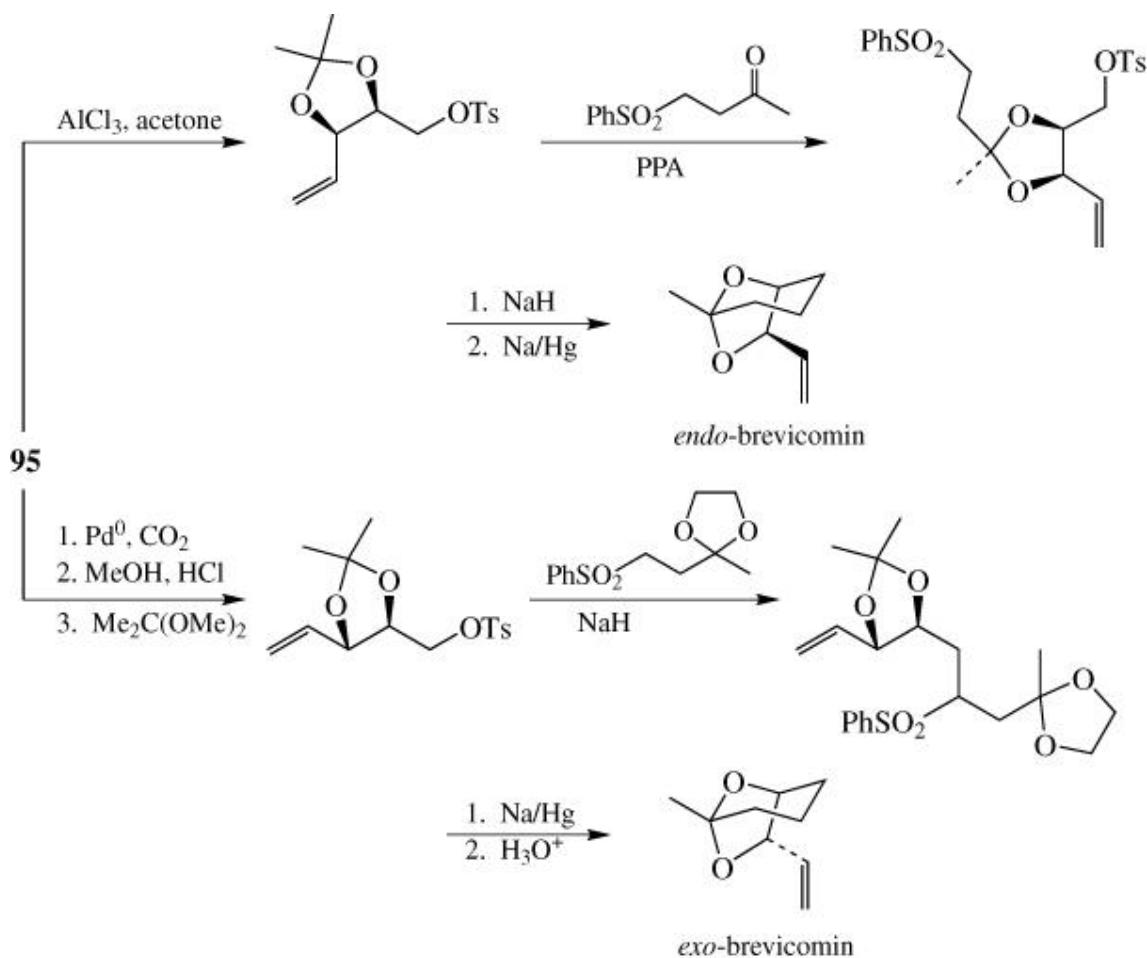
aldehydes with optically active (*S,S*)-(–)-diethyl tartrate as a chiral source provides *erythro* epoxy alcohols exclusively (Eq. 59). (247)

(59)
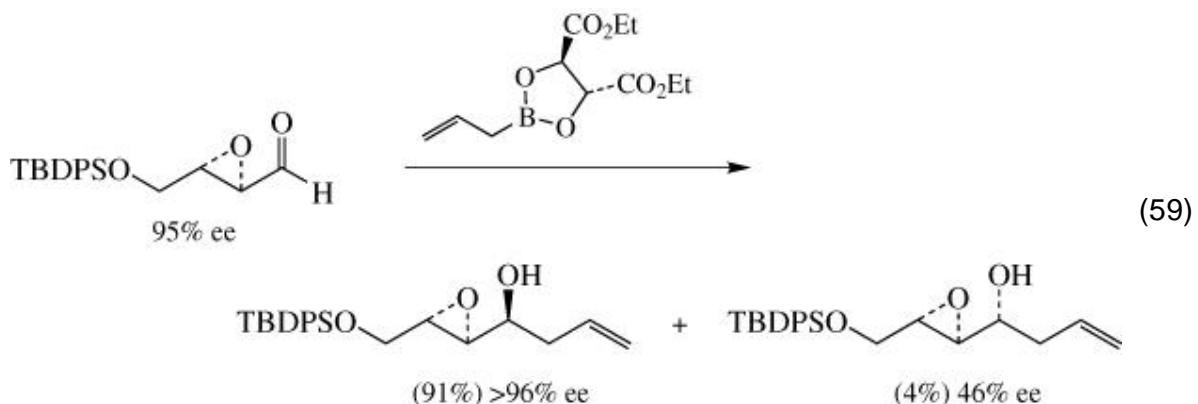
Reduction of epoxy ketones by sodium borohydride—diphenyl diselenide (248, 249) or samarium iodide (250, 251) provides β -hydroxy ketones regioselectively (Eq. 60).

(60)
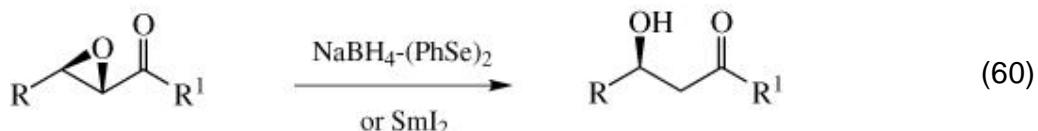
Epoxy aldehydes can be used as chiral sources in imine—ketene cycloadditions, which provide *cis*-substituted 3-amino-4-alkylazetidinones of high enantiomeric purity (Eq. 61). (252)

(61)
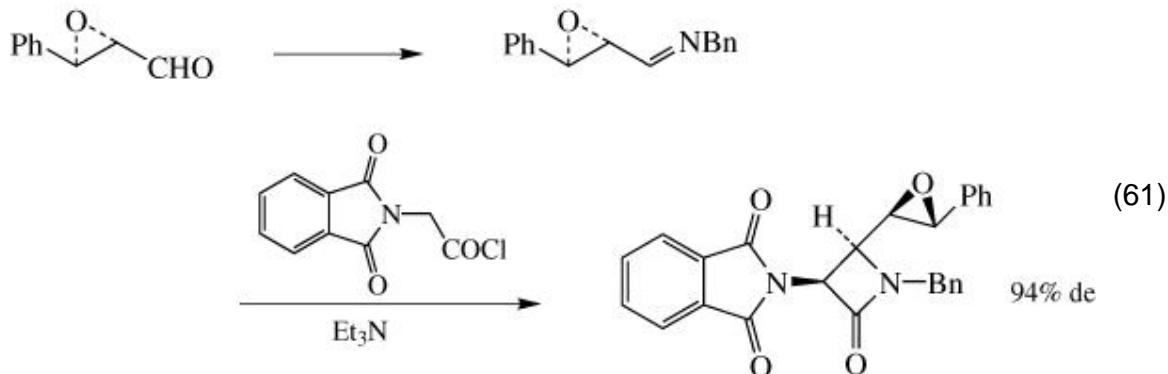
Epoxy alcohols can be oxidized directly without epimerization to epoxy acids by ruthenium tetroxide or potassium permanganate (Eq. 62). (253-255)

$$R \diagdown\!\!\!\diagup OH \xrightarrow[\text{2. RuCl}_3 - \text{H}_5\text{IO}_6]{\substack{\text{1. Ti(OPr-}i)_4, (S,S)\text{-(–)-DET,} \\ \text{TBHP}}} R \overset{O}{\triangle} CO_2H \quad (62)$$

(75~95%)
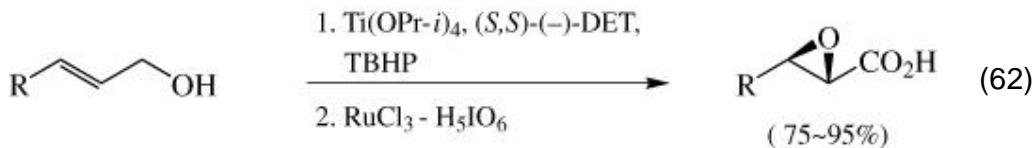
Epoxy acids can be further converted into γ -hydroxy- α , β - unsaturated esters via epoxy diazomethyl ketones (Eq. 63). (256, 257)

$$R \overset{O}{\triangle} CO_2H \xrightarrow[\text{2. CH}_2\text{N}_2]{\text{1. }i\text{-BuOCOCl}} R \overset{O}{\triangle}\overset{O}{\underset{\text{CHN}_2}{\|}} \xrightarrow[\text{EtOH}]{h\nu} R \overset{OH}{\underset{}{|}} \diagdown\!\!\!\diagup CO_2Et \quad (63)$$

(70%)   (53%)
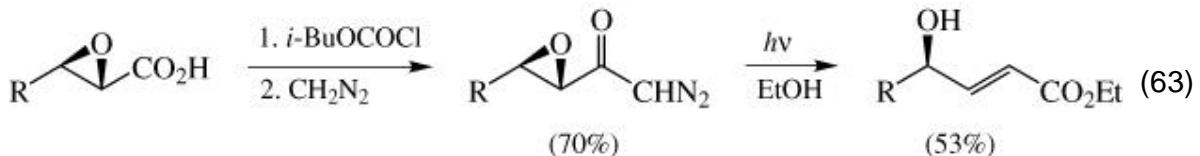
4.6.2. Payne Rearrangement–Epoxide-Opening Sequence

2,3-Epoxy alcohols are rapidly equilibrated with 1,2-epoxy alcohols under alkaline conditions (Payne rearrangement). (258) The equilibrium ratio of 1,2- to 2,3-epoxy alcohols is remarkably dependent on the substrate. However, as a 1,2-epoxide is considerably more reactive than a 2,3-epoxide, treatment of the equilibrium mixture with a nucleophile provides preferentially the product from the 1,2-epoxide (Eq. 64). (258, 259)

$$R \overset{O}{\triangle}\diagdown OH \rightleftharpoons R \overset{OH}{\underset{}{|}}\diagup\overset{O}{\triangle} \xrightarrow{\text{Nu}} R \overset{OH}{\underset{}{|}}\diagdown\overset{}{\underset{\text{OH}}{|}} Nu \quad (64)$$
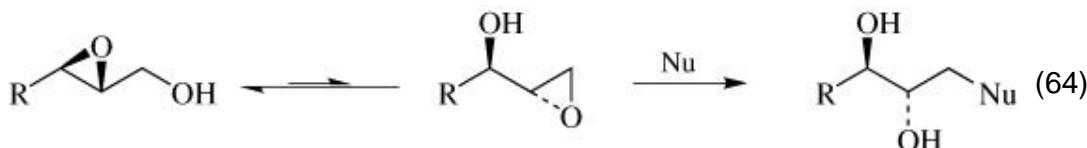
Thus the Payne rearrangement—epoxide-opening sequence is a useful alternative for activating C-1 for substitution, (7, 73, 260, 261) although this provides 2,3-diols while direct C-1 substitution provides 2,3-epoxides. For example, the Payne rearrangement—epoxide-opening sequence using phenylthiolate as the nucleophile has permitted the straightforward synthesis of sugars via iterative asymmetric epoxidation cycles (scheme 9). (73, 74) Other nucleophiles including OH^-, (73, 145, 148) BH_4^-, (145, 259) $TsHN^-$, (145) CN^-, (260, 262) N_3^-, (261, 263) and R_2NH (259) have also been used

successfully in Eq. 64.

scheme 9.
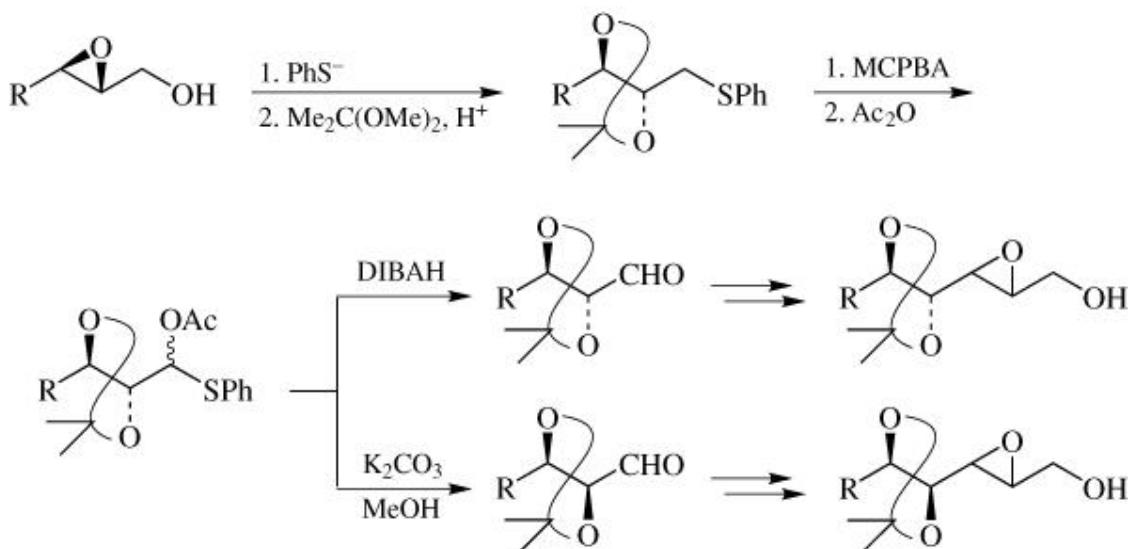
Use of the Payne rearrangement provides an easy approach to unstable vinyl epoxy alcohol **96**, which can be obtained in only moderate yield via the direct asymmetric epoxidation even under catalytic conditions. Epoxidation of 1,4-pentadien-3-ol (**97**) followed by Payne rearrangement gives **96** in good yield. (264-273) Another advantage of this procedure is that epoxidation of **97** gives **98** (and hence **96**) with extremely high enantiomeric purity. (274-280)

The major limitation of this Payne rearrangement—epoxide-opening strategy is that most organometallic reagents are not compatible with the aqueous conditions
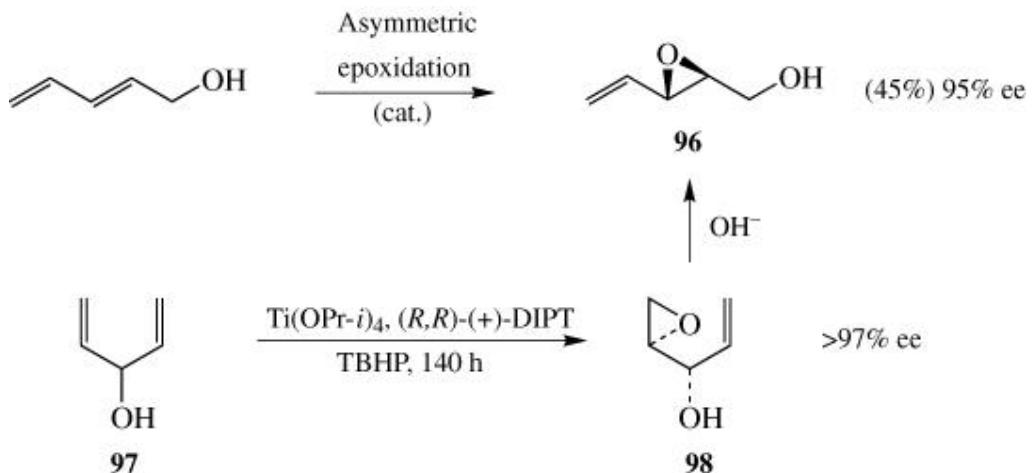
that are essential for the Payne rearrangement. This limitation can be overcome by isolating the 1,2-epoxy alcohols and then treating them with organometallic nucleophiles under nonaqueous conditions. (261, 281)

However, the equilibrium in the Payne reaction usually favors the 2,3-epoxy alcohols. Thus procedures for the synthesis of 1,2-epoxy alcohols have been developed. (261, 282, 283) For example, enantiomeric *erythro* 1,2-epoxy alcohols **99** and **100** can be derived
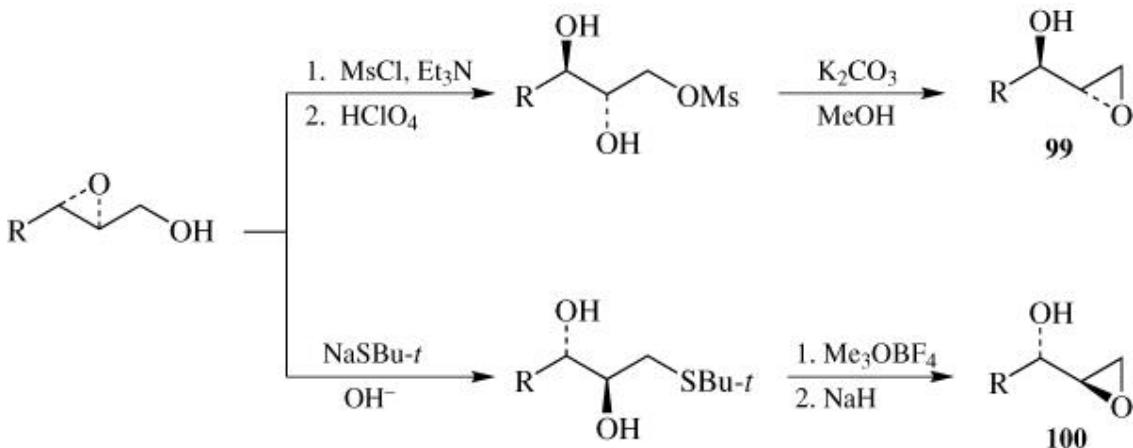
stereoselectively from common 2,3-epoxy alcohols via dihydroxy mesylate and dihydroxy sulfide intermediates, respectively. (259, 261) These *erythro* epoxides can be converted further to the *threo* 1,2-epoxides by the Mitsunobu reaction (Eq. 65). (208) The 1,2-epoxides thus obtained undergo nucleophilic epoxide opening at the terminal carbon. (259, 282)

(65)
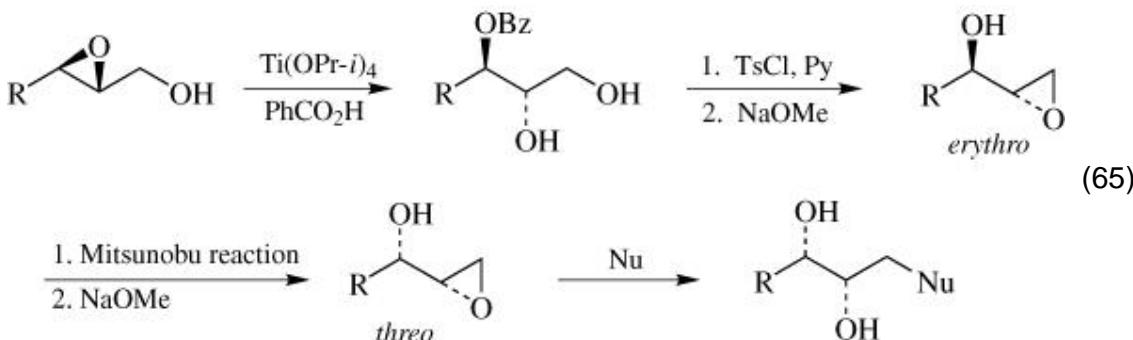
Recently it has been found that lithium chloride catalyzes the Payne rearrangement in tetrahydrofuran (Eq. 66). (284, 285) This enables the use of organometallic reagents like RCu or LiCuCNR as nucleophiles. However, the more reactive LiCuR$_2$ species react predominantly with the unrearranged 2,3-epoxide.

$$(66)$$
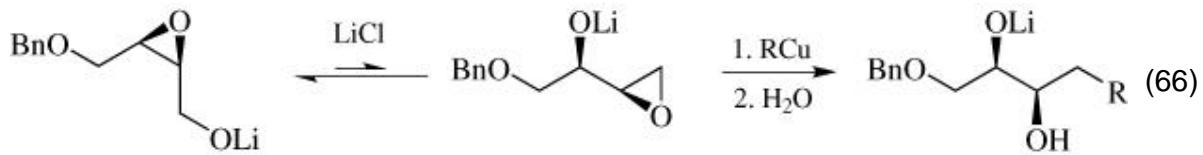
Treatment of epoxy alcohol with alkyllithium in the presence of boron trifluoride etherate gives a mixture of 1,2- and 1,3-diols (Eq. 67). (286, 287)

$$(67)$$
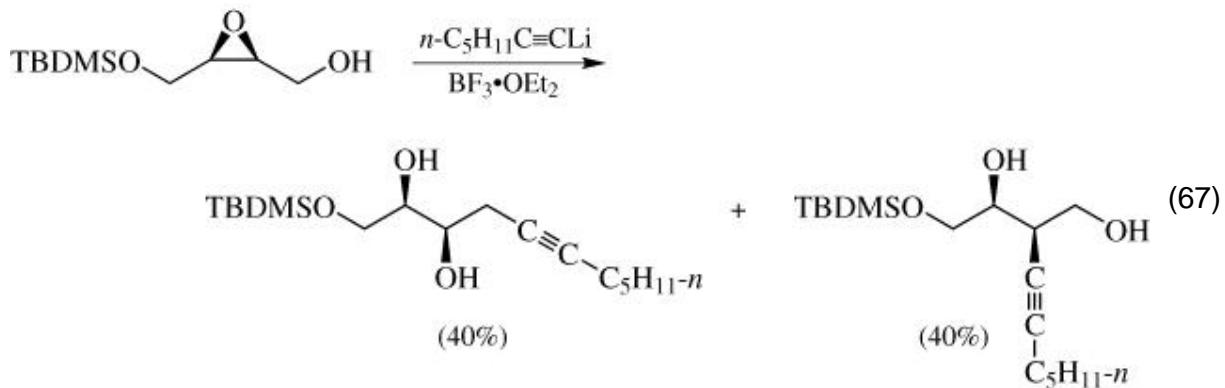
4.6.3. Epoxide Ring Opening at C-2 or C-3

Although the regio- and stereo-chemistry in epoxide-opening reactions of 2,3-epoxy alcohols depend on the steric and electronic factors in the substrates and on reaction conditions, the following general features are noted. Nucleophilic substitution under neutral and basic conditions occurs preferentially from the less-substituted side in an S_N2 manner, where the configuration of the attacked carbon is inverted. (7, 288, 289) Nucleophilic attack under acidic conditions occurs at the more-substituted side, also in an S_N2 manner. (7, 290) With sterically unbiased epoxy alcohols or their O-protected derivatives, epoxide opening with nucleophiles occurs preferentially at C-3 (Eq. 68). (7, 261, 291) This regioselectivity is attributed to the presence of the electro-negative

$$(68)$$
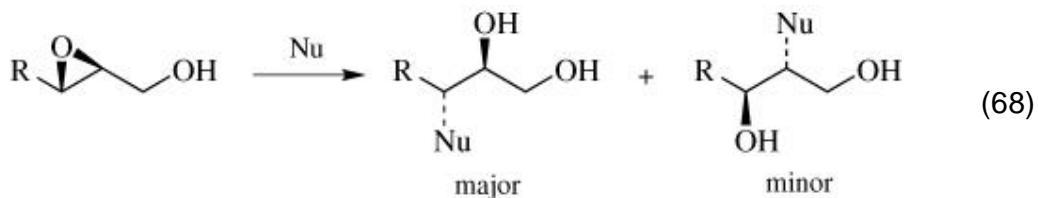
hydroxy group at C-1, (7, 261) which retards S_N2 substitution at the vicinal carbon.

The presence of an acetal group at C-1 also promotes epoxide opening at C-3 to give a 2-hydroxy acetal selectively (Eq. 69). (7, 261) The substituent at C-4, however,

$$\text{Nu} = \text{H}^-, \text{N}_3{}^-, \text{PhS}^-, \text{Me}^- \tag{69}$$
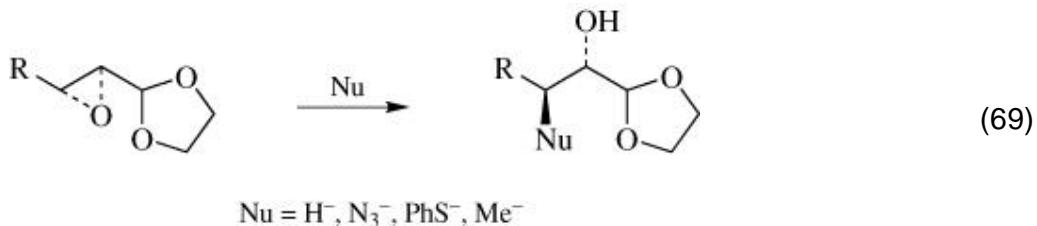
lowers selectivity for C-3 attack by differing degrees, depending on its size and electron-withdrawing ability. (7, 261)

Selectivity for nucleophilic opening at C-3 is greatly enhanced by the use of appropriate organometallic reagents. Alkyl, aryl, and alkynyl groups (292-295) as well as hydride (123, 292) can be introduced regioselectively at C-3 by using aluminum reagents (Eq. 70). The azide group is also introduced regioselectively

(70)
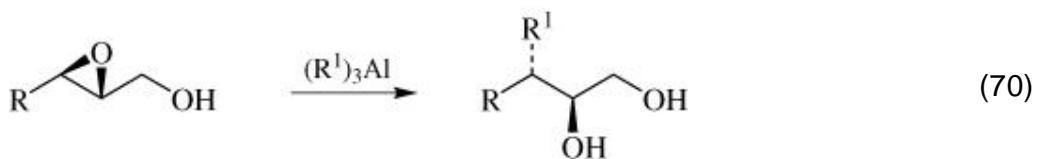
(98:2) with trimethylsilyl azide—diethylaluminum fluoride to give 3-azido diols (Eq. 71), (296) while reaction with sodium azide—ammonium chloride exhibits only modest C-3 selectivity. (261)

(71)
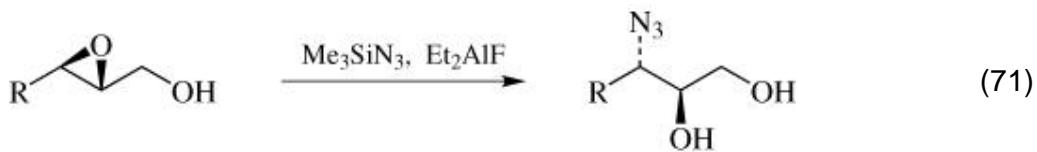
Treatment of epoxy alcohol **101** with trimethylaluminum, however, leads to the formation of a complicated mixture. With such a substrate, the sequence involving

101

1. Ph₃CCl, Py
2. LiCuMe₂

TsOH, MeOH, H₂O

(80%)   +   (14%)
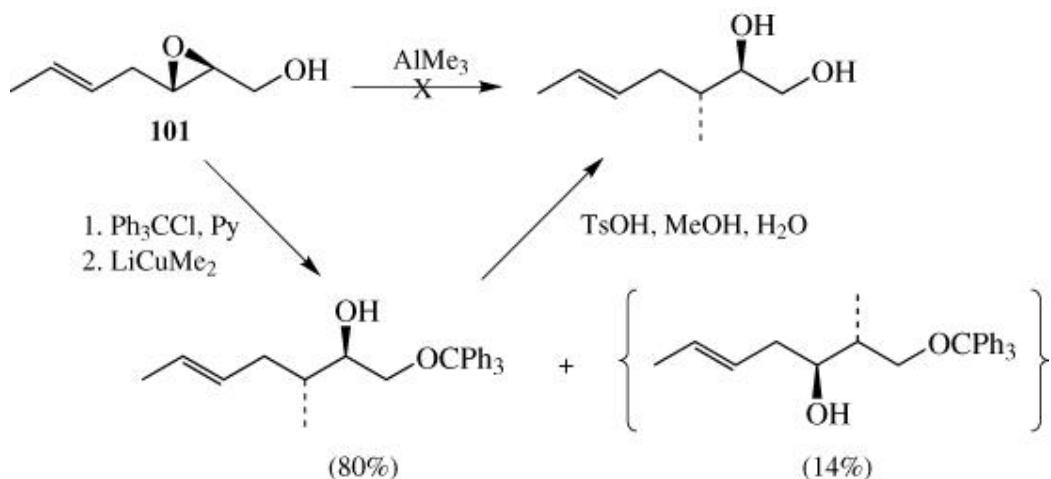
hydroxy protection as a trityl ether, alkylation with lithium dialkylcuprate, and deprotection is an effective alternative. (297-299) Although alkylative epoxide-opening with trialkylaluminum usually occurs in an S_N2 manner, reaction of 3-*p*-tolylglycidol (**102**) with trimethylaluminum proceeds with retention of the configuration to give **103**. Treatment of **102** with lithium dimethylcuprate gives the usual S_N2 reaction product **104**. (300)

102

AlMe₃

103

LiCuMe₂

104
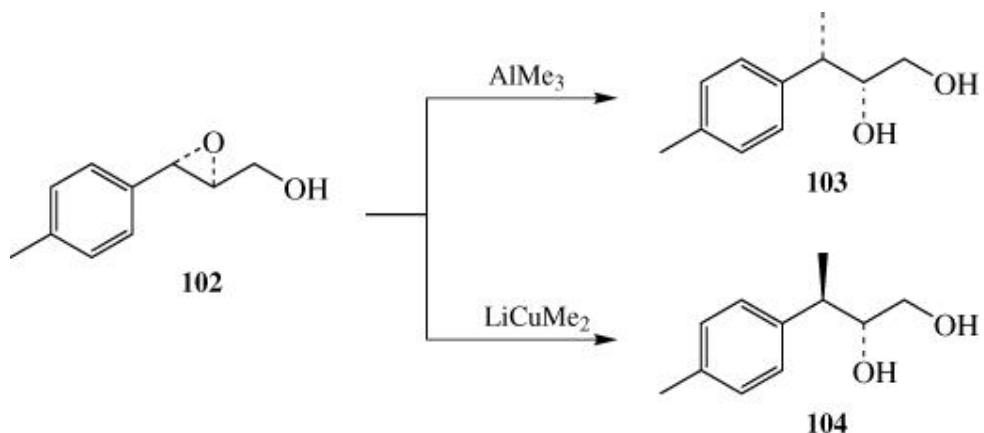
The formation of chelates of epoxy alcohols with metal ions also enhances C-3 selectivity in the nucleophilic opening as well as the reactivity of the substrate, especially when titanium tetraalkoxide is used as a mediator. (301) For example, the reaction of (2*S*, 3*S*)-epoxyhexan-l-ol with diethylamine in the presence of Ti(OPr-*i*)₄ proceeds to completion at room temperature, although the same reaction in the absence of Ti(OPr-*i*)₄ is sluggish even under reflux conditions (Eq. 72).
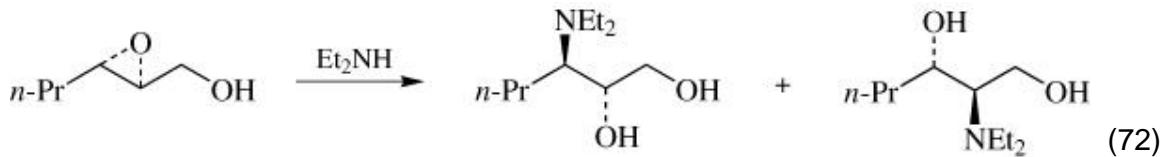
$$\text{Et}_2\text{NH (xs), reflux; (4\%) } 3.7:1$$
$$\text{Et}_2\text{NH (xs), Ti(OPr-}i)_4\text{, rt; (90\%) } 20:1$$

In the presence of Ti(OPr-i)$_4$, nucleophiles such as dialkylamines, (301) monoalkylamines, (301, 302) alcohols, (301) borohydrides, (303) and carboxylic acids (301, 304) also exhibit high C-3 selectivity (>100:1), while nucleophiles like thiols, (301) azides, (301) chlorides, (301, 305) bromides, (305) and cyanides (301) show moderate levels of C3-selectivity (5–15:1). For ring openings with azides, use of Ti(OPr-i)$_2$(N$_3$)$_2$ instead of Ti(OPr-i)$_4$ and NaN$_3$ is recommended. (306) C3-Selective halohydrin formation is also effected by the use of Ti(OPr-i)$_4$-halogen(Br$_2$,I$_2$), (307) TiCl$_4$-lithium halide, (308) or ClBH$_2$·SMe$_2$. (309) When the nucleophiles are chlorides, thiocyanides, or thiols, C3-selective opening is also promoted by tetrakis(triphenyl-phosphine) palladium. (310)

Treatment of 2,3-epoxy alcohols with lithium iodide at 70° affords *threo*-1-iodo-2,3-diols (Eq. 73). (311)
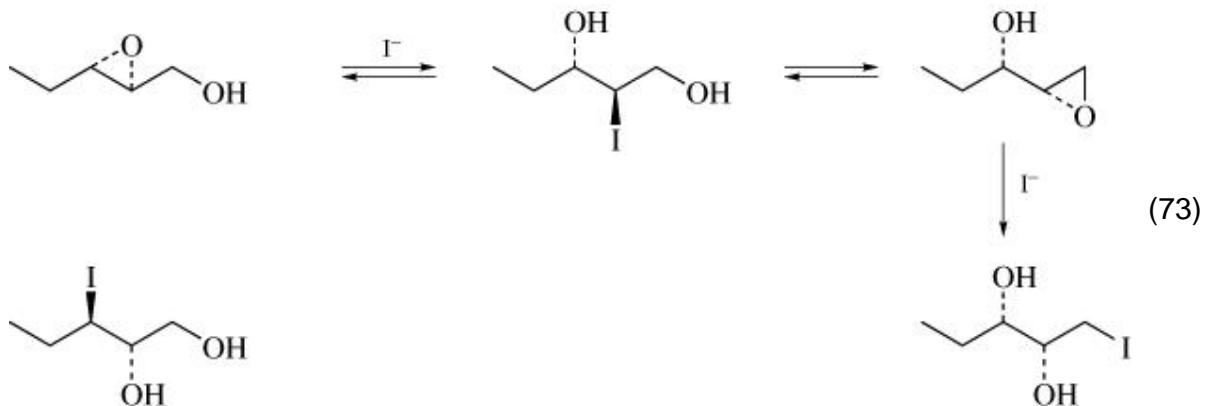
Since Ti(OPr-i)$_4$ is a weak Lewis acid, it promotes the rearrangement of some epoxy alcohols in the absence of an appropriate nucleophile. (312) For example, exposure of 2,3-epoxygeraniol and 2,3-epoxynerol to Ti(OPr-i)$_4$ leads stereoselectively to allylic alcohols **105** and **106**.

105 (70-80%)

106 (70-80%)
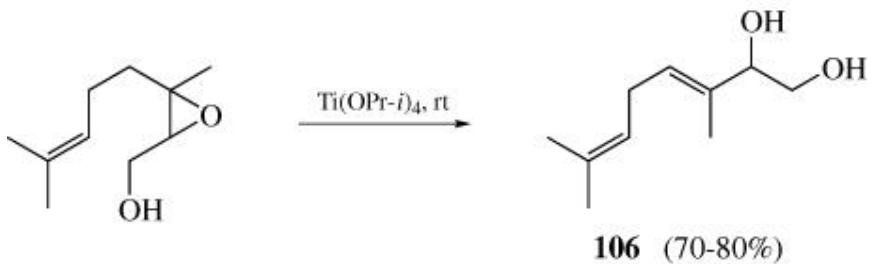
The titanium chelation effect is also observed in the epoxide opening reactions of epoxy acids (Eq. 74). (254)

	I + II	I:II
Ti(OPr-i)$_4$-Et$_2$NH (xs), rt	(92%)	>20:1
Et$_2$NH-H$_2$O (2:1), reflux	(95%)	1:6

(74)
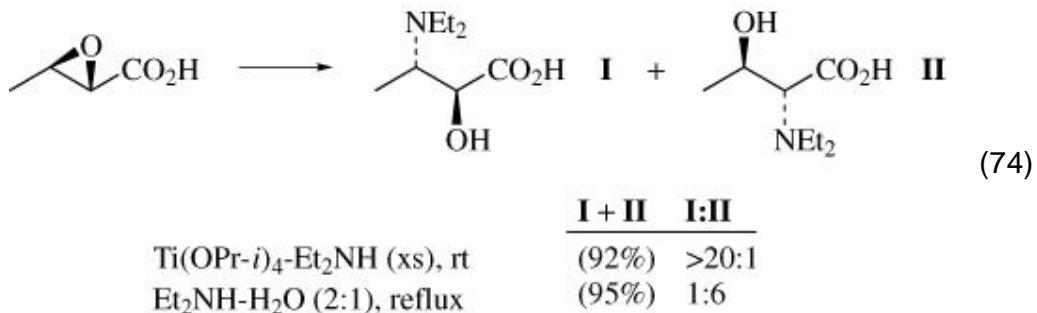
Treatment of epoxy ester **107** with azidotrimethylsilane in the presence of a catalytic amount of zinc chloride gives the 3-azido hydroxy ester exclusively. (313)

107
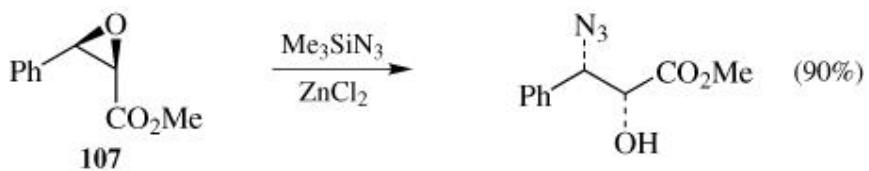
Nucleophiles supported on calcium ion-exchanged Y-type zeolite also react with epoxy alcohols regioselectively to give C-3-opened products (Eq. 75). (314-316)

$$\text{Nu} = \text{N}_3^-, \text{Cl}^-, \text{Br}^-, \text{PhS}^-$$

CaY = calcium ion-exchanged Y-type zeolite
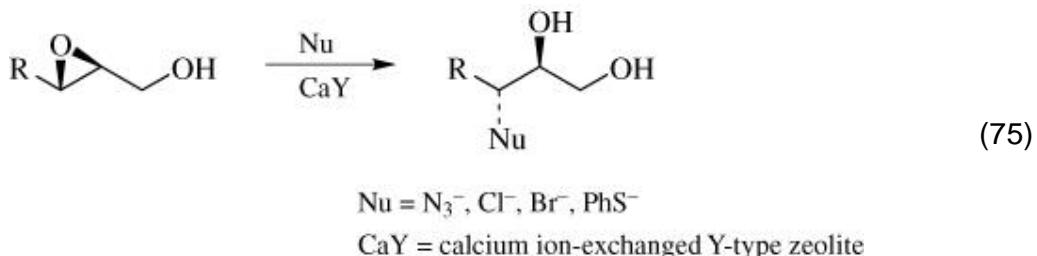
Magnesium iodide reacts regioselectively with epoxy alcohols to give iodohydrins that are further reduced to vicinal diols (Eq. 76). (317, 318)
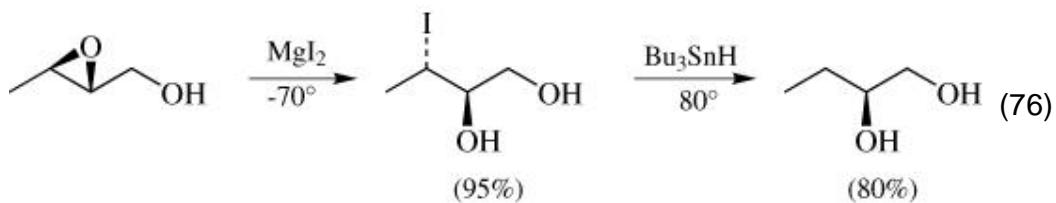
Intramolecular nucleophilic opening of an epoxy alcohol where the nucleophile is anchored to the hydroxy group is effective for selective epoxide opening at C-2. For example, epoxy carbonates **108** and epoxy urethanes **109**, obtained by treatment of epoxy alcohols with alkoxycarbonyl chlorides or isocyanates, undergo intramolecular epoxide opening under acidic conditions by attack on the carbonyl oxygen to give hydroxy carbonates **110** with inversion at
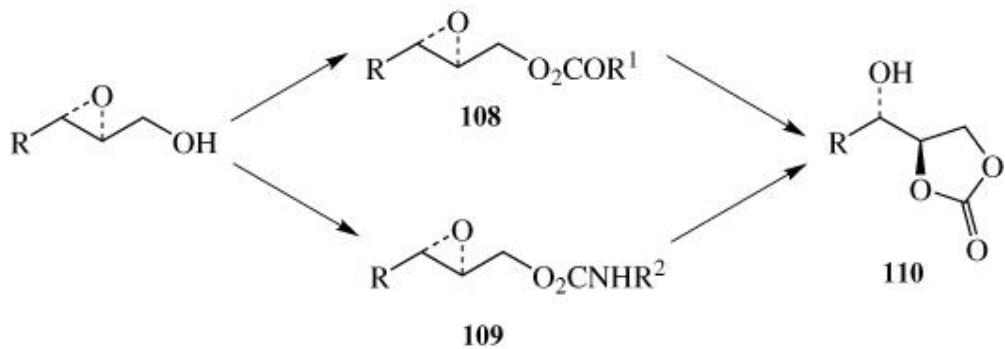
C-2. (105, 160, 183, 184, 319-322) Treatment of the carbamates derived from 3,3-disubstituted epoxy alcohols, however, provides a mixture of C-2 and C-3 ring-opened products, the ratio of which is dependent on the Lewis acid used (Eqs. 77, (323) 78 (324)).

(77)

(70%)

(17%)

(78)

I + II (53%) I:II = 1:3
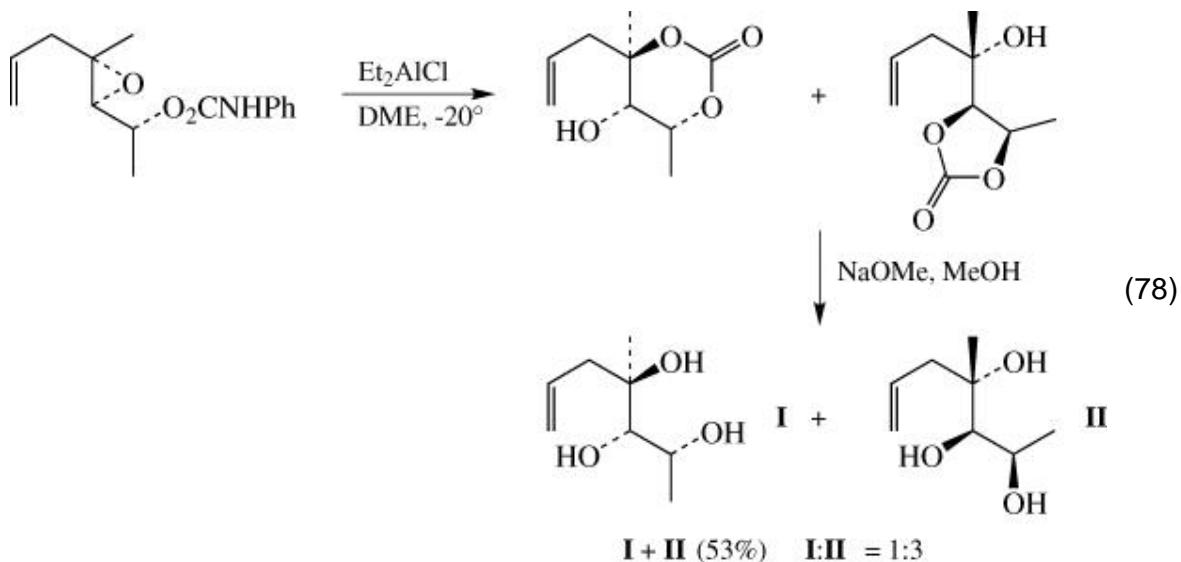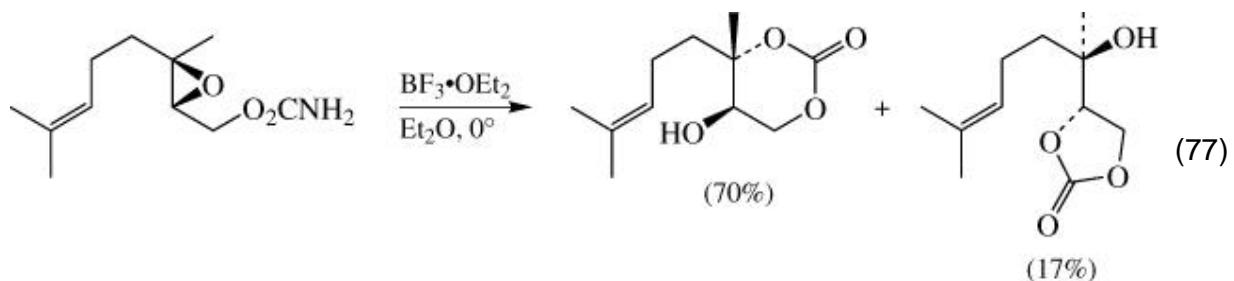
With acid-sensitive substrates such as **111**, treatment with cesium carbonate

and powdered 3-Å molecular sieves in dimethylformamide under carbon dioxide provides 3-hydroxy carbonate **112** together with a small amount of 1-hydroxy carbonate **113**. (325, 326)
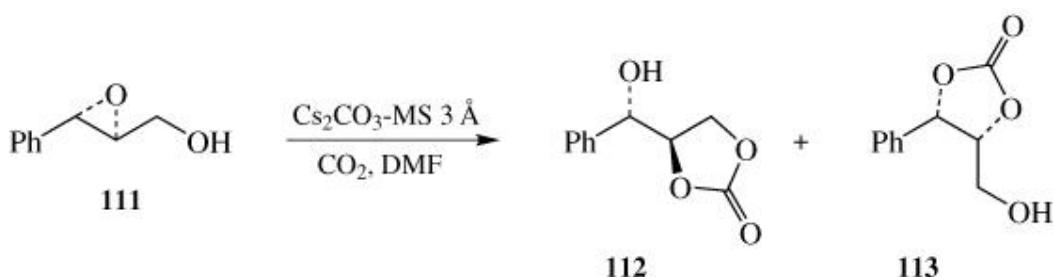
Treatment of epoxy alcohols with cesium carbonate and paraformaldehyde gives hydroxy dioxolanes in good yields (Eq. 79). (327)

$$(79)$$
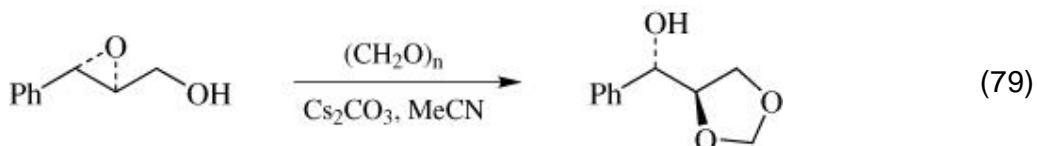
The reaction of epoxy alcohols with carbon disulfide in the presence of sodium hydride gives cyclic xanthates which can be transformed into episulfides (Eq. 80). (328)

$$(80)$$
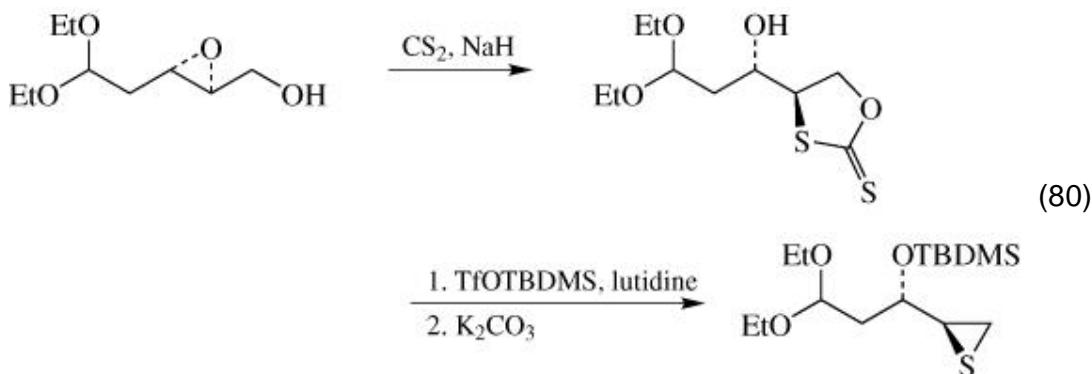
On treatment of **109** with a base such as sodium hydride, the urethane

nitrogen attacks the C-2 epoxide carbon to give hydroxy carbamates **114**. (160, 319, 321)

109

114
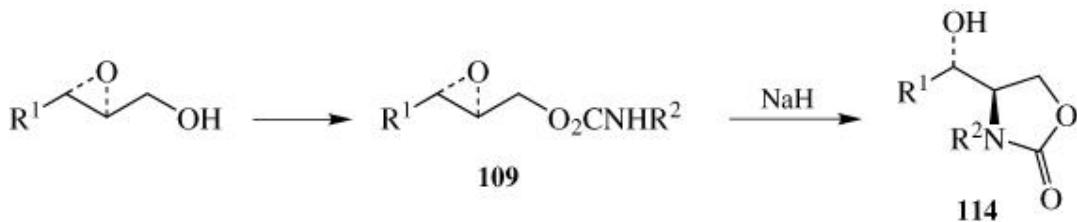
Nitrogen delivery can be effected under mild basic conditions when epoxy *N*-benzoylcarbamate **115** is used as a substrate (Eq. 81). (329)

115

(81)
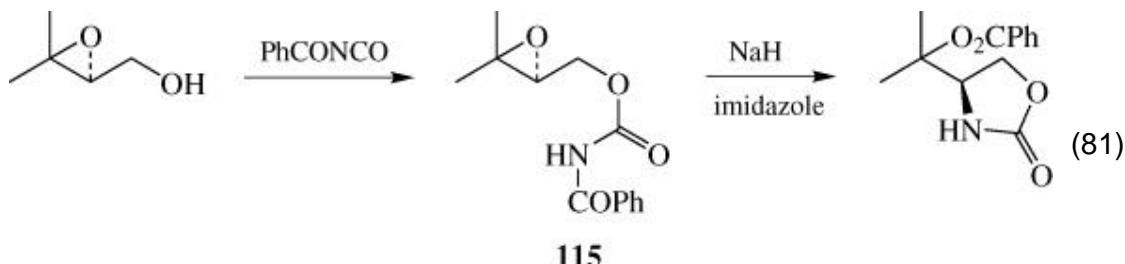
Reduction of epoxy alcohols with sodium bis(methoxyethoxy)aluminum hydride (Red-Al®) in tetrahydrofuran provides 1,3-diols selectively, presumably by a pathway in which hydride is delivered to C-2 from an intermediate epoxy alcohol-Al(OR)₂H⁻ complex (Eq. 82). (160, 330, 331) This notion is supported by the observation

(82)

(90%)
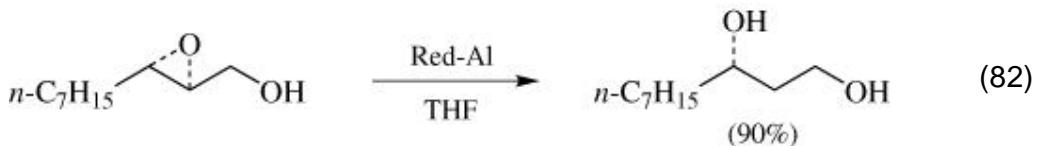
that reduction of the epoxy ether is slow and exhibits poor regioselectivity (Eq. 83). (331) In contrast, reduction of epoxy alcohols with diisobutylaluminum hydride (123)

$$\text{n-C}_7\text{H}_{15}\text{–(epoxide)–OBn} \xrightarrow[\text{THF}]{\text{Red-Al}} \text{n-C}_7\text{H}_{15}\text{–CH(OH)–CH}_2\text{–OBn} \quad + \quad \text{n-C}_7\text{H}_{15}\text{–CH}_2\text{–CH(OH)–OBn}$$

(50%) 1:1.5 (83)
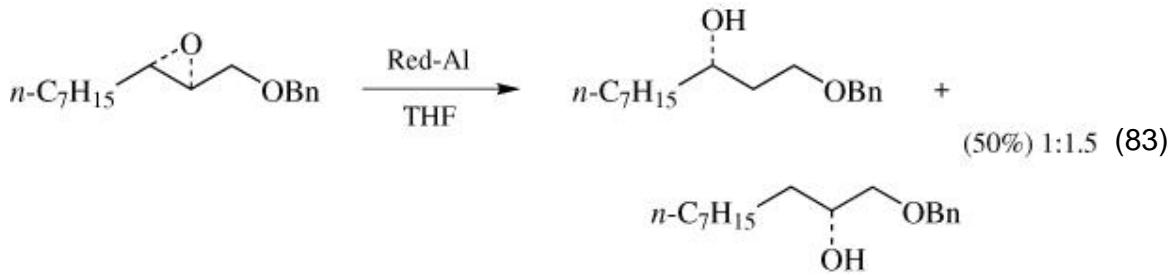
gives 1,2-diols preferentially (Eq. 70). Compound **116** with a C-2 substituent, however, undergoes opening at C-3 because of steric hindrance at C-2. (331)

$$\text{n-C}_7\text{H}_{15}\text{–(epoxide, C-Me)–OH} \xrightarrow[\text{THF}]{\text{Red-Al}} \text{n-C}_7\text{H}_{15}\text{–C(Me)(OH)–OH} \quad (70\%)$$

116
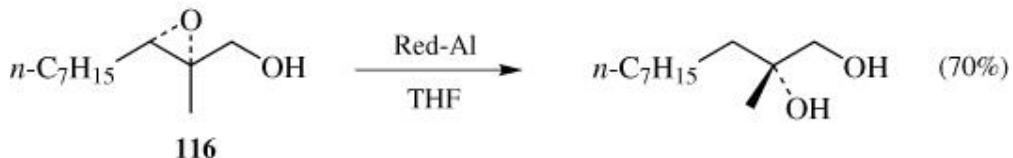
In contrast, C-4 branching causes hydride delivery to occur at C2 (Eq. 84). (332) In the reduction of 2,3-epoxycinnamyl alcohol by sodium bis(methoxyethoxy)aluminum hydride,

$$\text{BOMO–(chain, epoxide)–OH} \xrightarrow[\text{THF}]{\text{Red-Al}} \text{BOMO–(chain, OH)–OH} \quad (84)$$

(89%)
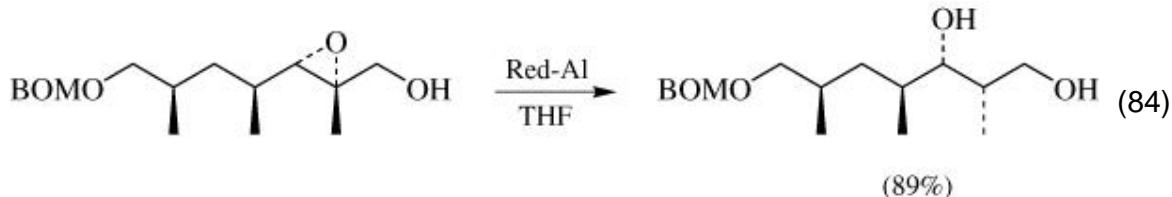
higher regioselectivity (22:1) is obtained by using dimethoxyethane instead of tetrahydrofuran as a solvent. (333)

Reaction of epoxy alcohol **117** with LiCuMe$_2$ gives C-2 methylated 1,3-diols selectively. (154, 334) With sterically unbiased epoxy alcohols, methylation with

$$\text{BnO–(chain, epoxide)–OH} \xrightarrow{\text{LiCuMe}_2} \text{BnO–(chain, OH)–OH} \quad (95\%)$$

117
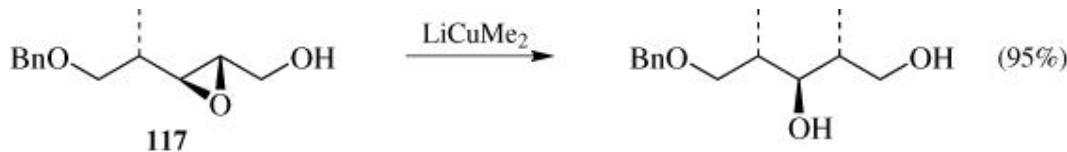
LiCuMe$_2$ is nonregioselective (Eq. 85), but reaction with Li$_2$Cu(CN)Me$_2$ prepared from methyllithium not contaminated with lithium chloride, in a coordinating solvent system [THF-1,3-dimethyl-2-imidazolidone (DMEU)], shows moderate C-2 selectivity (Eq. 86). (335, 336) Use of a Grignard reagent in the presence of a catalytic amount of CuI also shows moderate C-2 selectivity. (337)
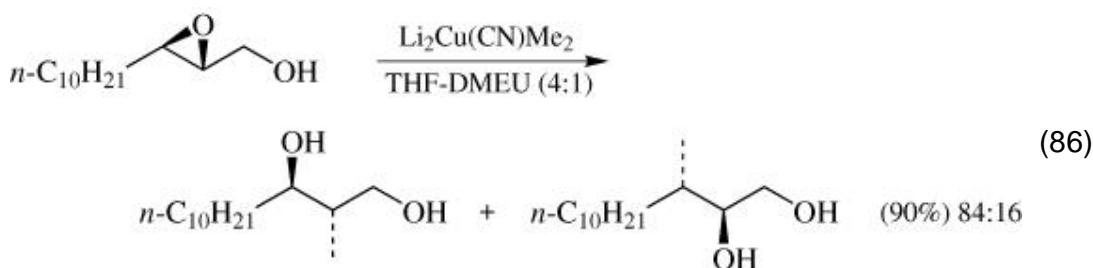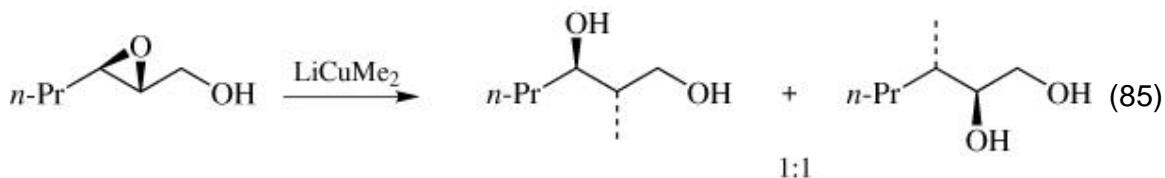
Treatment of 118, derived from epoxy alcohols, with titanium tetrachloride or boron trifluoride etherate promotes 1,2-migration of the vinyl group, providing the *anti-* β -hydroxy ketone stereoselectively. (338–339)
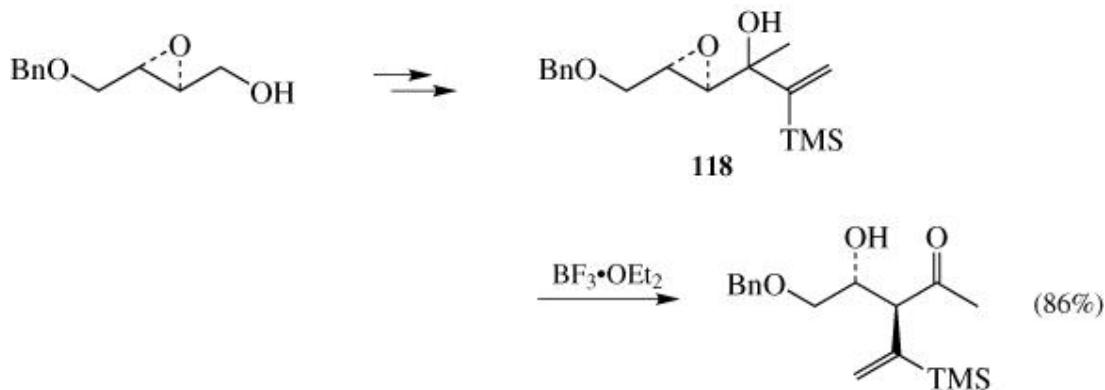
Treatment of epoxy silyl ethers with methylaluminum

bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) promotes rearrangement of the *tert*-butyldimethyl-siloxymethyl group to give β -hydroxy aldehyde derivatives (Eq. 87). (340-343)

$$
\text{(87)}
$$

(87%) 98% ee

Cyclization by intramolecular nucleophilic substitution of epoxides follows Baldwin's rule. (344, 345) For example, 3-7-*exo-tet* systems are favored and 5-6-*endo-tet* systems disfavored (Eq. 88).

$$
\text{(88)}
$$
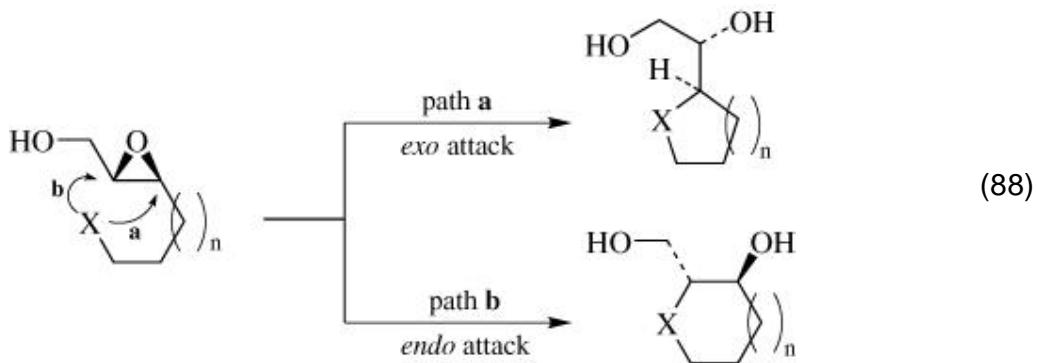
Epoxide opening with a hydroxy group leads to stereospecific formation of tetrahydrofuran (75, 76, 82, 83, 94, 346) or tetrahydropyran ring systems (Eqs. 89, 90). (82, 83, 347, 348) However, formation of a tetrahydropyran or oxepane ring is observed

$$
\text{(89)}
$$

(71%)

(90)
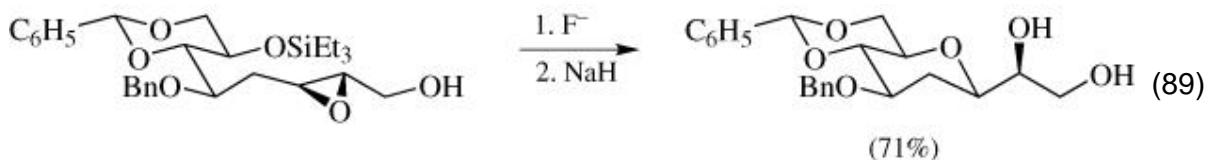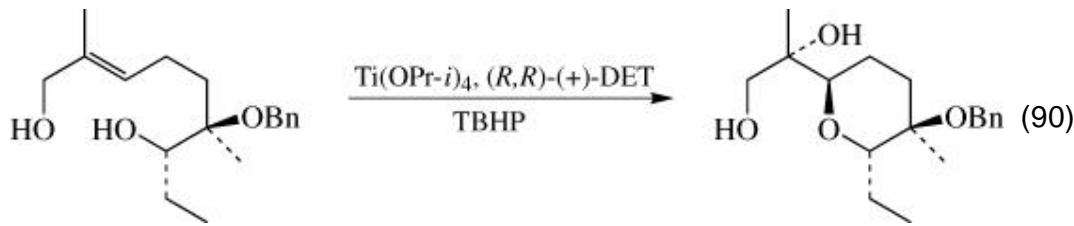
in the acid treatment of hydroxy vinylepoxides, which are readily derived from the corresponding epoxy alcohols (Eq. 91). (349, 350)

(91)
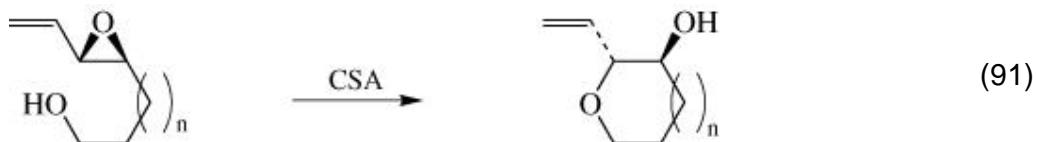
Although the vinyl carbanion derived from vinyl sulfone **119** cyclizes smoothly to give dihydrofuran **120**, cyclization of the cyano ester **121** to lactone **122** does not proceed because of the unfavorable stereoelectronic requirement

119

120 (72%)

121

122
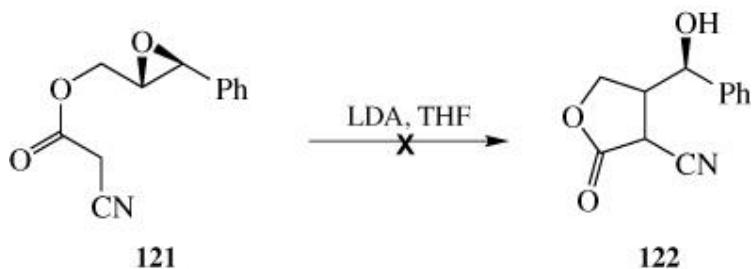
that the enolate π system must achieve colinearity with the oxirane C_2-O bond. (351-353)

Intramolecular nucleophiles such as carbonyl groups, alcohols, and carboxylic acids can react with the epoxide with C-3 selectivity if they are located at an

appropriate position. For example, alkaline treatment of epoxy ester **123** provides a triol derivative stereoselectively via an intermediate lactone. (354, 355)
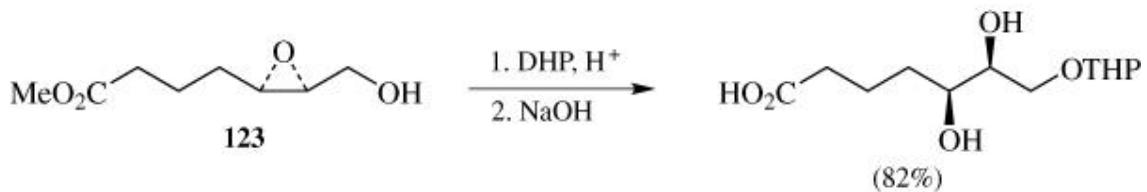
Amino groups can also serve as intramolecular nucleophiles (Eq. 92). (356)
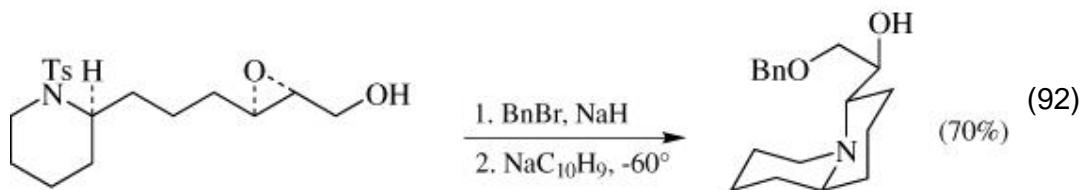
Nucleophilic π -bonds will also open epoxides. For example, treatment of epoxy ether **124** with boron trifluoride etherate gives the tricyclic compound **125**
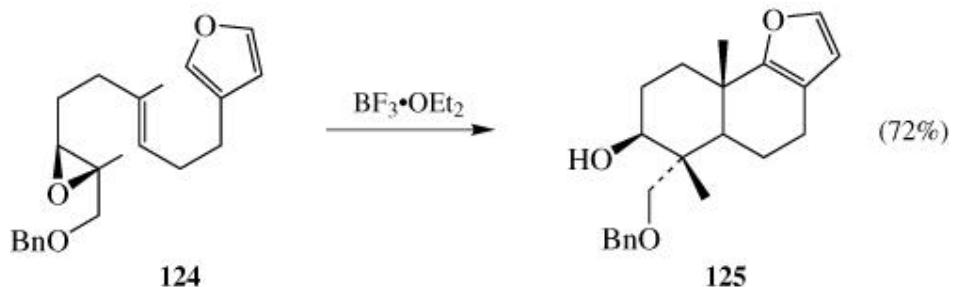
with high stereoselectivity. (357) Baker's yeast also catalyzes this type of cyclization. For example, epoxide **126** provides C-28 hydroxylated sterol **127** on treatment

126

127 (41%)
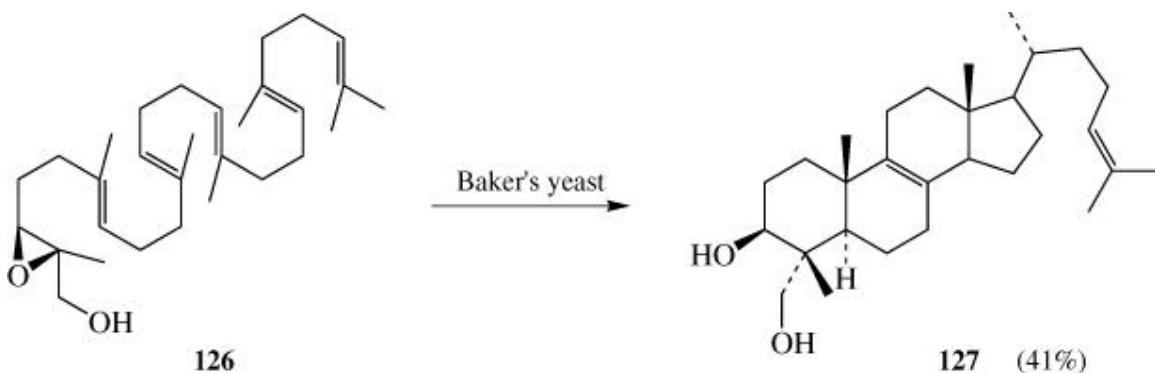
with Baker's yeast, but the enantiomer of **126** does not react under the same conditions. (358)

Treatment of unsaturated epoxy alcohols **128** or **129** with tin tetrachloride gives mixtures of diastereomeric cyclopropyl lactones in a ratio of 1.5:1, regardless of the geometry of the double bonds. (359)

128

or

129

SnCl₄

I

+

II

I:II = 1.5:1
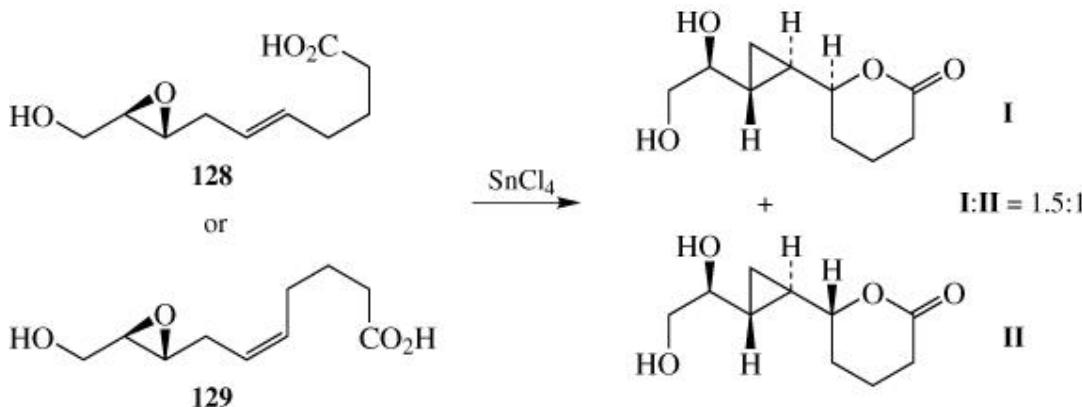
Reactions of alkynyl epoxy alcohols with dialkylbromomagnesium cuprates in the presence of dimethyl sulfide give dihydroxy allenes stereoselectively (Eq. 93). (101)

n-Bu₂CuMgBr•SMe₂

-60°

(68%) (93)
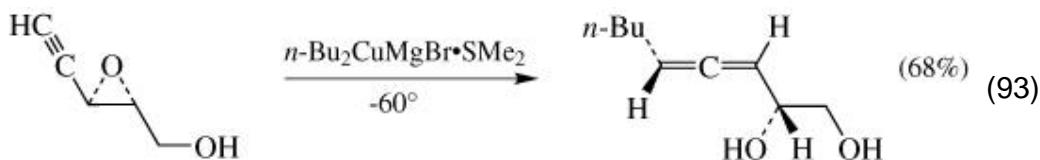
2,3-Epoxy alcohols can be converted into the corresponding 2,3-epithio alcohols and 2,3-aziridino alcohols stereoselectively. Treatment of epoxy alcohols with thiourea in the presence of Ti(OPr-i)$_4$ gives 2,3-epithio alcohols stereospecifically (Eq. 94). (360) Transformation of epoxy alcohols into aziridino alcohols

$$\text{(94)}$$
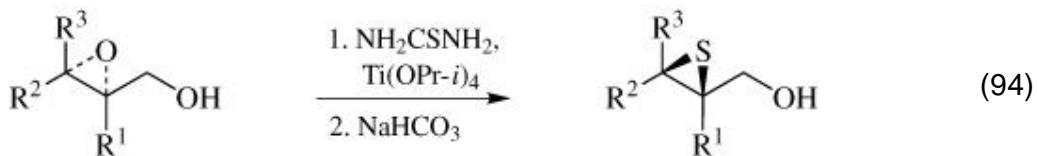
is also achieved in five steps by using the modified Blum procedure (Eq. 95). (361, 362)

$$\text{(95)}$$
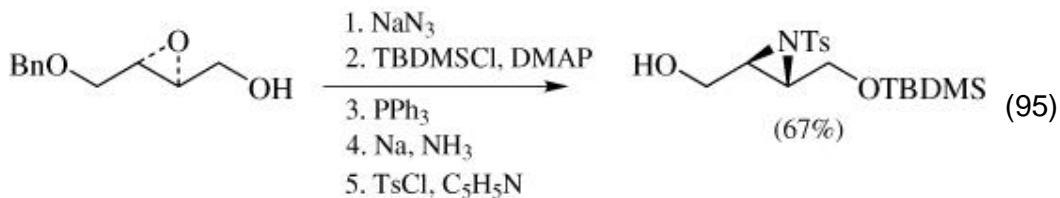
The selectivity of reactions of 2,3-epithio alcohols and 2,3-aziridino alcohols is similar to that of the corresponding epoxy alcohols. For example, reduction with sodium bis(methoxyethoxy)aluminum hydride provides 3-thio or 3-amino alcohols regioselectively (Eqs. 96, 97). (361, 363) Treatment of an aziridino alcohol with LiCuEt$_2$ provides a 3-amino-2-ethyl alcohol exclusively (Eq. 98). (362)

$$\text{(96)}$$

$$\text{(97)}$$

(80%)   (98)
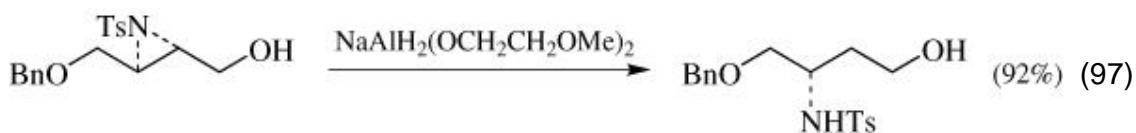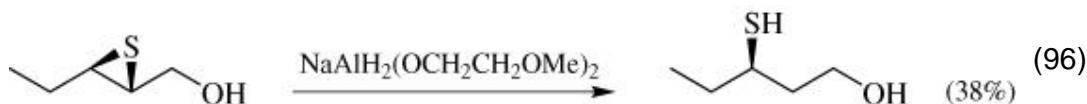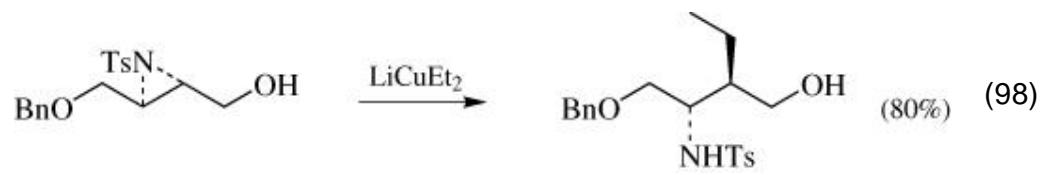
5. Other Methods for Synthesis of Nonracemic Epoxides

Epoxides can be prepared in various ways, including epoxidation of olefins, reaction of carbonyl compounds with sulfur ylides or with α -halo esters, and alkaline closure of halohydrins. Among these methodologies, the epoxidation of olefins is the most practical from the viewpoint of easy availability of olefins and mildness of the reaction. Three classes of asymmetric epoxidation of olefins are summarized in this section.

1. Epoxidation with chiral peracids or related compounds. (364-368) This includes the first example of asymmetric epoxidation using an optically active peroxycamphoric acid (Eq. 99), though the enantioselectivity of the reaction is poor (<10% ee). (364)

(99)
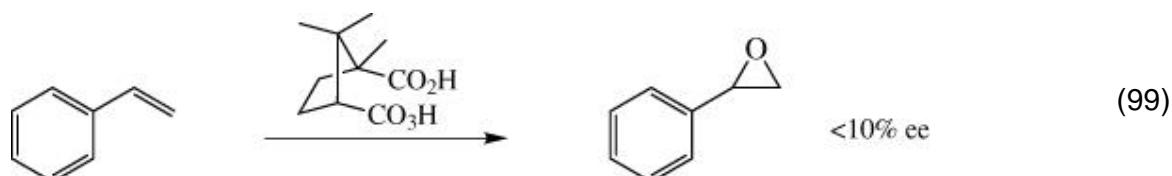
Several optically active peracids were examined for asymmetric epoxidation but the optical yields did not exceed 5% ee. (365-368) However, the enantiomerically pure *N*-sulfamyloxaziridine derivatives have proven quite effective for asymmetric epoxidation of unfunctionalized alkenes: good enantioselectivities (up to 65% ee) have been observed (Eq. 100). (369-371)

(100)
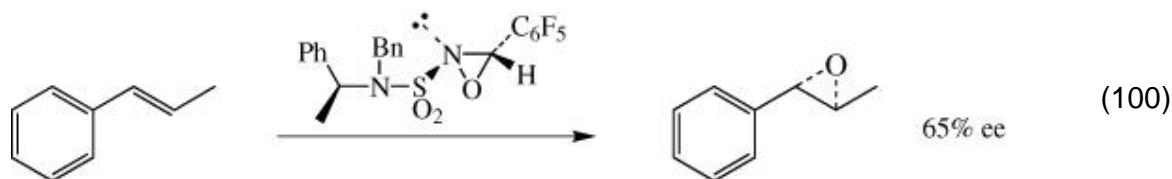
2. Epoxidation of conjugated enones with hydrogen peroxide in the presence of a chiral phase transfer reagent (Eq. 101). (372-376)

(101)
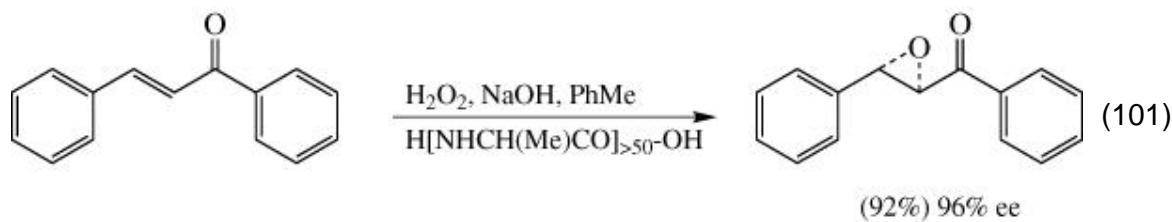
3. Epoxidation using a metal catalyst bearing chiral ligand(s). In 1970, it was found that the epoxidation of allylic alcohols with an alkyl hydroperoxide under catalysis by VO(acac)$_2$ proceeds smoothly in comparison with that of isolated olefins. (377) These metal-catalyzed epoxidations of allylic alcohols are chemo-, regio-, and stereoselective (Eqs. 102, 103). (61, 378, 379) Reaction occurs in the coordination

(102)

(103)
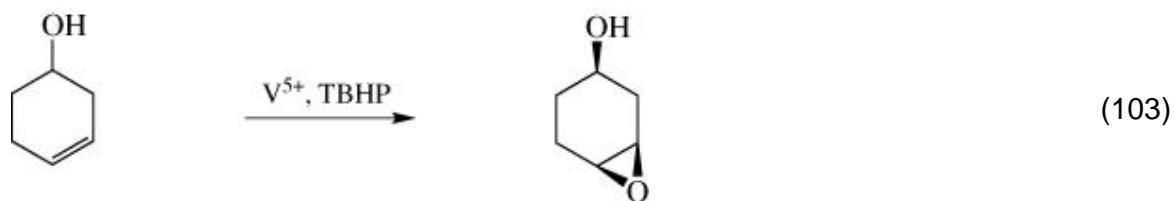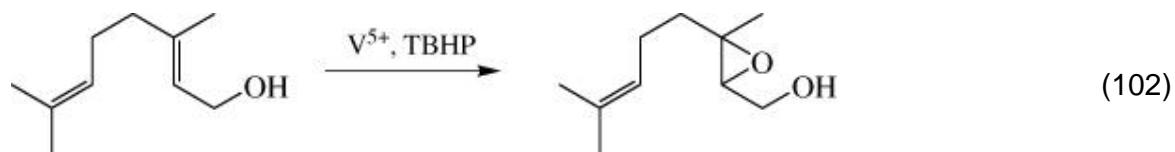
sphere of the metal, and the reacting ligand sites are located adjacent to the bystander ligand (L) sites of complex **130**. (30) Therefore, the use of chiral bystander

130
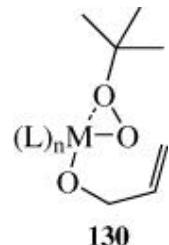
ligands has the effect of placing the reaction site in an asymmetric environment, and several approaches using chiral metal catalysts have been examined. (30, 380-383) Although optical yields were unsatisfactory from a practical point of view, these initial results indicated the potential of chiral metal complex-catalyzed asymmetric epoxidation and, in this context, the titanium-mediated epoxidation discussed in this chapter was discovered.

In contrast to the success realized in the asymmetric epoxidation of allylic alcohols, there is still considerable room for improvement in the asymmetric epoxidation of olefins lacking coordinating functional groups, though several precedent studies have been reported. (384, 385) However, chiral porphyrin complexes were shown to be effective catalysts for the epoxidation of mono-

and *Z*-disubstituted olefins. (386-392) Furthermore, quite recently the chiral salen complexes **131** were
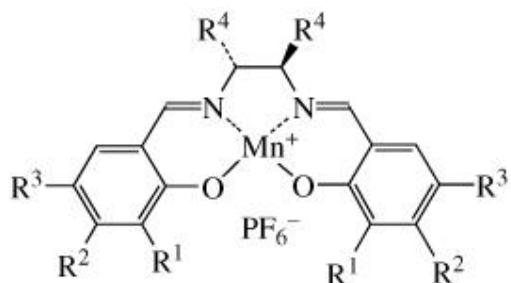
	R¹	R²	R³	R⁴
131a	*t*-Bu	H	H	Ph
131b	*t*-Bu	H	*t*-Bu	–(CH₂)₄⁻
131c	(*S*)-1-phenylpropyl	H	H	Ph
131d	(*S*)-1-(4-*tert*-butylphenyl)propyl	Me	H	–(CH₂)₄⁻

found to be very effective catalysts for this purpose, and the highest enantioselectivity to date was realized. (393-403) For example, 2,2-dimethylchromene **132** was converted to the corresponding epoxide with 98% ee.
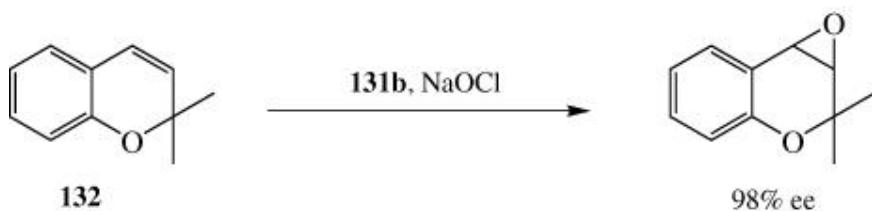
Highly enantioselective dihydroxylation of olefins proceeds in a catalytic manner by using K₂OsO₂(OH)₄-phthaladine (**133** or **134**) complex as a catalyst (Eq. 104). (404) This dihydroxylation reaction can be applied to a wide range of

(104)

133

134
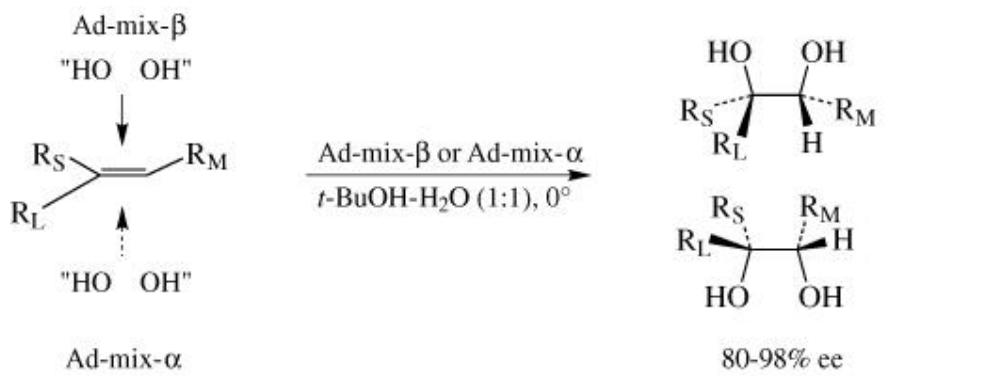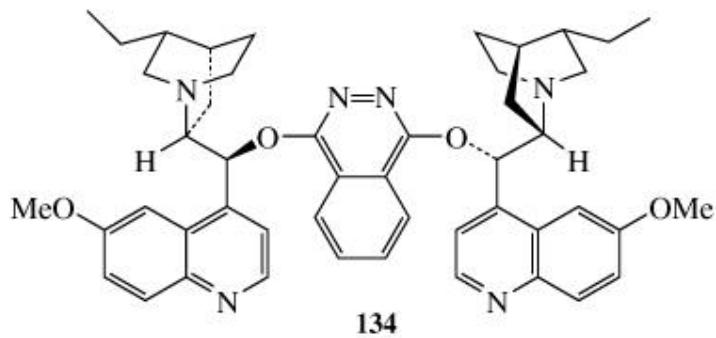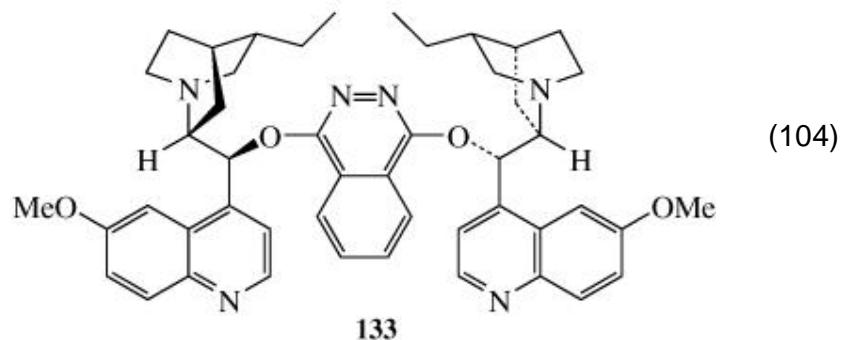
olefins irrespective of the presence or absence of coordinating functional groups, except for *cis*-disubstituted and tetrasubstituted olefins which show decreased enantioselectivity to some extent. The resulting diols are stereospecifically converted into epoxides (Eq. 105). (405, 406)

1. MeC(OEt)$_3$, TMSCl
2. KOH, MeOH

(89%)

(105)

1. MeC(OEt)$_3$, TMSCl
2. KOH, MeOH

(89%)
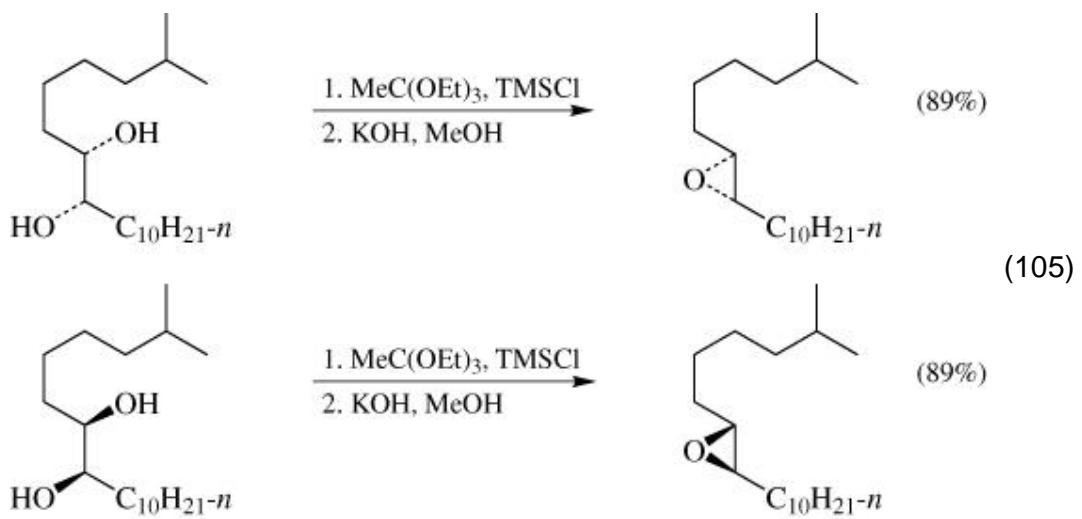
6. Experimental Conditions

6.1. Reagents
6.1.1. Titanium Alkoxide
Titanium tetraisopropoxide, Ti(OPr-i)$_4$, has been almost the only metal alkoxide used in asymmetric epoxidation and kinetic resolution reactions. It can be distilled under vacuum (bp 78–79.5°/1.1 mm Hg) and stored under an inert gas for long periods of time (~1 year) without decomposition. This reagent can be used for most any epoxidation as received from commercial sources, but if poor percentages of ee are obtained, especially in the catalytic procedure, purification by distillation is recommended. Titanium tetraisopropoxide can be transferred to the reaction vessel via syringe or cannula, avoiding exposure to atmospheric moisture, which would quickly destroy the metal alkoxide. Ti(OBu-t)$_4$ can be used in the epoxidation of primary allylic alcohols when epoxide opening is problematic (see Experimental Procedures). However, use of Ti(OBu-t)$_4$ is not recommended when the substrate is a secondary allylic alcohol because the relative rate constant obtained with Ti(OBu-t)$_4$ is low relative to that with Ti(OPr-i)$_4$. (38)

6.1.2. Dialkyl Tartrates
Diethyl tartrate (DET) and diisopropyl tartrate (DIPT) are the chiral auxiliaries most often used in either stoichiometric or catalytic asymmetric epoxidation, the choice being irrelevant in terms of the enantioselectivity except in the asymmetric epoxidation of allyl alcohol. (18) Dimethyl tartrate (DMT) is useful when a water-soluble tartrate is needed (e.g., when the epoxy alcohol needs to be purified without tartrate hydrolysis). The choice of tartrate ester is more critical in kinetic resolution since k_{rel} increases in the order DMT < DET < DIPT. In the catalytic procedure, dicyclohexyl tartrate (DCHT) (18) and dicyclododecyl tartrate (DCDT) (18) have shown greater enantioselectivity than DIPT, although DIPT is usually the first choice because it is most readily available and gives acceptable selectivity.

Like titanium tetraisopropoxide, the tartrate ester usually can be used as received from commercial sources, but if substandard enantioselectivity is observed, distillation under high vacuum followed by storage under an inert gas is recommended (DMT, mp 48–50°, bp 163°/23 mm Hg; DET, bp 89°/0.5 mm Hg; DIPT, bp 76°/0.1 mm Hg). The distillation temperature should be kept below 100° in order to avoid polymerization of the tartrate. Both DCHT (mp 69.5–70.5°) and DCDT (mp 122–123°) can easily be prepared by Fisher esterification of tartaric acid with the corresponding alcohol. (18) Liquid tartrates can be handled by syringe. However, since they are extremely viscous, a more convenient method is to weigh the amount required into a flask, dissolve it in a minimum amount of dichloromethane, and transfer the solution to the reaction vessel via syringe or cannula.

6.1.3. Organic Peroxide

tert-Butyl hydroperoxide is the most often used oxidant in asymmetric epoxidation and kinetic resolution reactions. It is available as a 70% solution in water, but preparation of anhydrous organic solutions is necessary. Anhydrous isooctane solutions (18) are commercially available (Aldrich Chemical Company). However, care must be taken when an isooctane solution is used. Some reactions using TBHP in isooctane with higher substrate concentrations produce lower reaction rates and/or percent ee. Introduction of too much isooctane into the reaction medium (dichloromethane) changes the solvent polarity, with negative effects on the rate and percent ee. (18) Accordingly, use of > 5 M solutions of TBHP in isooctane is highly recommended. Other organic solvents such as dichloromethane, dichloroethane, heptane, and toluene can also be used. Anhydrous TBHP solutions can be prepared by extraction of the commercial 70% aqueous solution with the chosen solvent and by azeotropic distillation of the organic phase to ensure the removal of all remaining water. (17, 18, 30, 407) The concentration of hydroperoxide is determined by iodometric titration, (17, 18, 30) and the solutions are stored with refrigeration (0–5°) over 3 Å molecular sieves (dichloromethane) or at room temperature (isooctane) without zeolites in high-density polyethylene bottles. The latter are recommended instead of glass bottles because of possible pressurization by gas evolution. Although TBHP solutions have proved to be safe during manipulation, peroxides are potentially hazardous with respect to violent decomposition, so special care should be taken when handling them. Thus, never add transition metal salts or strong acid to the concentrated peroxide solutions. In the same sense, never work with pure hydroperoxide, and avoid high concentrations of TBHP whenever possible. *All heating of peroxide solutions should be done behind an adequate blast shield in a well-ventilated fume hood.* The desired amount of TBHP solution should be added to a flask or graduated cylinder containing activated 3 or 4 Å molecular sieves. After standing several minutes in the stoppered flask, the solution can be transferred to the reaction vessel by syringe, by cannula, or simply by pouring. The syringe or cannula should never be inserted directly into the stock solution.

Commercially available cumyl hydroperoxide (Aldrich Chemical Company, 80% solution in cumene) can be used without further treatment. Asymmetric epoxidations using cumyl hydroperoxide are faster than those using TBHP. However, in general, TBHP solutions are recommended because the products are more easily isolated.

6.1.4. Reaction Solvent

Dichloromethane is the solvent used in all asymmetric epoxidation and kinetic resolution reactions. When dichloromethane is methanol free, it can be prepared for use just by storing over activated 3 Å molecular sieve pellets (4-Å should not be used since pressurization in bottles has been observed). A simple check of the dichloromethane by ^{1}H NMR can show whether it contains

methanol. In general, care must be taken to avoid contamination by chelating solvents (alcohols, esters, nitriles, amines, ketones) which decrease the rate, yield, and enantioselectivity of the epoxidation reaction.

Although most allylic alcohols have sufficient solubility in dichloromethane, some long-chain allylic alcohols are poorly soluble. For example, (*E*)-octadec-2-en-4-yn-1-ol is scarcely soluble in dichloromethane at – 20°, but use of a 1:1 mixture of 2,3-dimethyl-2-butene and dichloromethane as a solvent allows smooth epoxidation. (102, 103)

6.1.5. Molecular Sieves

The use of 3 or 4 Å molecular sieves (zeolites) is essential to accomplish both asymmetric epoxidation and kinetic resolution in a catalytic manner. Their use in the stoichiometric reaction is also highly recommended. The amount of molecular sieves added to the reaction mixture is not critical, so long as the allylic alcohol and TBHP solutions are predried. Tartrates and Ti(OPr-i)$_4$ should not be stored over molecular sieves. Molecular sieves should be preactivated in a vacuum oven (160° and 0.05 mm Hg pressure for at least 3 hours) and crushed. Preactivated, powdered 4 Å molecular sieves are commercially available (Aldrich Chemical Company). Either 3 or 4 Å molecular sieves can be used, except for epoxidations of low molecular weight substrates (e.g., allyl alcohol) where 3 Å sieves are recommended.

6.1.6. Reaction Conditions

Asymmetric epoxidation and kinetic resolution reactions can be run either stoichiometrically (50% or more catalyst) or catalytically (5–10% catalyst). The stoichiometric procedure is useful when very unreactive substrates are oxidized or when the reaction product is not amenable to further percent ee enrichment by recrystallization. In general, use of the minimum amount of catalyst is recommended because the reaction products are more easily isolated. Reaction conditions are similar in both procedures. The catalyst is unstable if stored over long periods of time, and thus should be prepared in situ. It is prepared by mixing the tartrate with Ti(OPr-i)$_4$ at – 20°, in any order of addition, and adding either the allylic alcohol or the TBHP solution in a second step. *The use of at least 10% excess of tartrate over Ti(OPr-i)$_4$ is essential to obtain optimum results (a ratio of 1.2:1 is recommended).* The three components should be aged at this temperature for 20–30 minutes. Although this aging period is important for the catalytic procedure, most stoichiometric reactions have been run after aging for only 1–5 minutes. After aging, the precooled (especially important in large-scale reactions) fourth component (the allylic alcohol or the TBHP solution) is added to the reaction mixture. It is recommended that TBHP be the last component added to maintain more control over the reaction temperature. This is especially important in large-scale procedures because its addition is slightly exothermic. The use of 2.0 equivalents of TBHP is generally suitable, although 3 equivalents may be

used for sluggish substrates. In kinetic resolution reactions, 0.6 equivalent of TBHP is the normal amount used. However, if very unreactive substrates are resolved, more TBHP can be used (about 2 equivalents), as long as substrate conversion is monitored (e.g., GLC with an internal standard). The temperature of the reaction mixture must be adjusted to within the range – 40 to 0°, depending on the substitution pattern of the substrate. If the epoxidations are rapid enough, lower temperatures are recommended to avoid side reactions such as transesterification and epoxide opening. Most asymmetric epoxidations and kinetic resolutions are carried out at – 20° (carbon tetrachloride/dry ice slurry).

The concentration of the substrate is another factor to be considered. The highest suggested concentration for the stoichiometric reaction and for the catalytic procedure in which the product is very reactive (e.g., cinnamyl alcohol epoxide) is 0.1 M in order to minimize side reactions (mainly epoxide opening). For some substrates the concentration for the catalytic procedure can be up to 1.0 M, although substrate solubility can be a limitation.

Finally, since asymmetric epoxidation and kinetic resolution are sensitive to humidity, these reactions must be run under dry conditions, usually under a dry nitrogen or argon atmosphere.

6.1.7. Workup
Choice of the appropriate isolation procedure is essential to the success of an asymmetric epoxidation or kinetic resolution reaction and depends on the nature of the product. The development of workup procedures has paralleled the development of the asymmetric epoxidation and kinetic resolution procedures. (1, 18, 41, 59, 347, 408, 409) The most important factors to be considered in workup are: (1) hydrolysis of the titanium complex; (2) destruction of excess oxidant; (3) tartrate removal; and (4) purification of the product, having in mind the possibility that the product might be water soluble or react with the reagents used.

Hydrolysis of the titanium complex has been effected with aqueous solutions of hydroxy carboxylic acids, (1, 17, 18) water/acetone, (10) saturated sodium sulfate/ether, (4, 348) sodium fluoride solution, (59) triethanolamine, (347) anhydrous citric acid/ether (or acetone/ether), (18) and sodium hydroxide in saturated brine. (17, 18) Hydrolysis of the complex can also be combined with destruction of the tartrate and/or the excess TBHP. Tartrate removal can be carried out either by alkaline hydrolysis of the ester to give a water-soluble tartrate salt or by chromatographic separation at the purification step. Excess TBHP can be reduced with dimethyl sulfide, (59, 347) trimethyl phosphite, (18) aqueous sodium thiosulfate, (30, 363) aqueous sodium sulfite, (30) sodium borohydride, (408) triphenylphosphine, (409) or aqueous ferrous sulfate. (18)

These steps are followed by a product purification step involving chromatographic separation, distillation, or recrystallization, either alone or in combination. Although various combinations of these procedures have led to an adequate workup method for most epoxy alcohols, an ideal method has not yet been found to isolate very water-soluble or reactive epoxy alcohols. Thus in situ derivatization of the reaction products can sometimes be useful because more stable and easily isolable products are obtained. (18, 135, 136) Such in situ derivatization is one of the most important advantages of the catalytic procedure, since it is impractical to perform in the stoichiometric reaction because of the large amount of hydroxylic contaminants. (18) The most water-soluble glycidol, however, can be extracted into water and purified by distillation when tributylphosphine is used as a reducing agent for excess TBHP. (410) A few standard workup procedures are presented here that can be used for any epoxy alcohols included in the group indicated in each case.

6.1.7.1. Aqueous Acidic Workup

This is the most common procedure for water-insoluble products from either asymmetric epoxidation or kinetic resolution. (1) The reaction mixture is poured into a precooled (0°) aqueous solution of tartaric acid (10% w/v) or citric acid (11% w/v), (18) using 5–20 mL of the acid solution per 1 mmol of Ti(OPr-i)$_4$. This mixture is vigorously stirred until a clear organic phase is obtained (10–30 minutes). In small-scale reactions the excess TBHP can be ignored because it can be easily removed by azeotropic distillation with toluene or carbon tetrachloride (up to 0.5 mol has been removed by this procedure) or in the product purification step. However, oxidant destruction may be desired to avoid peroxide hazard and is essential in large-scale reactions. If so, the solution of tartaric or citric acid should include ferrous sulfate heptahydrate (30% w/v), in which case the resulting organic phase contains only the reaction product, the tartrate, and *tert*-butyl alcohol. Further alkaline treatment (30% NaOH w/v in saturated brine, approximately 2 mL for 1 mmol of tartrate) at 0° (approximately 1 hour) with vigorous stirring leads, after solvent removal, to a crude reaction product that contains fairly pure epoxy alcohol, or epoxy and allylic alcohols from kinetic resolution reactions. Although the original workup procedure[1] used aqueous alkali for tartrate hydrolysis, the saturation of this solution with sodium chloride is strongly recommended to avoid losing partially water-soluble products and to suppress Payne rearrangement. (258)

6.1.7.2. Aqueous Nonacidic Workup

Modified workup procedures have been developed to simplify the acidic procedure and to accommodate the instability of some water-insoluble epoxy alcohols. (18, 42, 59, 347) Thus an alternative procedure entails adding water [20–30 times the weight of Ti(OPr-i)$_4$] to hydrolyze the titanium complex and stirring (30–60 minutes) until room temperature is reached. Hydrolysis of the tartrate is performed in situ by adding an alkaline hydroxide solution (30%

NaOH w/v in saturated brine) (1 mL for 1 mmol of tartrate) and stirring vigorously until phase separation occurs (addition of a small amount of methanol, ca. 5% v/v, can help achieve the separation). After drying the organic phase over sodium sulfate or magnesium sulfate, removal of the solvent gives a crude reaction mixture containing the epoxy alcohol, TBHP, and *tert*-butyl alcohol.

When dealing with very acid-sensitive products, the alkaline solution (10% NaOH w/v in saturated brine, 1–2 mL for 1 mmol of tartrate) and diethyl ether (10% v/v) are added directly to the reaction and the mixture is stirred to hydrolyze both the complex and the tartrate ester. The addition of magnesium sulfate and Celite gives a solution containing the epoxy alcohol and TBHP; the latter can be removed as described above. (18)

6.1.7.3. Nonaqueous Workup
When the product is very water soluble, a nonaqueous workup procedure must be used. A solution of citric acid monohydrate [1 equivalent relative to Ti(OPr-i)$_4$] in acetone-ether (11% w/v in 1:9 mixture) or ether (4% w/v) is added to the reaction mixture. After stirring, solvent removal, and filtration through a pad of Celite, a crude reaction product is obtained that contains the water-soluble epoxy alcohol, tartrate, and TBHP. These last two substances must be removed in the purification step. It is important for acid-sensitive compounds that the molar amount of citric acid used be equal to or slightly less than that of Ti(OPr-i)$_4$ to avoid excess acid in the solution.

An alternative workup useful for both acid-sensitive and water-soluble epoxy alcohols uses triethanolamine [1.5 equivalents relative to Ti(OPr-i)$_4$] to neutralize the acidity of the titanium species, and dimethyl sulfide to reduce the excess TBHP. (347) The cold reaction mixture is then quickly filtered through a pad of silica gel and eluted with ether. Removal of solvents under vacuum leads to a crude mixture containing the product, tartrate, and *tert*-butyl alcohol.

6.1.7.4. In Situ Derivatization
This procedure is useful only for the products of a catalytic asymmetric epoxidation; the amounts of isopropyl alcohol and tartrate present in the stoichiometric procedure make in situ derivatization impractical. It is also necessary to destroy excess TBHP before doing any in situ derivatization because the hydroperoxide reacts with most alkylating and acylating agents, whereas *tert*-butyl alcohol does not.

Trimethyl phosphite is the recommended reagent for reducing excess TBHP because it reacts completely and rapidly at low temperature, and because both trimethyl phosphite and trimethyl phosphate are volatile and can be removed under high vacuum. Care should be taken not to use excess trimethyl phosphite, particularly for a subsequent sulfonation, because epoxy sulfinates

could be formed. The destruction of TBHP should be monitored by TLC eluting with 40% ethyl acetate/hexane using tetramethylphenylenediamine spray (10% w/v in methanol:water:ethyl acetate 128:28:1 mixture).

Two important derivative classes are the *p*-nitrobenzoates (PNB) and *p*-toluenesulfonates. Although both derivatives are useful synthetic intermediates, *p*-nitrobenzoates are especially useful because they are easily isolated and are usually crystalline. Enhancement of optical purity is often possible by recrystallization of *p*-nitrobenzoates. Furthermore, epoxy alcohol *p*-nitrobenzoates undergo most of the ring-opening reactions of the free substance. (137)

Derivatization is carried out on the catalytic epoxidation mixture when the reaction is found to be completed (TLC). The mixture is cooled to – 20°, and trimethyl phosphite is carefully added until all TBHP is destroyed, taking care that the temperature does not rise above – 20°. The mixture is then treated with triethylamine (1.2 equivalents to the original amount of allylic alcohol), 4-(*N,N*-dimethylamino)pyridine (0.05 equivalent), and a solution of the derivatizing agent (acyl or sulfonyl chloride, 1 equivalent) in dichloromethane, and allowed to stand (usually at – 20°) until the reaction is completed. The reaction mixture is filtered through a pad of Celite. The filtrate is successively washed with aqueous tartaric acid (10% w/v), saturated sodium bicarbonate and saturated brine, dried over magnesium sulfate, and concentrated. Chromatographic purification and/or crystallization of the crude mixture yields the pure derivatives.

7. Experimental Procedures

7.1.1. (2R,3R)-2,3-Epoxy-1-octadecanol (Stoichiometric Epoxidation of an E Allylic Alcohol) (321)

Freshly distilled titanium tetraisopropoxide (3.8 mL, 12.7 mmol) was added to dichloromethane (115 mL), and the resulting solution was cooled to a temperature between – 30 and – 20° (dry ice/ CCl_4). Freshly distilled (S,S)-(–)-diethyl tartrate (2.89 mL, 16.9 mmol) was then added. The resulting mixture was stirred for 15 minutes, and then a solution of (E)-octadec-2-en-1-ol (2.83 g, 10.6 mmol) in dichloromethane (20 mL) was added. Ten minutes later tert-butyl hydroperoxide solution (8.7 mL of a 3.64 M solution in toluene, 31.7 mmol) was added, and the reaction mixture was then stored in a – 20° freezer for 24 hours. The reaction was quenched by addition of dimethyl sulfide (3 mL, 41 mmol). The resulting mixture was stirred at – 20° for 30 minutes, and then saturated aqueous Na_2SO_4 (13 mL) was added. This suspension was allowed to warm to room temperature, then filtered through a pad of Celite and washed with diethyl ether. Concentration of the filtrate provided an oil, which was purified by chromatography on a flash silica gel column with solvent, increasing the polarity from hexane to 5:1 hexane-diethyl ether. The appropriate fractions were combined and concentrated under reduced pressure to give 2.65 g (88%) of the crystalline product, mp 77–78°;

$[\alpha]_D^{23}$ +22.5° (c 0.79, $CHCl_3$) (>95% ee); IR (CH_2Cl_2) 3780, 2915, 2860, 1420, 1250, 1110 cm^{-1};^{1}H NMR δ 3.90 (ddd, J = 12.6, 5.5, 2.5 Hz, 1 H, H_{1a}), 3.61 (ddd, J = 12.6, 4.2, 3.1 Hz, 1 H, H_{1b}), 2.91 (m, 2 H, $H_{2,3}$), 1.65 (dd, J = 7.3, 5.6 Hz, 2 H), 1.23–1.57 (m, 27 H), 0.86 (t, J = 6.6 Hz, 3 H, CH_3); mass spectrum, m/z 284 (M$^+$).
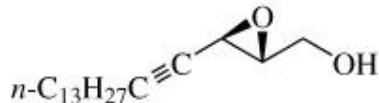
7.1.2. (2R,3R)-2,3-Epoxyoctadec-4-yn-1-ol (Stoichiometric Asymmetric Epoxidation of an E Unsaturated Allylic Alcohol) (103)

A solution of freshly distilled titanium tetra-tert-butoxide (41.1 mL, 107.6 mmol) in absolute dichloromethane (100 mL) was cooled to – 25°. (S,S)-(–)-Diethyl tartrate (35 mL of a 3.14-M solution in absolute dichloromethane, 110 mmol)

was added over 15 minutes. After an additional 15 minutes at – 25°, a solution of (E)-octadec-2-en-4-yn-1-ol (15.0 g, 56.7 mmol) in absolute dichloromethane was added at such a rate (approximately 60 minutes) that the mixture remained homogeneous. This was followed by the addition of *tert*-butyl hydroperoxide (34 mL, 3.79 M in absolute toluene, 129 mmol). After 4–5 hours at – 30°, 10% aqueous tartaric acid (500 mL) was added and the mixture was warmed to room temperature. Dilution with diethyl ether (1 g/L), washing with 10% aqueous tartaric acid (2 × 500 mL) and saturated NaCl solution (2 × 750 mL), drying (MgSO$_4$), and concentration under reduced pressure afforded a yellow oil. Separation of the product by flash silica gel column chromatography gave 1.05 g (6.6%) of unreacted (E)-octadec-2-en-4-yn-1-ol and 12.6 g [86%, based on recovered (E)-octadec-2-en-4-yn-1-ol] of the crystalline product. Two recrystallizations from hexane (–10°) gave pure

(2R,3R)-2,3-epoxyoctadec-4-yn-1-ol, mp 55–56°; $[\alpha]_D^{25}$ –41.5° (c 2.05, CHCl$_3$)

(100% ee); IR (KBr) 3300 (br), 3180, 3000, 2960, 2850, 2240, 1460, 1320, 1070, 1030, 875, 725 cm^{-1};^{1}H NMR (CDCl)$_3$ δ 3.94 (ddd, J = 12.9, 4.9, 2.2 Hz); with D$_2$O : dd, J = 12.9, 3.4 Hz, H-C1), 3.70 (ddd, J = 12.9, 7.9, 3.4 Hz; with D$_2$O : dd, J = 12.9, 2.2 Hz, H-C1), 3.43 (q, J = 1.7 Hz, H-C3), 3.27 (ddd, J = 3.4, 2.2, 1.7 Hz, H-C2), 2.20 (td, J = 7.0, 2, 1.7.Hz, H-C6), 1.55 (m, exchangeable with D$_2$O , OH), 1.26 (m, 22 H), 0.88 (t, J = 6.7 Hz, 3 H-C18); ^{13}C NMR δ 85.6, 75.8 (2 s, C-4, C-5), 60.4 (t, C-1), 60.0 (d, C-3), 43.1 (d, C-2), 31.9 (t, C-16), 29.6–28.3 (9 t, C-7–C-15), 22.6 (t, C-17), 18.7 (t, C-6), 14.0 (q, C-18); CI-mass spectrum, m/z 281 (M + 1)$^+$. Anal. Calcd for C$_{18}$H$_{32}$O$_2$: C, 77.09; H, 11.50. Found: C, 76.81; H, 11.44.
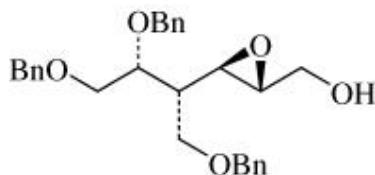
7.1.3. 4,5-Anhydro-3-deoxy-3-[(phenylmethoxy)methyl]-1,2-bis-O-(phenyl methyl)galactiol (Stoichiometric Asymmetric Epoxidation of a Chiral E Allylic Alcohol) (87)

(2E,4R,5R)-5,6-bis(Phenylmethoxy)-4-[(phenylmethoxy)-methyl]-2-hexen-1-ol (12.5 g, 28.7 mmol) was dissolved in anhydrous dichloromethane (287 mL) and cooled to – 20° under argon. To this stirred solution were sequentially added (S,S)-(–)-diethyl tartrate (8.88 g, 43.1 mmol), titanium tetraisopropoxide (9.79 g, 34.4 mmol), and *tert*-butyl hydroperoxide (21.0 mL of a 3.4 M solution in dichloromethane, 63.1 mmol). The reaction mixture was kept at – 20° for 16 hours, quenched at that temperature with 10% aqueous tartaric acid solution (75 mL), and vigorously stirred for 1 hour at 25°. The resulting precipitate was

filtered (Celite), and the filtrate was dried over Na_2SO_4. Filtration followed by concentration gave an oily residue, which was diluted with diethyl ether (250 mL), cooled to 0°, and treated with NaOH solution (1 N, 80 mL). The resulting two-phase mixture was vigorously stirred at 0° for 30 minutes, and the organic phase was separated and washed with aqueous HCl (1 N, 30 mL), saturated aqueous $NaHCO_3$ (2 × 25 mL), and brine (50 mL). Drying ($MgSO_4$), concentration and flash column chromatography (silica, 30% ethyl acetate in petroleum ether) gave 9.65 g (75%) of the product, $[\alpha]_D^{20}$ +13.6° (c 0.73, MeOH);

IR (film) 3460, 3080, 3060, 3030, 2940, 2860, 1600, 1580, 1500, 1480, 1450, 1360, 1200, 1100, 1020, 900, 670 cm^{-1}; ^{1}H NMR(C_6D_6) δ 7.40–7.05 (m, 15 H, aromatic), 4.82 (d, J = 11.6 Hz, 1 H, PhCH$_2$O), 4.56 (d, J = 11.6 Hz, 1 H, PhCH$_2$O), 4.37 (s, 2 H, PhCH$_2$O), 4.19 (s, 2 H, PhCH$_2$O), 4.05 (m, 1 H, CHO), 3.75–3.50 (m, 5 H, CHO, CH$_2$O), 3.06 (dd, J = 8.6, 2.1 Hz, 1 H, CH epoxide), 2.83 (m, 1 H, CH epoxide), 1.89–1.81 (m, 1 H, CH), 1.61 (br s, 1 H, OH); CI-mass spectrum, m/z calculated for $C_{28}H_{32}O_5$ + H, 449.2328, found 449.2321 (M + H).
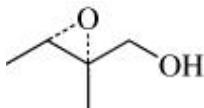
7.1.4. (2s,3s)-2,3-Epoxy-2-methyl-1-butanol (Stoichiometric Asymmetric Epoxidation of a 2,3-Disubstituted E Allylic Alcohol) (347)

To a solution of (E)-2-methyl-2-buten-1-ol (2.57 g, 29.8 mmol) in dichloromethane (100 mL) at – 20° were added (R,R)-(+)-diethyl tartrate (1.43 mL, 1.78 g, 8.35 mmol) and titanium tetraisopropoxide (1.77 mL, 1.69 g, 6.00 mmol). After 15 minutes, the solution was cooled to – 30°, and *tert*-butyl hydroperoxide (8.2 mL of a 4.0 M solution in benzene) was added in one portion. The solution was stirred at – 40 to – 30° for 30 minutes and then placed in a – 20° freezer. After 10 hours at – 20°, dimethyl sulfide (3.6 mL) was added, and the reaction mixture was kept at – 20° an additional 5 hours. Triethanolamine (9 mL of a 1.0 M solution in dichloromethane) was added, and the solution was stirred for 30 minutes at 0°. The solution was filtered through silica gel (75 g) in a sintered glass funnel and eluted with diethyl ether (500 mL). Concentration of the filtrate and bulb-to-bulb distillation (oven temperature 120°, 5 mm Hg) of the residue gave 2.33 g (77%) of the product as a colorless oil, $[\alpha]_D^{20}$ –22.2° (c 3.0, CH$_2$Cl$_2$) (94% ee); IR (film) 3420 (br), 3000, 2970, 2930, 2880, 1460, 1380, 1030, 855 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 3.68 and 3.55 (AB quartet, 2 H, J = 12.3 Hz, CH$_2$OH), 3.16 (q, 1 H, J = 6.6 Hz, CHCH$_3$), 2.64 (br s, 1 H, OH), 1.32 (d, 3 H, J = 6.6 Hz, CHCH$_3$), 1.29 (s, 3 H, CHCH$_3$); ^{13}C NMR(CDCl$_3$) d 65.5, 60.9, 55.9, 13.8, 13.4.
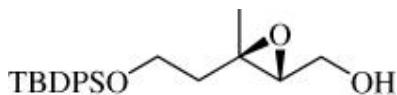
7.1.5. 5-[(tert-Butyldimethylsilyl)oxy]-3-methyl-(2R,3R)-2,3-epoxypentan-1-ol (Stoichiometric Asymmetric Epoxidation of a 3,3-Disubstituted Allylic Alcohol) (255)

Freshly distilled (S,S)-(–)-diethyl tartrate (3.6 mL, 20.6 mmol) was added to a – 20° solution of titanium tetraisopropoxide (4.13 mL, 13.8 mmol) in dichloromethane (60 mL). The solution was stirred for 20 minutes at – 20°. A solution of (2E)-5-[(tert-butyldimethylsilyl)oxy]-3-methyl-2-penten-1-ol (3.02 g, 13.1 mmol) in dichloromethane (50 mL) followed by tert-butyl hydroperoxide (26.2 mmol, 6.6 mL of 3.98 M solution in toluene) was then added dropwise. The mixture was left in a – 20° freezer for 17 hours before being quenched with saturated aqueous Na_2SO_4 (5 mL). The mixture was stirred vigorously and then filtered through Celite and evaporated. The residue was partitioned between diethyl ether (80 mL) and saturated aqueous NaCl (80 mL) and then cooled to 0°. Aqueous NaOH (10 mL of 0.5 N solution) was added and the mixture was stirred vigorously for 1.5 hours at 0° until analytical TLC showed complete disappearance of (S,S)-(–)-diethyl tartrate. The layers were separated and the aqueous phase was washed with ether (50 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The crude epoxide was purified by flash chromatography (50-mm column, 1:1 hexane–ether) to afford 2.63 g (81%) of the product, $[\alpha]_D^{19}$ +2.1° (c 1.59, $CHCl_3$ (>95% ee); IR (film) 3340, 2950, 2926, 2858, 1470, 1256, 1098, 872, 772 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91–3.63 (m, 4 H, H_1 and H_5), 3.06 (dd, J = 7, 4 Hz, 1 H, H_2), 1.90 (dt, J = 14, 6 Hz, 1 H, H_{4a}), 1.71 (t, J = 7 Hz, 1 H, OH), 1.65 (dt, J = 14, 6 Hz, 1 H, H_{4b}), 1.34 (s, 3 H, H_6), 0.90 (s, 9 H, t-Bu), 0.06 (s, 6 H, $SiMe_2$); ^{13}C NMR($CDCl_3$) δ 63.2, 61.3, 59.8, 59.5, 41.4, 25.8, 18.1, 17.2, – 5.5; mass spectrum, m/z 246 (M^+). Anal. Calcd for $C_{12}H_{26}O_3Si$: C, 58.49; H, 10.63. Found: C, 58.28; H, 10.89.
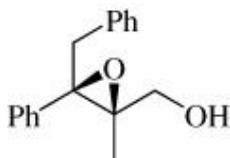
7.1.6. (2R,3R)-3,4-Diphenyl-2-methyl-2,3-epoxybutan-1-ol (Stoichiometric Asymmetric Epoxidation of a 2,3,3-Trisubstituted Allylic Alcohol) (411)

To a stirred solution of titanium tetraisopropoxide (698 mg, 2.45 mmol) in dichloromethane (20 mL) at – 20° was added (S,S)-(–)-diethyl tartrate (698 mg, 3.07 mmol). The pale yellow solution was stirred at – 20° for 5 minutes followed by the addition of (E)-3,4-diphenyl-2-methyl-2-buten-l-ol (487 mg, 2.04 mmol) and tert-butyl hydroperoxide (0.63 mL of 6.54 M solution in dichloromethane). The solution was stirred at – 20° for 5 hours and the reaction was stopped by addition of saturated Na_2SO_4 (0.5 mL) and diethyl ether (1.5 mL). The mixture was warmed to room temperature and stirred for 3 hours, then filtered through Celite, dried over $MgSO_4$, filtered, and evaporated to give a colorless oil. This residue was dissolved in diethyl ether (20 mL) and this solution stirred vigorously for 30 minutes with a 10% solution of NaOH in saturated NaCl at room temperature. The organic phase was separated, washed with NaCl (2 × 10 mL), dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by flash chromatography to afford 469 mg of the product as a colorless oil (94% ee): IR (film) 3420 (br), 3080, 3060, 3030, 2960, 2920, 1600, 1580, 1490, 1450, 1445, 1375, 1265 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.87–7.15 (m, 10 H), 3.71 (br s, 2 H), 3.14 (ABq, 2 H), 1.67 (s, 1 H, D_2O exchange), 1.00 (s, 3 H).

7.1.7. (2S,3S)-Epoxycinnamyl Alcohol [(2S-trans)-3-Phenyloxiranemethanol] (Catalytic Asymmetric Epoxidation of an Aromatic E Allylic Alcohol) (18)

A flame-dried, 5-L, three-necked flask was fitted with an overhead mechanical stirrer, thermometer, and dropping funnel, flushed with nitrogen, and charged with (R,R)-(+)-diethyl tartrate (6.55 g, 0.028 mol) and dichloromethane (3.5 g/L). After the mixture was cooled to – 20°, activated powdered 4 Å molecular sieves (20 g), titanium tetraisopropoxide (5.55 mL, 5.30 g, 0.019 mol), and tert-butyl hydroperoxide (96.9 mL of 7.7 M solution in dichloromethane, 0.746 mol) were added sequentially. The mixture was stirred at – 20° for 1 hour and a solution of freshly distilled (E)-3-phenylpropen-l-ol (cinnamyl alcohol) (50.0 g, 0.373 mol) in dichloromethane (70 mL) was added dropwise over a period of 1 hour. After 3 hours at – 20°, the reaction was quenched at – 20° with 30 mL of a 10% aqueous solution of sodium hydroxide saturated with sodium chloride. After diethyl ether (400 mL) was added, the cold bath was allowed to warm to 10°. Stirring was maintained at 10°, while $MgSO_4$ (30 g) and Celite (4 g) were added. After a final 15 minutes of stirring, the mixture was allowed to settle and the clear solution was filtered through a pad of Celite and washed with diethyl ether. Azeotropic removal of the tert-butyl hydroperoxide with toluene at reduced pressure and finally subjection

of the residue to high vacuum (0.2 mm Hg) gave a yellow oil. Recrystallization of this material from petroleum ether/ethyl ether at − 20° gave 50.0 g (89%) of slightly yellow crystals, mp $[\alpha]_D^{25}$ −49.6° (c 2.4, CHCl$_3$) (>98% ee); IR (CHCl$_3$) 3580, 3450, 2980, 2920, 2870, 1600, 1450, 1380, 1100, 1070, 1020, 880, 860, 845 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.2–7.5 (m, 5 H), 4.18 (dd, 1 H, J = 3,13 Hz), 3.95 (d, 1 H, J = 3 Hz), 3.81 (dd, 1 H, J = 5.13 Hz), 3.25-3.3 (m, 1 H), 2.2 (br s, 1 H, w$_{1/2}$ = 40 Hz).
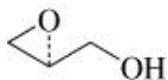
7.1.8. (S)-2,3-Epoxypropanol (Glycidol) (Catalytic Epoxidation to Obtain a Water-Soluble Epoxy Alcohol) (18, 304)

To a stirred mixture of powdered activated 3 Å molecular sieves (3.5 g) and dichloromethane (190 mL) were added (R,R)-(+)-diisopropyl tartrate (1.39 g, 1.25 mL, 5.95 mmol) and allyl alcohol (5.81 g, 6.8 mL, 100 mmol, stored over 3 Å sieves). The solution was stirred and cooled to − 5°, and titanium tetraisopropoxide (1.4 g, 1.5 mL, 5 mmol) was added. The reaction mixture was stirred at − 5 ± 2° for 10–30 minutes, and then 80% technical grade cumene hydroperoxide (36 mL, » 200 mmol, dried over 3 Å sieves prior to use) was added slowly (30 minutes) via a dropping funnel. The mixture was stirred under N$_2$ at − 5 ± 2° for 5 hours. Triethanolamine (10 mL of 1 M solution in dichloromethane) was added, and the mixture was stirred for 30 minutes at − 5°. The cooling bath was removed, and after 15 minutes the mixture was filtered through a pad of Celite over a layer (0.5 cm) of flash silica gel. The pad was rinsed with diethyl ether (500 mL). After the solvent was removed on a rotary evaporator, the crude product was distilled quickly through a Bantamware simple distillation apparatus, collecting all material with a boiling point of about 50° at 7–8 mm Hg of pressure. This distillate was redistilled through a Bantamware 10-cm Vigreux column, and 3.77 g (51%) of the product was collected at bp 49–50° (7.7 mm Hg). [α]$_D$ − 13.02° (neat) (>86% ee). The ^{1}H NMR (CDCl$_3$) spectrum was identical with that of glycidol except that it showed the presence of small amounts of cumyl alcohol and cumene.

7.1.9. (R)-2,3-Epoxypropyl p-Nitrobenzoate (Catalytic Asymmetric Epoxidation With in situ Derivatization) (18)

Epoxidation of allyl alcohol was carried out as described above on a 1.0 mol scale with (R,R)-(+)-diisopropyl tartrate. After 6 hours at – 5 ± 2°, the mixture was cooled to – 20° and carefully treated with trimethyl phosphite (180 mL, 189 g, 1.5 mol) added over a period of 1 hour, taking care that the temperature did not rise above – 20°. The mixture was then treated with triethylamine (170 mL, 123 g, 1.2 mol) and a solution of p-nitrobenzoyl chloride (185.6 g, 1 mol) in dichloromethane (250 mL) and stirred for 1 hour at 0°. After filtration through a pad of Celite, the filtrate was washed with 10% aqueous tartaric acid (2 × 250 mL), saturated NaHCO$_3$ (3 × 250 mL), and brine (2 × 250 mL). The organic phase was dried over Na$_2$SO$_4$, filtered through a small pad of silica gel, and concentrated to an oil (first at 12 mm Hg, then at 0.2 mm Hg at 60°) to remove any remaining cumene, 2-phenylpropan-2-ol, trimethyl phosphite, and trimethyl phosphate. The oil solidified on standing and was recrystallized twice from diethyl ether to give 135.7 g (61%) of the product, mp 59.5–60.0°; $[\alpha]_D^{20}$ –38.8° (c 3.02, CHCl$_3$) (92–94% ee); IR: 3120, 2970, 2920, 2860, 1730, 1610, 1520, 1460 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.21–8.37 (m, 4 H), 4.76 (dd, 1 H, J = 3, 13 Hz), 4.21 (dd, 1 H, J = 7, 13 Hz), 3.37 (m, 1 H), 2.96 (t, 1 H, J = 5 Hz), 2.77 (dd, 1 H, J = 5, 3 Hz). Anal. Calcd for C$_{10}$H$_9$NO$_5$: C, 53.81; H, 4.06; N, 6.28. Found: C, 53.68; H, 4.20; N, 6.23.

7.1.10. (1S,2S)-(2-Methyl-1,2-epoxycyclotetradecyl)methanol (Stoichiometric Asymmetric Epoxidation of a Cyclic Allylic Alcohol) (412)

To dichloromethane (80 mL) at – 23° solution under an argon atmosphere was added titanium tetraisopropoxide (2.76 mL, 9.28 mmol), followed by dropwise addition of (R,R)-(+)-diethyl tartrate (2.07 mL, 12.07 mmol). The mixture was stirred for 5 minutes, and then (E)-(2-methyl-1-cyclotetradecenyl)methanol (2.211 g, 9.28 mmol) in dichloromethane (15 mL) was added dropwise followed by anhydrous tert-butyl hydroperoxide (3.18 mL of 3.5 M solution in 1,2-dichloroethane, 11.14 mmol) at – 23°. The reaction mixture was stirred for 1.5 hours at – 23° and then stored in a freezer at – 30° for 18.5 hours. The mixture was poured into a – 23° solution of water (5.0 mL) and acetone (195 mL) and stirred at – 23° for 45 minutes and at room temperature for 2 hours. The clear solution was filtered through Celite, concentrated, and extracted with dichloromethane. The combined extracts were dried over potassium carbonate, filtered, and concentrated under reduced pressure. Flash chromatography on silica gel (7:1 hexane–diethyl ether) afforded 1.815 g (77%) of the product as a white solid, mp 62.5 – 65.0° $[\alpha]_D^{25}$ –7.13° (c

3.49, CHCl$_3$) (>90% ee). IR (film) 3350, 2920, 2850, 1470, 1050 cm^{-1}; ^{1}H NMR δ 1.23–1.60 (env, ring CH$_2$), 1.61–2.13 (m), 2.26 (t, J = 6.0 Hz, CH$_2$), 3.80 (ABq, J = 3.6 Hz, CH$_2$O). Anal. Calcd for C$_{16}$H$_{30}$O$_2$: C, 75.54; H, 11.89. Found, C, 75.47; H, 11.94.
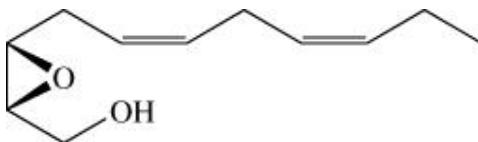
7.1.11. (2R,3S)-(5Z,8Z)-2,3-Epoxy-5,8-undecadien-1-ol (Stoichiometric Asymmetric Epoxidation of a Z-Allylic Alcohol and Derivatization to Increase Optical Purity) (110)

Titanium tetraisopropoxide (2.15 mL, 7.23 mmol) was added dropwise to stirred dry dichloromethane (60 mL) at – 23° under an argon atmosphere. To this was added (*S,S*)-(–)-diethyl tartrate (1.74 g, 8.43 mmol). The mixture was stirred for 5 minutes at 23°. A solution of (2*Z*,5*Z*,8*Z*)-2,5,8-undecatrien-1-ol (1.0 g, 6.02 mmol) in dry dichloromethane (2 mL) and 4.4 M *tert*-butyl hydroperoxide (3.42 mL, 15.1 mmol, dichloromethane) were added to the stirred mixture at – 23°. The mixture was left to stand for 42 hours at – 23°. The reaction was quenched by the addition of 10% aqueous tartaric acid (15 mL) at – 23° with stirring. After stirring for 30 minutes at – 23°, the mixture was warmed to room temperature and stirred for 1 hour. The organic layer was separated, washed with water, dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The residue was purified by silica gel chromatography and distilled (bp 96–97°/0.15 mm Hg) to afford 886 mg (81%) of the product, $[\alpha]_D^{23}$ +9.27° (*c* 0.90, CHCl$_3$) (81% ee). To a solution of this material (852 mg, 4.68 mmol) in dry diethyl ether (20 mL) was added 3,5-dinitrobenzoyl chloride (1.4 g, 6.09 mmol) and dry pyridine with stirring and ice cooling. The stirring was continued overnight at – 0°. The mixture was poured into ice water and extracted with diethyl ether. The ether solution was washed with saturated aqueous CuSO$_4$, water and brine, dried (MgSO$_4$), and concentrated under reduced pressure. This residue was repeatedly recrystallized from *n*-hexane-ether (9:1) until constant optical rotation was reached, giving 793 mg (45.1 mmol) of pure (2*R*,3*S*,5*Z*,8*Z*)-2,3-epoxy-5,8-undecadienyl 3, 5-dinitrobenzoate as colorless leaflets, mp 38–39°; $[\alpha]_D^{22}$+5.68° (*c* 0.37, diethyl ether). K$_2$CO$_3$ (60 mg, 0.43 mmol) was added to a solution of (2*R*,3*S*,5*Z*,8*Z*)-2,3-epoxy-5,8-undecadienyl 3,5-dinitrobenzoate (610 mg, 1.62 mmol) in methanol (6 mL) with stirring and ice cooling. The stirring was continued for 30 minutes at 0°. The mixture was concentrated under reduced pressure to remove MeOH. The residue was diluted with water and extracted

with diethyl ether. The ether solution was washed with water and brine, dried (MgSO$_4$), and concentrated under reduced pressure. The residue was chromatographed over silica gel and distilled (bp 90–91°/0.11 mm Hg) to give 257 mg (87%) of the product, $[\alpha]_D^{122}$+11.6° (*c* 0.84, CHCl$_3$ (>99% ee); IR 3450 (br), 3040, 2990, 2960, 2900, 1655, 1460, 1400, 1040, 975, 920 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 0.96 (t, *J* = 7 Hz, 3 H), 1.70–2.50 (m, 4 H), 2.50–3.20 (m 4 H), 3.25–3.80 (m, 3 H), 5.0–5.7 (m, 4 H); Anal. Calcd for C$_{11}$H$_{18}$O$_2$; C, 72.49; H, 9.96. Found: C, 72.22; H, 10.11.
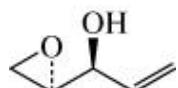
7.1.12. (2R,3S)-1,2-Epoxy-4-penten-3-ol [catalytic Asymmetric Epoxidation and Kinetic Resolution of a meso-Allylic Alcohol] (279)

To a – 23° (dry ice– CCl$_4$) cooled mixture of powdered 4 Å molecular sieves (4.3 g) and dichloromethane (250 mL) were added titanium tetraisopropoxide (5.0 mL, 16.8 mmol) and (*R,R*)-(+)-diisopropyl tartrate (4.50 mL, 21.5 mmol) via syringe. After stirring at – 23° for 10 minutes, divinyl carbinol (20 g, 238 mmol) was added via cannula, followed by *tert*-butyl hydroperoxide (160 mL of 3.0 M solution in isooctane, 480 mmol) in several portions via syringe. The reaction vessel was then placed in a – 15° freezer and stored for 118 hours. At freeze temperature, aqueous Na$_2$SO$_4$ (17 mL) was added, and the mixture was diluted with diethyl ether (250 mL). After stirring at ambient temperature for 2 hours, the resulting slurry was filtered through a pad of Celite, washing with several portions of ether. The Celite pad was transferred to an Erlenmeyer flask, heated gently with diethyl ether, and the supernatant filtered through a second fresh pad of Celite. Most of the solvent was removed on a rotary evaporator with cooling to avoid undue loss of the somewhat volatile product. The resulting oil was subjected to flash column chromatography followed by distillation at aspirator pressure to afford 23.6 g of the desired epoxide, which was about 50% pure by NMR. A second flash column chromatography (3:1 pentane—ether) in two batches provided 13.1 g (50%) of the product as a clear, colorless oil, $[\alpha]_D^{23}$+48.8° (c 0.73, CHCl$_3$) (> 99% ee), IR (film) 3400 (br), 3019, 1108 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 5.75-5.89 (ddd, *J* = 17.2, 10.5, 6.2 Hz, 1 H), 5.34 (dt, *J* = 17.2, 1.4 Hz, 1 H), 5.22 (dt, *J* = 10.5, 1.3 Hz, 1 H), 4.26 (br s, 1 H), 3.05 (dd, *J* = 3.3, 3.1 Hz, 1 H), 2.70–2.78 (m, 2 H), 2.61 (br s, 1 H); ^{13}C NMR(CDCl$_3$) δ 135.6, 117.3, 70.3, 53.9, 43.5; mass spectrum m/z (percent) 99 (M-H, 0.4), 57 (100).
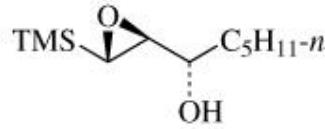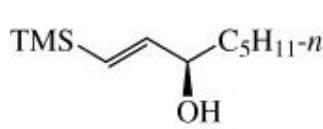
7.1.13. (1E,3R)-1-Trimethylsilyl-1-octen-3-ol And (1S,2S,3S)-1-Trimethylsilyl-1,2-epoxyoctan-3-ol (Stoichiometric Kinetic Resolution of a Secondary E Allylic Alcohol) (13)

To a solution of titanium tetraisopropoxide (4.6 mL, 15.6 mmol) in dichloromethane (140 mL) was added (R,R)-(+)-diisopropyl tartrate (3.94 mL, 18.72 mmol) and the resulting solution was stirred for 10 minutes at – 20°. After addition of (E)-1-trimethylsilyl-1-octen-3-ol (6.29 g, 15.6 mmol), the mixture was stirred for an additional 10 minutes. *tert*-Butyl hydroperoxide (4.46 mL of 3.5 M solution in dichloromethane, 15.6 mmol, 1 equiv) was added slowly and the solution was stirred at – 20° for 7 hours. Dimethyl sulfide (3.94 mL, 46.8 mmol) was added slowly and the mixture was stirred for 30 minutes at – 20°. tartaric acid aqueous solution (10%, 280 mL), diethyl ether (280 mL), NaF (10.9 g), and Celite (6.2 g) were added sequentially. The resulting mixture was stirred for 30 minutes at room temperature, filtered through a pad of Celite with diethyl ether, and concentrated. The residue was chromatographed on triethylamine-deactivated silica gel to afford 2.64 g (42%) of (R)-(E)-1-trimethylsilyl-1-octen-3-ol, $[\alpha]_D^{25}$ –9.8° (c 1.10, CHCl$_3$) (> 99% ee),

and 2.75 g (42%) of (1S,2S,3S)-1-trimethylsilyl-1,2-epoxyoctan-3-ol, $[\alpha]_D^{25}$ –7.5° (c 1.04, CHCl$_3$) (> 99% ee), IR (neat) 3420, 2390, 1247 cm^{-1}; ^{1}H NMR(CCl$_4$, C$_6$H$_6$, D$_2$O) δ 0.03 (s, 9 H), 0.93 (t, 3 H, J = 4.8 Hz), 1.07–1.72 (m, 8 H), 2.26 (d, 1 H, J = 4.0 Hz), 2.71 (t, 1 H, J = 4.0 Hz), 3.30–3.70 (m, 1 H).
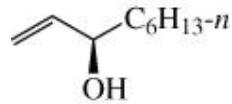
7.1.14. (R)-Non-1-en-3-ol (Catalytic Kinetic Resolution of a Secondary Allylic Alcohol) (18)

To a room-temperature solution of (±)-1-nonen-3-ol (284 mg, 2 mmol) and (R,R)-(+)-dicyclododecyl tartrate (135.6 mg, 0.3 mmol) in dichloromethane (8 mL) were added powdered and activated 3 Å molecular sieves (60 mg) and a saturated hydrocarbon internal standard (n-decane, 80 µL) for gas chromatographic (GC) monitoring of percent conversion. The stirred mixture, maintained under an inert atmosphere, was cooled to – 10 to – 20°, treated with titanium tetraisopropoxide (60 µL, 0.2 mmol) and allowed to stir for 20–30

minutes at – 20°. During this time, a small aliquot (ca. 100 μL) was removed, diluted with 100 μL of ether, and quenched into 200 μL of a freshly prepared aqueous solution of $FeSO_4 \cdot 7\,H_2O$ (330 mg, 1.2 mmol) and citric acid (110 mg, 0.6 mmol) diluted to 10 mL with deionized water at ~ 0°, to provide a T_0 GC reference sample. The reaction was then treated with *tert*-butyl hydroperoxide [190 μL, 5.8 M solution in isooctane (dried with freshly activated 3 Å pellets for 30 minutes prior to use), 1.1 mmol] added by gastight syringe. The reaction was maintained at – 22 ± 2° and periodically monitored by GC. After 13 days (51% conversion), the reaction was quenched with 2 mL of an aqueous solution of $FeSO_4$ and citric acid at – 20° and stirred vigorously without cooling for 30 minutes until two clear phases appeared. The phases were separated and the aqueous phase was extracted twice with dichloromethane. The combined organic phases were washed with saturated brine and dried ($MgSO_4$). After precipitation of most of the crystalline dicyclododecyl tartrate, the crude product was then purified by flash chromatography to give 95 mg of

(*R*)-non-1-en-3-ol (99% based on percent conversion, 33% overall), $[\alpha]_D^{25}$

–19.1° (*c* 6.7, EtOH) (>98%ee).
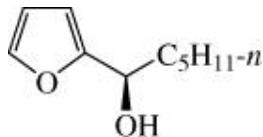
7.1.15. (R)-1-(2-Furyl)hexan-1-ol (Catalytic Kinetic Resolution of a Secondary Furyl Carbinol) (413)

To a mixture of crushed 4 Å molecular sieves (5 g) and 0.2 equiv of titanium tetraisopropoxide (7.35 mL, 24.7 mmol) in dichloromethane (100 mL) at – 21° was added 0.24 equiv of (*R,R*)-(+)-diisopropyl tartrate (6.23 mL, 29.6 mmol). The mixture was stirred for 10 minutes at – 21° and cooled to – 30°. (±)-1-(2-Furyl)hexan-1-ol (20.7 g, 123 mmol) dissolved in dichloromethane (20 mL) was added and the mixture was stirred at temperatures between – 30 and – 20° for 30 minutes. The mixture was cooled again to – 30°, and 0.6 equiv of *tert*-butyl hydroperoxide (17.0 mL, 4.35 M solution in dichloromethane, 74.0 mmol) was added slowly. After stirring for 14 hours at – 21°, dimethyl sulfide (5.43 mL, 74.0 mmol) was added slowly and the mixture was stirred for 30 minutes at – 21°. To this mixture were added 10% aqueous tartaric acid (5 mL), diethyl ether (100 mL), and NaF (30 g), and the resulting mixture was vigorously stirred for 2 hours at room temperature. The white precipitate was filtered through a pad of Celite and washed with diethyl ether (100 mL). The filtrate was concentrated to give an oil, which was dissolved in diethyl ether (200 mL) and treated with NaOH (3 N, 100 mL) for 30 minutes at 0° with vigorous stirring. The organic layer was washed with brine, dried ($MgSO_4$),

and concentrated to give an oil, which was passed through a short silica gel column to afford 7.94 g (38 %) of the product, $[\alpha]_D^{25}$ +13.8° (c 1.07, CHCl$_3$)(>95%ee).
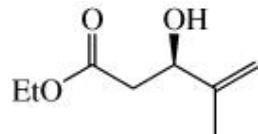
7.1.16. Ethyl (3R)-3-Hydroxy-4-methyl-4-pentenoate (Stoichiometric Kinetic Resolution of a Secondary 2-Substituted Allylic Alcohol) (414)

A solution of (R,R)-(+)-diisopropyl tartrate (42 g, 179 mmol) in anhydrous dichloromethane (1 g/L) at – 25° was treated with freshly distilled titanium tetraisopropoxide (40.8 g, 143 mmol). After 15 minutes, (±)-ethyl 3-hydroxy-4-methyl-4-pentenoate (18.9 g, 119 mmol) was added, and the mixture was stirred for an additional 15 minutes. tert-Butyl hydroperoxide (358 mmol, 125 mL of a 2.86 M solution in 1,2-dichloroethane) was added slowly, and the reaction temperature was maintained at – 25° for 96 hours (at which time the reaction was 57% complete by GC analysis). The reaction mixture was poured into a stirred solution of water (50 mL) in acetone (2 g/L) at – 50° and, after being allowed to reach ambient temperature, was filtered through Celite. Removal of the solvents in vacuo followed by fractional distillation (60–65°, 1 mm Hg) gave a mixture of ethyl (3R)-3-hydroxy-4-methyl-4-pentenoate and the corresponding epoxy ester, which were separated by silica gel flash chromatography to afford 2.95 g (16 %) of the pentenoate as a clear oil, $[\alpha]_D^{25}$ +14.6° (c 2.31, EtOH) (>99% ee).
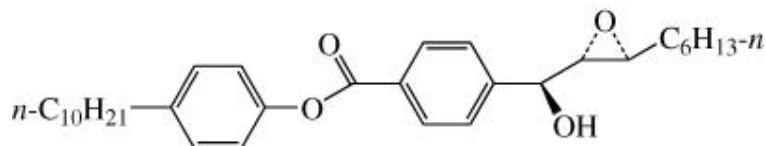
7.1.17. 4-(n-Decyloxy) phenyl 4-[(1S, 2S, 3S)-2,3-Epoxy-1-hydroxynonyl]-benzoate (Stoichiometric Kinetic Resolution of a Secondary Aromatic Allylic Alcohol) (415)

To a cooled solution (–30°) of titanium tetraisopropoxide (5.49 g, 18.44 mmol) in dry dichloromethane (100 mL) was added with stirring (R,R)-(+)-diisopropyl tartrate (4.65 g, 22.1 mmol). The mixture was stirred for 20 minutes. A precooled – 20° solution of 4¢-(n-decyloxy)phenyl 4-[(E)-1-hydroxy-2-nonenyl]benzoate (9.12 g, 18.44 mmol) in dry

dichloromethane (50 mL) was added, and dichloromethane (34 mL) was used to transfer all residual allylic alcohol. The reaction mixture was stirred for 10 minutes before *tert*-butyl hydroperoxide (3.32 mL of a 2.5 M solution in toluene, 8.3 mmol) was added. The reaction flask was stored in a freezer (–25°) for 18 hours. The reaction mixture was then poured over an ice-cold solution of $FeSO_4$ (9.22 g) and water (37 mL). The mixture was then warmed to ambient temperature and stirred for 1 hour. The two layers were separated, and the aqueous layer was washed three times with 50 mL portions of diethyl ether. The combined organic layers were dried over Na_2SO_4, and the solvent was removed in vacuo. The oil obtained was dissolved in a minimum amount of 20% ethyl acetate/hexane solution and was filtered through a pad of silica gel, which was then washed thoroughly with 20% ethyl acetate/hexane. The combined filtrate was concentrated and the crude product was purified by flash chromatography on silica gel with 25% ethyl acetate/hexane as eluant. The product was then recrystallized from hexane at – 20°. The gel obtained was centrifuged at – 20° and the solvent was decanted to afford 3.73 g (79%) of the product, mp 68.9–69.5°; IR (CHCl₃) 3350, 3010, 2930, 2850, 1736, 1510, 1270, 1235, 1185 cm^{-1}; ^{1}H NMR (CDCl₃) δ 0.87 [m 6 H, (RCH_3)₂], 1.15–1.60 [m, 24 H, ArOCH₂CH₂(CH_2)₇CH₃, CHOCH(CH_2)₅CH₃], 1.73 (quint), J = 6.8 Hz, 2 H, ArOCH₂CH_2), 2.40 (d, J = 1.8 Hz, 1 H, ArCHOH), 3.0 (t, J = 3.0 Hz, ArCHOHCHOCH, 1 H), 3.12 (m, 1 H, ArCHOHCHOCH), 3.94 (t, J = 6.5 Hz, 2 H, ArOCH_2), 4.97 (s, 1 H, ArCHOH), 6.91 (d, J = 9.1 Hz, 2 H, ArH), 7.08 (d, J = 9.0 Hz, 2 H, ArH), 7.50 (d, J = 8.2 Hz, 2 H, ArH), 8.18 (d, J = 8.3 Hz, 2 H, ArH); ^{13}C NMR δ 13.9, 14.0, 22.4, 22.6, 25.8, 26.0, 28.8, 29.3, 29.4, 29.5, 31.3, 31.6, 31.9, 55.3, 61.0, 68.6, 70.7, 115.2, 115.3, 126.2, 129.5, 130.4, 144.4, 145.6, 157.0, 165.2; mass spectrum m/z (percent) 510 (M^+,0.49), 147.1 (92), 133.1 (100). Anal. Calcd for $C_{32}H_{46}O_5$: C, 75.42; H, 9.10. Found: C, 75.33; H, 9.15.
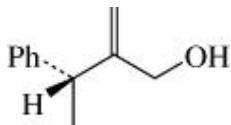
7.1.18. (R)-2-[1-(Phenyl)ethyl]propenol (Stoichiometric Kinetic Resolution of a 2-substituted Chiral Primary Allylic Alcohol) (*416*)

To a cooled (–20°), stirred solution of titanium tetraisopropoxide (5.95 mL, 20 mmol) in dry dichloromethane (200 mL) were added (*R,R*)-(+)-diisopropyl tartrate (5.616 g, 24 mmol) and (±)-2-[1-(phenyl)ethyl]propenol (3.22 g, 20 mmol). The mixture was stirred for 10 minutes and treated with *tert*-butyl hydroperoxide (3.75 mL of a 3.73 M solution in dry dichloromethane, 14 mmol). The reaction was stored in a freezer (–20°) for 18 hours. Acetone (50 mL) was added at – 20° and the mixture was stirred for 5 minutes. Then water (6 mL)

was added and the reaction mixture was vigorously stirred at ambient temperature for 1 hour. The resulting slurry was filtered through a pad of Celite, washing with several portions of diethyl ether. The filtrate was concentrated to give an oil, which was dissolved in ether (50 mL) and treated with NaOH (15% in brine, 20 mL) for 30 minutes at 0° with vigorous stirring. The organic layer was washed with brine, dried (MgSO$_4$), and concentrated to give an oil, which was passed through a silica gel column to afford 700 mg (35%) of the product, $[\alpha]_D^{25}$+98.0° (c 3.20, EtOH) (>95% ee).
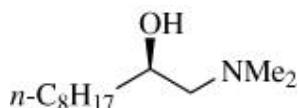
7.1.19. (R)-N,N-Dimethyl(2-hydroxydecyl)amine (kinetic Resolution of Racemic β -Hydroxyamines) (21)

To a mixture of (±)-N,N-dimethyl(2-hydroxydecyl)amine (404 mg, 2.01 mmol) and (R,R)-(+)-diisopropyl tartrate (2.43 mmol, 1.21 equiv) was added dichloromethane (20 mL) followed by titanium tetraisopropoxide (1.20 mL, 4.09 mmol, 2.04 equiv). The mixture was stirred for 30 minutes at room temperature. After this aging period, the flask was cooled, while stirring, in a dry ice/ CCl$_4$ bath (ca. – 20°). To this solution was added tert-butyl hydroperoxide (365 mL, 1.20 mmol, 3.29 M solution in toluene, 0.6 equiv). After stirring for 2 hours at – 20°, the reaction was quenched by adding diethyl ether (20 mL), water (0.8 mL), and a 40% NaOH solution (0.8 mL). This mixture was vigorously stirred for 4–5 hours at room temperature, yielding a gelatinous precipitate which was filtered through a pad of Celite. The precipitate was stirred vigorously in refluxing chloroform for 3 minutes before filtering it again through the Celite pad. The combined filtrates were concentrated to leave a pale yellow viscous oil, which was dried under high vacuum. This oil was triturated with n-hexane (20 mL). The clear supernatant solution was filtered and the filtrate was washed with n-hexane (20 mL). The filtered solid was the optically active N-oxide of dimethyl(2-hydroxydecyl)amine (233 mg, 54%). The hexane extracts were diluted with ether (5 mL), washed with water (~200 mL × 2), and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated to afford 144 mg, (36%) of the product as an oil, $[\alpha]_D^{20}$–3.58° (c 1.65, EtOH) (91% ee).
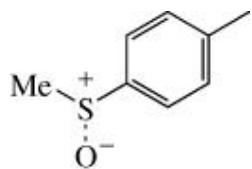
7.1.20. (R)-Methyl p-Tolyl Sulfoxide (Asymmetric Oxidation of a Sulfide) (23)

Titanium tetraisopropoxide (1.49 mL, 5 mmol) and (R,R)-(+)-diethyl tartrate (1.71 mL, 10 mmol) were dissolved at room temperature in dichloromethane (50 mL) under nitrogen. Water (90 mL, 5 mmol) was introduced via syringe. Stirring was maintained until the yellow solution became homogeneous (15–20 minutes) and 0.7 g (5 mmol) of methyl p-tolyl sulfide was added. The solution was cooled to – 20° and *tert*-butyl hydroperoxide (2.75 mL, 2 M solution in dichloromethane, 5.5 mmol) was then introduced. After the reaction was completed (4 hours), water (0.9 mL, 10 equiv) was added dropwise via microsyringe to the solution at – 20°. The mixture was stirred vigorously for 1 hour at – 20° and for 1 hour at room temperature. The white gel was filtered (a small amount of alumina added to the solution helps the filtration) and thoroughly washed with dichloromethane. The filtrate was kept in the presence of NaOH (5%) and brine for 1 hour and then separated. The organic phase was dried over Na_2SO_4 and concentrated to give the crude product, which did not contain sulfone. Chromatography (ethyl acetate, cyclohexane 1:1) of the crude product on silica gel afforded 0.70 g (80%) of the product, $[\alpha]_D^{20}$+132° (c 2, acetone) (90% ee) ($[\alpha]_D^{20}$ +145.5° for enantiomerically pure R isomer).

8. Tabular Survey

Asymmetric oxidations of allylic alcohols, amines, sulfides, and selenides are grouped in Tables I–XVII. Allylic alcohols are classified as nonchiral or chiral and are further subdivided according to their substitution patterns. Within each table, entries are in the order of increasing number of carbon atoms in the substrate, omitting the carbon atoms in nonreacting groups attached to the substrate through a heteroatom. The literature has been reviewed through April 1992.

Reactions were carried out in dichloromethane using *tert*-butyl hydroperoxide as oxidant, titanium tetraisopropoxide as the titanium tetraalkoxide, and dialkyl tartrate as the chiral auxiliary unless noted otherwise. Workup conditions are not described. A dash in the Conditions column indicates that no conditions were given, and a dash in a Product column of the kinetic resolution tables means that the indicated product was not reported. The symbol (—) after a product means that no yield was reported. Optical rotations were measured with the Na D line in chloroform unless noted otherwise.

The following abbreviations are used in the tables:

Ac	acetyl
Aib	α -aminoisobutyryl
Ala	alanyl
Bn	benzyl
Boc	benzyloxycarbonyl
BOM	benzyloxymethyl
Bz	benzoyl
catalytic	catalytic amounts of Ti(OPr-i)$_4$ and DAT were used
CUHP	cumene hydroperoxide
DAT	dialkyl tartrate
(–)-DAT	(*S,S*)-(–)-DAT
(+)-DAT	(*R,R*)-(+)-DAT
DBTA	*N,N¢*-dibenzyltartramide
DCHT	dicyclohexyl tartrate
DCDT	dicyclododecyl tartrate
DET	diethyl tartrate
DIPT	diisopropyl tartrate
DMT	dimethyl tartrate

DNB	3,5-dinitrobenzoyl
EE	1-ethoxyethyl
MEM	methoxyethoxymethyl
MMTr	*m*-methoxytrityl
MOM	methoxymethyl
MPM	*p*-methoxyphenylmethyl
MS	molecular sieves
Nap	naphthyl
Nps	naphthalenesulfonyl
Phe	phenylalanyl
PNB	*p*-nitrobenzoyl
Pro	prolyl
Pyr	pyridyl
SEM	(2-trimethylsilylethoxy)methoxy
stoichiometric	stoichiometric amounts of Ti(OPr-*i*)$_4$ and DAT were used
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
TBHP	*tert*-butyl hydroperoxide
TES	triethylsilyl
THP	tetrahydropyranyl
TI	titanium(IV) isopropoxide
TIPS	triisopropylsilyl
TMS	trimethylsilyl
Tr	trityl
Ts	*p*-toluenesulfonyl

Table I. Asymmetric Epoxidation of Primary Allylic Alcohols

View PDF

Table II. Asymmetric Epoxidation of Bisallylic Alcohols

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Table III. Asymmetric Epoxidation of Alkenylsilanols

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Table IV. Kinetic Resolution of Racemic Primary Allylic Alcohols

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Table V. Asymmetric Epoxidation of Homo-, Bishomo-, and Trishomoallylic Alcohols

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Table VI. Kinetic Resolution of Racemic Secondary Allylic Alcohols

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Table VII. Asymmetric Epoxidation of Chiral Secondary Allylic Alcohols

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Table VIII. Epoxidation and Kinetic Resolution of *meso*-Secondary Allylic Alcohols

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Table IX. Kinetic Resolution of α -Hydroxy-Furans, -Thiophenes, and -Pyrroles

View PDF

Table X. Kinetic Resolution of α -Tosylaminofurans

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Table XI. Epoxidation of Allylic Alcohols with in situ Hydroxy Derivatization

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Table XII. Epoxidation of Allylic Alcohols with in situ Epoxide Opening

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Table XIII. Asymmetric Oxidation of Sulfides and Disulfides

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Table XIV. Asymmetric Oxidation of β -Hydroxy Sulfides

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Table XV. Asymmetric Oxidation of Dithioacetals

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Table XVI. Kinetic Resolution of a Racemic Sulfide

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Table XVII. Asymmetric Oxidation of Selenides

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Table XVIII. Kinetic Resolution of β -Hydroxyamines

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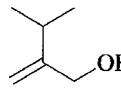TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C₃ ⟍⟍OH	TI (0.05), (+)-DIPT (0.06), 5 hᵃ	O⟍⟍OH (65) 90-92% ee	18, 304
	TI (1.2), (+)-DIPT (1.4), 0°, 24 h	" (15)ᵇ 73% ee	1
TMS⟍⟍OH	TI (1), (−)-DIPT (1.05), −23°	TMS⟍O⟍OH (60) >95% ee	145, 417, 418
	TI (0.03), (+)-DIPT (0.036), −20°, 3.5 d	TMS⟍O⟍OH (90) 99% ee, [α] −25.3°	419
TBDMS⟍⟍OH	(+)-DET	TBDMS⟍O⟍OH (75) >98% ee, [α] −26.9°	420
TIPS⟍⟍OH	(+)-DET	TIPS⟍O⟍OH (70) 98% ee, [α] −12.7°	421
Ph₃Si⟍(D)⟍OH (D)	TI (1), (+)-DIPT (1.25), −20°, 16 h	Ph₃Si⟍O(D)⟍OH (D) (96) 94% ee	422
	TI (1), (−)-DIPT (1.25), −20°, 16 h	(Ph₃)₃Si⟍O(D)⟍OH (D) (—) 92% ee	422
C₄ ⟍⟍OH	TI (1), (+)-DET (1), −20°, 3 d	O⟍⟍OH (—) 88% ee	423
	Catalytic	" (—) 93% ee	424

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (Continued)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TIᶜ (0.08), (−)-DET (0.1), 4 Å, −40 to −20°	O⟍⟍OH (47) >95% ee, [α] +10.62°	131, 425, 426
	TI (1), (−)-DET (1), −30°, 40 h	" (32) >94% ee, [α] +9.8°ᵈ	409, 427, 428
	TI (0.1), (−)-DIPT (0.12)	" (—) 87% ee	429
	TI (1.4), (−)-dibutyl tartrate (1.6), SiO₂, CaHᵃ	" (81) 91% ee	430
CD₂OAc ⟍⟍OH	—, Stoichiometric	O⟍CD₂OAc⟍OH (—) 90% ee	431
CD₂OBn ⟍⟍OH	TI (0.08)ᶜ, (+)-DET (0.1), 4 Å, −20°, overnight	O⟍CD₂OBn⟍OH (75) [α] −10.9° ᵈ	132
	TI (0.08)ᶜ, (−)-DET (0.1), 4 Å, −20°, overnight	O⟍CD₂OBn⟍OH (74) [α] +11.0° ᵈ	131
⟍⟍⟍OH	TI (0.05), (+)-DIPT (0.06), 3 Å, −20°, 2 h	⟍O⟍OH (70) 91% ee, [α] −50.1°	18
	TI (1), (+)-DIPT (1), −20°, 20 h	" (58) [α] −49° ᵉ	432
	(+)-DIPT, −20°, 24 h	" (40) 95% ee, [α] −53.1° ᵉ	433-437
	(+)-DET, (catalytic)	" (—) >91% ee, [α] −35.8°	438
	TI (0.03)ᶠ, (+)-DIPT (0.06), −20 to −15°, 4.2 h	" (91) 95% ee	138

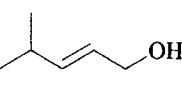TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (Continued)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (–)-DIPT (1), -23°	OH (45) >95% ee, [α] +55° [e]	59, 436, 437
	(–)-DET (catalytic), 3 Å, -23°	" 90%ee	129
(structure) OH / D	TI (0.05), (+)-DIPT (0.06), 4 Å, -15°, overnight	OH (52) [α] -54° [e] / D	439
(structure) D / OH / D	TI (0.05), (+)-DIPT (0.06), 4 Å, -15°, overnight	D / OH (43) [α] -51° [e] / D	439
	TI (0.05), (–)-DIPT (0.06), 4 Å, -15°, overnight	D / OH (43) [α] +48° [e] / D	439
BnO OH	TI (0.05), (+)-DIPT (0.08), -20 to 0°	BnO OH (85) 88% ee	224, 440
	(+)-DIPT	" (—) >95% ee	441
	(+)-DET (stoichiometric), -20°, 24 h	" (84) 98% ee	73, 161, 162, 171
	(+)-DET (stoichiometric),	" (74) [α] -20.3°	282, 442
	TI (1.1), (–)-DET (1.1), -23°, 5 h	BnO OH (80) 98% ee [α] +21.8°	85, 87, 295, 443
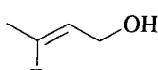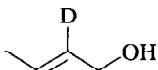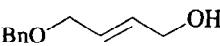
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (Continued)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
MMTrO OH	(+)-DET	MMTrO OH (84) 97% ee	444
	(–)-DET	MMTrO OH (79) 93% ee	444
OBn / O OH	TI (1), (+)-DET (1), -20°, overnight	OBn / O OH (86) 92% ee [α] -15.8°	445, 446
	TI (1), (–)-DET (1), -20°, overnight	OBn / O OH (86) >96% ee [α] +16.4°	445, 446
TBDPSO OH	TI (0.14), (+)-DET (0.2), -20°, 3 d	TBDPSO OH (86) >95% ee [α] -15.3° [d]	247
	Stoichiometric	" (—) >95% ee, [α] -9.6°	438
MeO / MeO OH	TI (1), (+)-DET (1), -23°, 20 h	MeO / MeO OH (81) >97% ee [α] -37.5° [g]	57, 447, 448
Ts(Bn)N OH	TI (1.2), (–)-DIPT (1.5), -20°, 2.5 h	Ts(Bn)N OH (91) 95% ee [α] +20°	98
Ph₂P OH / O	TI (1), (+)-DET (1.2), 4 Å, -16°	Ph₂P OH / O (76) 82% ee	449
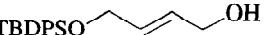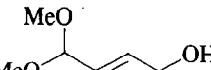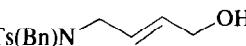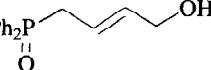
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
NC⌒⌒OH	TI (0.3), (+)-DIPT (0.37), 4 Å, 5°, 10 d	NC△⌒OH (81) 91% ee	106, 108
$C_2H_5O_2C$⌒⌒OH	TI (1), (–)-DIPT (1.2), 3 Å, -25°, 72 h	$C_2H_5O_2C$△⌒OH (85) 90% ee	450
⌒⌒OH	TI (0.05), (+)-DIPT (0.06)	△⌒OH (68) 92% ee	18
BnO⌒⌒OH	TI (0.1), (+)-DET (0.14), 4 Å, -20°, 43 h	BnO⌒△⌒OH (—)[h] 85% ee	18
	TI (1), (–)-DIPT (1), -20°, 40 h	BnO⌒△⌒OH (86) 89% ee [α] +25°	63, 442
	(–)-DET (stoichiometric)	" >95% ee, [α] +25°	451, 73, 353
p-BrC$_6$H$_4$⌒O⌒⌒OH	TI (0.1), (+)-DET (0.13), 4 Å, -20°, 2 h	p-BrC$_6$H$_4$⌒O⌒△⌒OH (73) 100% ee[i], [α] -17.3°[j]	62
	TI (0.1), (–)-DET (0.13), 4 Å, -20°, 2 h	p-BrC$_6$H$_4$⌒O⌒△⌒OH (86) [α] +14.7°; (71) 100% ee[i], [α] +17.4°[j]	62
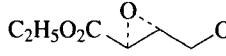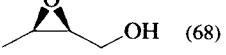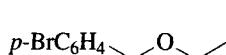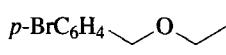
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
Ph₂CH-O⌒⌒OH	TI (1.2), (+)-DIPT (1.5), -20°, 18 h	Ph₂CH-O⌒△⌒OH (92) [α] -17.6°	162
MMTrO⌒⌒OH	(+)-DET	MMTrO⌒△⌒OH (78) 97% ee	444
	(–)-DET	MMTrO⌒△⌒OH (73) 94% ee	444
TBDMSO⌒⌒OH	(+)-DET, -25°	TBDMSO⌒△⌒OH (90) 98% ee	89
TBDPSO⌒⌒OH	(+)-DET	TBDPSO⌒△⌒OH (—) 75% ee [α] -4.4°[d]	452, 453
AcO-sugar-O⌒⌒OH	TI (0.2), (+)-DET (0.24), 4 Å, -16°, 6 d	AcO-sugar-O⌒△⌒OH (65) 96% de	454
	TI (0.2), (–)-DET (0.24), 4 Å, -16°, 6 d	AcO-sugar-O⌒△⌒OH (79) 80% de, [α] -9.8°	454
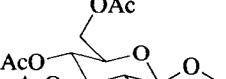
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)
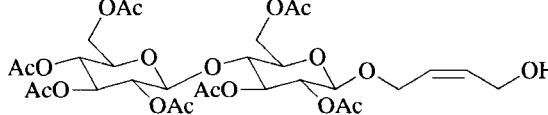
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.1), (+)-DET, (0.2), 4 Å	(75) [α] -23.7°	454
	TI (0.1), (−)-DET, (0.2), 4 Å	(65) [α] -17.0°	454
C₅ TBDMS—⋯—OH	(+)-DET	TBDMS—⋯—OH (78) >98% ee [α] -24.9°	420
—OH	TI (0.048), (+)-DET (0.06), 4 Å, -20 to -15°, 1 h	(97) 86% ee	455-457
	TI (0.048), (−)-DET (0.06), 4 Å, -20 to -15°, 1 h	(97) 86% ee [α] +32°	455-457
⋯⋯OH	TI (1), (−)-DIPT (1.2), -23°	⋯OH (80) >95% ee [α] +32.1°	332
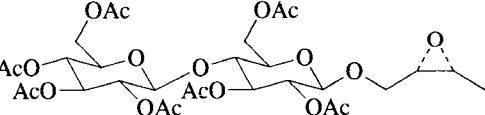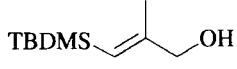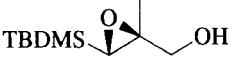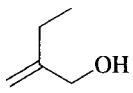
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
⋯⋯OH	Catalytic	OH (40)[b] 95% ee	19
	(+)-DIPT (catalytic), -25°	" (56) >91% ee, [α] -164°	244
HC≡C⋯⋯OH	(−)-DET, -28°, 12 h	HC≡C⋯OH (43) [α] -10.3°	101
BnO⋯⋯OH	(+)-DIPT, 4 Å	BnO⋯OH (80) >90% ee [α] -33.3°	458
	TI (1), (−)-DET (1.002), -25°, 12 h	BnO⋯OH (80) [α] +29.76°	459
	TI (0.1), (−)-DET (0.12), 4 Å, -20°, 12 h	" (89) 91% ee	460-462
	(−)-DIPT, 4 Å	" (72) >90% ee, [α] +32.3°	458
⋯O⋯⋯OH	(+)-DET, -20°, 3 h	O⋯OH (72), 98% ee	463
TBDPSO⋯O⋯⋯OH	(+)-DET (stoichiometric)	TBDPSO⋯O⋯OH (93) 97% ee, [α] -17.56° [d]	362, 464
	TI (0.06), (+)-DIPT (0.08), 4 Å, -20°, 20 h	" (85) >95% ee	221
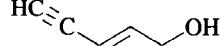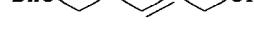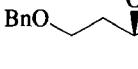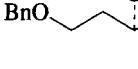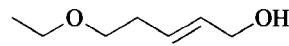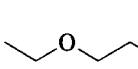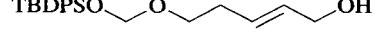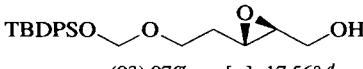
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
TrO⌁⌁OH	(+)-DET (stoichiometric)	TrO⌁△OH (—) >95% ee [α] -23.8°	438
Me₂Si(t-Bu)O⌁⌁OH	TI (1.1), (+)-DET (1.3), 4 Å, -23°, 18 h	Me₂Si(t-Bu)O⌁△OH (—) 99% ee, [α] -28.5°	465
	TI (1.1), (–)-DET (1.3), 4 Å, -23°, 18 h	Me₂Si(t-Bu)O⌁△OH (78) 96% ee, [α] +28.6°	465
(dioxane acetal)⌁OH	(–)-DIPT (catalytic)[a], 4 Å, -20°, 22 h	(dioxane acetal)△OH (90)	466
MeO(CH(OMe))⌁⌁OH	TI (1), (+)-DET (1.2), -20°, 20 h	MeO(CH(OMe))⌁△OH (81) [α] -37.5°[g]	447
	(–)-DIPT (stoichiometric), -20°, SiO₂, 2 d	" (74-90) >95% ee	467

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
BnO(CH(OBn))⌁⌁OH	(–)-DET, 4 Å, -20°	BnO(CH(OBn))⌁△OH (91) >97% ee	468
TBDMSO(CH(OBn))⌁⌁OH	TI, (–)-DIPT	TBDMSO(CH(OBn))⌁△OH (98) 90% de	228
(dioxolane)⌁⌁OH	TI (0.05), (+)-DIPT (0.08), -23 to 0°	(dioxolane)△OH (83) 91% de	224
	(+)-DET, -23°, 2 d	" (74) 87% de, [α] -21.5°	160, 2, 73
	TI (0.05), (–)-DIPT (0.08), -23 to 0°	(dioxolane)△OH (73) 92% de	224
	(–)-DIPT	" (–) 98% ee	162
	(–)-DET, -23°, 2 d	" (77) 95% de, [α] +38.6°	160, 2, 73
TBDMSO(CH)⌁⌁OH	TI (0.05), (+)-DET (0.07), -12°	TBDMSO(CH)△OH (80)	243
⌁⌁OH	(+)-DIPT	△OH (60) 80% ee [α] -11.8°[d]	60, 469
	(+)-DIPT (stoichiometric)	" (42) [α] -3.0°[k]	210

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)
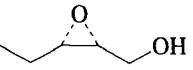
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(–)-DIPT, stoichiometric	[α] +3.1° [k]	210
	(–)-DIPT, stoichiometric	" (67) [α] +8.1°	470
BnO⁀⁀⁀OH	(+)-DIPT, 4 Å	BnO⁀⁀⁀OH (88) 92% ee [α] -6.7°	458
	(–)-DIPT, 4 Å	BnO⁀⁀⁀OH (75) 92% ee [α] +8.5°	458
MPMO⁀⁀⁀OH	(+)-DIPT, -20°, 48 h	MPMO⁀⁀⁀OH 92% ee [α] -9.02°	471
TBDMSO⁀⁀⁀OH	TI (1.06), (–)-DIPT (1.06), 4 Å, -30°, 64 h	TBDMSO⁀⁀⁀OH (90) [α] -7.81°	472
	TI (1.10), (–)-DET (1.13), 4 Å, -30°, 4 d	" (95)	294
TBDPSO⁀⁀⁀OH	(–)-DET, -20°	TBDPSO⁀⁀⁀OH (87)	473
	(+)-DET (stoichiometric), -20°, 14 d	(55) >94% de	73
	TI (1), (+)-DET (1), -23°, 11 d	" (57) 85% de	160
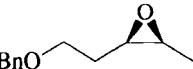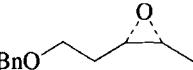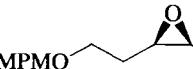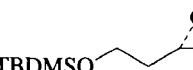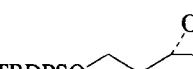
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

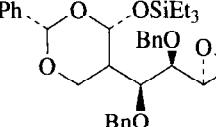| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (–)-DET (1), -23°, 11 d	(—) 20% de	160, 73
⁀⁀OH	TI (0.2), (+)-DET (0.28), -20°	OH (77)[l] 94% ee [α] -22.2° [d]	347
	TI (0.05), (–)-DET (0.07), -23°	OH (—)	242
BnO⁀⁀OH	(+)-DET (catalytic)	BnO⁀⁀OH (—) 80-90% ee	235
	(–)-DIPT, -15°	BnO⁀⁀OH (87) 90% ee [α] +22°	263
BnO⁀⁀OH	TI (1), (+)-DET (1.42), -20°, 14 h	BnO⁀⁀OH (80) 80% ee [α] -10.86°	235
⁀OH	TI(1), (+)-DET (1), -20°, 24 h	OH (55) >93% ee [α] -20.1°	474
	TI(0.05)[a], (+)-DIPT (0.075), 4 Å, -20°, 0.5 h	" (90) [α] -18°	475, 476
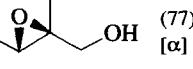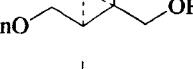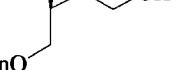
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

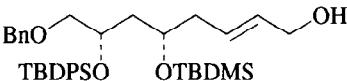| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.05), (–)-DIPT (0.075)	(—) 90% ee	252
	TI(1), (–)-dibutyl tartrate (1), -20°	" (25) 90% ee, [α] +17.1°	477
	TI(1), (+)-DET (1.2), 4 Å, -16°	(91) 96% ee	449
	TI(1), (+)-DET (1.2), 4 Å, -16°	(85) 92% ee	449
C₆	TI (0.05), (+)-DET (0.06), 3 Å, -12°, 11 h	(88) 95% ee [α] -25.9°	18
	TI (0.65), (+)-DET (1.2)	(56) 86% ee	478
	TI (0.1), (+)-DET (1.3), 4 Å, -20°, overnight	(79) 98% ee	426
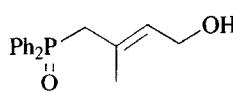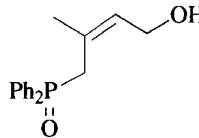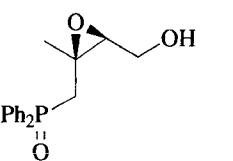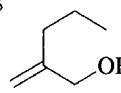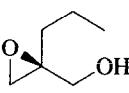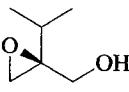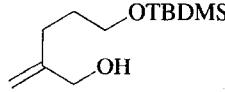
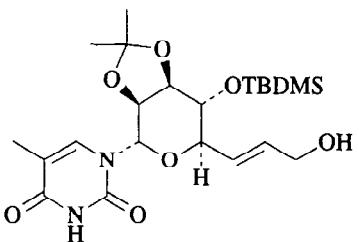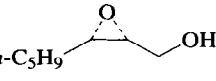TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)
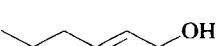
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.05), (+)-DET (0.06), 4 Å, -20°, 2.5 h	(85) 94% ee [α] -46.3°	18, 479
	TI (1.1), (+)-DET (1.1), -20°, 14 h	" (90) 92% ee, [α] -44.6°	480-483, 363
	TI (0.03)ᶠ, (+)-DIPT, -20 to -15°, 3.5 h	" (86) 94% ee	138
	TI (1.1), (+)-DIPT (1.11), -20°, 24 h	" (63.5) 93.5% ee, [α] -45°	484
	TI (1), (–)-DET (1)	(—) [α] +40.8°	363
	(–)-DET	" (63) >96% ee	482
	TI (0.05), (+)-DET (0.06), 4 Å, -20°, 2.5 h	(82) >95% ee [α] -32.7°	485
	(+)-DET	" (64) >90% ee	336, 483
	(–)-DET, -20°	(48) >90% ee	486
	(–)-DET	" (59) [α] +32.2°	487
	(+)-DET, -20°	(85) >95% ee [α] -15.2°	488
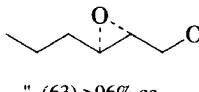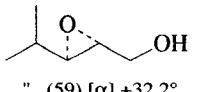
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(BnO, Z-alkene allylic alcohol)	(–)-DET	(epoxy alcohol, BnO) (72)	489
(diphenyl oxazole allylic alcohol)	(+)-DET, -23°	(0)	105
(TBDPSO allylic alcohol)	(+)-DET (stoichiometric)	(TBDPSO epoxy alcohol) (61) >95% ee, [α] -10.0°	438, 490
(Br allylic alcohol)	(+)-DET	(Br epoxy alcohol) [α] -23.3°	491
(dioxinone dioxane allylic alcohol)	TI (1.2), (–)-DIPT (1.2), 4 Å, -20°, 24 h	(epoxy alcohol) (94) >98% ee [α] +36.8°	492, 493
(dioxolane allylic alcohol)	(+)-DET (catalytic), -20°	(epoxy alcohol) (92)[m] [α] -34° [d]	494

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(dioxolane diethyl allylic alcohol)	(–)-DET (stoichiometric), -20°	(epoxy alcohol) (77)	495
(cyclohexyl spiro dioxolane allylic alcohol)	TI (1.19), (+)-DIPT (1.59), -20°, overnight	(epoxy alcohol) (75) [α] -22.5°	496
	TI (1.19), (–)-DET (1.59), -20°, overnight	(epoxy alcohol) (72) [α] +19.8°	496
(BnO allylic alcohol)	TI (1.1), (+)-DET (1.1), -23°, 0.7 h	(BnO epoxy alcohol) (88) 90% de, [α] -27.7°	154, 158, 159
	TI (1.1), (–)-DET (1.1), -23°, 0.7 h	(BnO epoxy alcohol) (—) 90% de, [α] +32.4°	154, 158, 159
(BnO allylic alcohol)	(–)-DET (stoichiometric)	(BnO epoxy alcohol) (98) 80% de	497

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

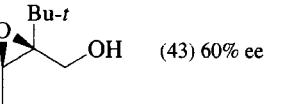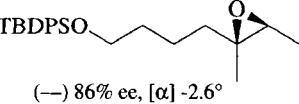| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
BOMO...OH	—	BOMO...OH (87)	498
THPO...OH	(+)-DIPT, -25°	THPO...OH (—)	499
TBDPSO...OH	TI (0.1), (–)-DET (0.13), 4 Å, -20°, 32 h	TBDPSO...OH (96) >95% de	221
...OH, OTBDMS	(+)-DET	...OH, OTBDMS (90)	500
	(–)-DET	...OH, OTBDMS (95)	500
BnO...OH	(–)-DET (stoichiometric), -20°, 18 h	BnO...OH (76) >98% de	330
...OH, OBn	(–)-DET (stoichiometric), -20°, 3 h	...OH, OBn (70) >98% de	330
TBDMSO...OH	TI (1.4), (+)-DET (1.4), 4 Å, -20°, 14 h	TBDMSO...OH (78)[a] [α] -22.4°	501

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
BnO...OH	(+)-DIPT (stoichiometric), -20°, 36 h	BnO...OH (70) >90% de	73, 161, 162, 257
	(–)-DIPT (stoichiometric), -20°, 36 h	BnO...OH (70) >90% de	161, 162, 257
BnO...OH	(+)-DET (stoichiometric)	BnO...OH (71) >90% de	161, 162
	(–)-DET (stoichiometric)	BnO...OH (73) >90% de	161, 162
Ph, Ph...O...OH	TI (1.2), (–)-DIPT (1.5), -20°	Ph, Ph...O...OH (84) [α] +14.7°	162

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
BnO—, TBDPSO, OH	TI (1.1), (–)-DET (1.1), -23°, 5 h	BnO—, TBDPSO, OH (60) 82% dc [α] -1.2°	85, 87
BocNH, CO$_2$CH$_2$C$_6$H$_4$OMe, H, OH	TI (1.1), (+)-DET (1.1), -23°, 18 h	HN, O, MeOC$_6$H$_4$CO$_2$, H, OH, OH (55-60)	502
OH	TI (1.1), (+)-DIPT (1.2), -20°, 3 d	OH (57) 87% ee; 97% ee[n] [α] -5.73°	64, 484
	TI (1.1), (–)-DIPT (1.2), -20°, 3 d	OH (56) 80% ee [α] +4.91°; 99% ee[n] [α] +5.69°	64
OH	(+)-DET	OH (54) 66% ee, [α] -9.9°	8
TBDPSO, OH	(–)-DET , -20°	TBDPSO, OH (88) 89% ee	503
BnO, OH	TI (1.1), (+)-DET (1.1), -23°, 24 h	BnO, OH (79) 67% ee	154
	TI (1.1), (–)-DET (1.1), -23°, 24 h	(0)	154

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

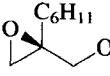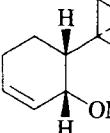| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
BnO, O, O, OH	(+)-DET (stoichiometric)	BnO, O, O, OH (—)	73
OH	TI (1), (+)-DMT (1.05), -20°, 16 h	OH (79) >95% ee	59
	TI (1), (+)-DET (1), -20°	" [α] -13.5°	504
	TI (0.05), (+)-DET (0.06), 3 Å, -25°, 3 d	" (85) >98% ee	505
	TI (0.1), (+)-DET (0.1), 4 Å, -23°, 2 h	" (91) >98% ee, [α] -21.3°	506, 507
	(–)-DMT, 3 Å, -20°	OH (78) >98% ee	508
	TI (1), (–)-DET (1), -20°	" (—) [α] +14.3°	504
OH	(+)-DET (stoichiometric)	OH (38) >95% ee [α] -23.92°	509
BnO, OH, OBn, BnO, OH	TI (1), (+)-DIPT (1.26), -23°	BnO, O, OBn, BnO, OH, OH (66) 34% de	510

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

	Conditions		
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (+)-DIPT (1.26), -23°	(64) 90% de	510
	TI (1), (−)-DIPT (1.26), -23°	" (71)[a] 80% de	510
	TI (1), (+)-DIPT (1.26), -23°	(63) 50% de	510
	TI (1), (−)-DIPT (1.26), -23°	" (65) 70% de	510
	TI (0.1), (−)-DIPT (0.15), 4 Å, -20°, 8 h	(90) 95% ee [α] +19° [g]	511
	TI (0.1), (+)-DIPT (0.12), 3 Å, -15°, overnight	(89) 80% ee [α] +15.3°	512

	Conditions		
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(+)-DET, -20°, 4 h	(80) [α] +11.36°	513
	—	(—) 60% ee	104
	TI(1.05), (−)-DET (1.57), -20°, 17 h	(81) 95% ee [α] +2.1°	255
	TI (1), (+)-DET (1), -20°, 24 h	(90) [α] -13.3° [g]	288, 514
	TI(1), (−)-DET (1.04), -20°	(—)	288
	TI (1), (+)-DET (1)	(83) 92% ee	288, 514

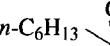TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

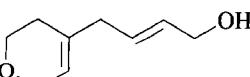| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI(1), (–)-DET (1.04), -20°	(structure, EEO) (82) [α] +2.9°	288
(TBDMSO... structure, =C(CH₃)...OH)	(+)-DET (stoichiometric), -30°, 12 h	(structure, TBDMSO) (98) 89% ee [α] -22°	515
	(–)-DET (stoichiometric), -30°, 12 h	(structure, TBDMSO) (98) 88% ee [α] +24°	515, 89
(cyclopropylidene structure ...OH)	TI (1), (+)-DIPT (1.2), -50°, 24 h	(structure) (54) 92% ee, [α] +18.2°	133
	TI (1), (–)-DIPT (1.2), -50°, 24 h	(structure) (38) 93% ee, [α] -18.5°	133
	TI (1), (–)-DET (1.2), -50°, 24 h	" (53) 89% ee, [α] -17.9°	133
C₇ (Bu-*n* structure ...OH)	TI (1), (+)-DET (1.2), -20°, 24 h	(structure, Bu-*n*) (67) [α] -6.2°[k]	516

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(Bu-*t* structure ...OH)	TI[c] (1.2), (+)-DET (1.5), -20°	(structure, Bu-*t*) (42) 85% ee	57
	TI[c] (1.1), (+)-DET (1.1),	" (79)[p] 72% ee	180
n-Bu ...OH	Stoichiometric[c]	*n*-Bu ...OH (90) >95% ee [α] -49.9°[e]	298, 299
	TI (1)[p], (+)-DET (1.2), -23°, 1 h	" (76) 95% ee, [α] -29.7°	140
(isopentyl structure ...OH)	(+)-DIPT	(structure) ...OH (90) 90% ee	517
t-Bu ...OH	TI (1.2), (+)-DET (1.5), -20°	*t*-Bu ...OH (52) >95% ee	57
MeC≡C ...OH	TI (0.075), (+)-DET (0.11), 4 Å, 0 to 23°, overnight	MeC≡C ...OH (74) [α] -20.3°[j]	518
TBDMSO ...OH	TI (0.1), (–)-DET (0.15), 4 Å, -40°, 8 h	TBDMSO ...OH (85) 97% ee	350
MOMO ...OH	(+)-DIPT, -23°	MOMO ...OH (57) 96% ee, [α] -24.7°	519

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions Ti (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
BnO⟶⟶OH (gem-dimethyl)	Ti (0.2), (–)-DET (0.26), 4 Å, 0°, 8 h	BnO⟶epoxide⟶OH (85) 92% ee [α] +8.38°	520, 521
Ph, Ph oxazole ⟶OH	(+)-DET, -23°	Ph, Ph oxazole ⟶epoxide⟶OH (75) 99% ee, [α] -16.8°	105
⟶⟶OH (methyl branch)	(–)-DET (stoichiometric), -45°	⟶epoxide⟶OH (74)	522, 523
AcO⟶⟶OH	(+)-DET, MS	AcO⟶epoxide⟶OH (77)	524
	(–)-DET, MS	AcO⟶epoxide⟶OH (83)	525
OTBDPS ⟶⟶OH	(+)-DIPT, -30°	OTBDPS ⟶epoxide⟶OH (89) 90% de	526
	(–)-DET, MS, -20°, 24 h	OTBDPS ⟶epoxide⟶OH (88) 88% de	527

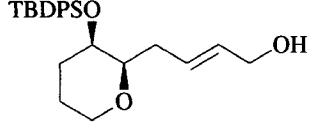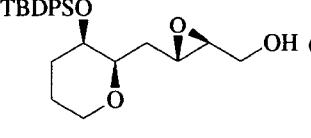TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions Ti (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
BnO– isopropylidene furanose ⟶OH, H	Ti (1.2), (+)-DIPT (1.5), -23°, overnight	BnO– isopropylidene furanose ⟶epoxide⟶OH (88)[m] [α] +43°	528
TBDPSO⟶C=C=C⟶OH (allene)	(+)-DET (stoichiometric), -20°, 3 h	TBDPSO⟶C=C=C⟶epoxide⟶OH (83)	346
BnO, BnO Ts(Bn)N⟶⟶OH	Ti (1.2), (+)-DET (1.5), -20°	BnO, BnO Ts(Bn)N⟶epoxide⟶OH (—) >99.5% de	98
	Ti (1.2), (–)-DIPT (1.5), -20°, 21 h	BnO, BnO Ts(Bn)N⟶epoxide⟶OH (93) >99.4% de	98
OBn BnO⟶BnO⟶OH	Ti (1.2), (–)-DET (1.5), -20°, 16 h	OBn BnO⟶BnO⟶epoxide⟶OH (75)[m] [α] +13.6°g	86, 87

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(–)-DET	(89)	529
	(+)-DET	(0)	529
	(+)-DET	(80) 95% ee [α] -5.2°	530
t-Bu	TI (1.2), (+)-DET (1.5), -20°	*t*-Bu (77) 25% ee	57
TMS	TI (0.23), (+)-DET (0.3), 4 Å, 4°, 15 h	TMS (78) 81% ee [α] -4.73°	111
BnO	(+)-DET	BnO (—)	531
	TI (1), (–)-DET (1), -20°, 48 h	BnO (—) (73) 86% ee, [α] +1.55°	532
MeO₂C	TI (1), (+)-DET (1), -20°, 8 h	MeO₂C (57) 94% ee, [α] -2.5°	354, 355

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

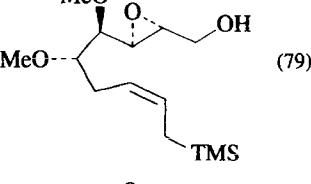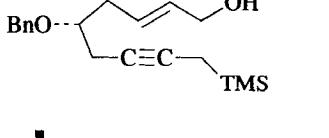| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.24), (+)-DET (0.34), 3 Å, -15°, overnight[a]	(77) [α] -45.9°	533
	TI (0.05), (+)-DET (0.075), -12°	(77) 93% ee, [α] -22.8°	18
	(+)-DET	" (—)	534
	(–)-DET, -40°	(70) 92% ee, [α] +22.4°	535, 536
TBDMSO	TI (0.75), (–)-DET (1), -20°, 12 h	TBDMSO (88) 93% ee, [α] +10.7°	490
TMSC≡C	Catalytic, (–)-DET, -5°, 36 h	TMSC≡C (83) 93% ee	537
n-Bu	(+)-DET	*n*-Bu (91)	538

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
BnO⋯OH	TI (1), (+)-DET (1.05), -25°, overnight	BnO⋯O⋯OH (93) 99% de [α] -14.03°	173, 174
TBDMSO⋯OH	TI (0.045), (+)-DET (0.065), 3 Å, -20°, 10 h	TBDMSO⋯O⋯OH (94) 50% de	539
TBDPSO⋯OH	TI (1), (–)-DET (1.2), -20°, overnight	TBDPSO⋯O⋯OH (97) [α] +17.33°	540, 459
(cyclopropylidene)⋯OH	TI (1), (–)-DIPT (1.2), -50°, 24 h	(cyclobutanone)⋯OH (80) 96% de, [α] +46.0°	133
(dioxolane)⋯OH	TI (1), (+)-DIPT (1), -23°, 72 h	(dioxolane)⋯O⋯OH (80) [α] -10.8°	541
n-C₅H₁₁⋯OH	TI (0.05), (+)-DET (0.08), -20 to 0°	*n*-C₅H₁₁⋯O⋯OH (75) 95% ee	250, 251
	TIᵖ (1), (+)-DET (1.2), -40°	" (76) 95% ee, [α] -29.7°	542
	Stoichiometric	" >95% ee, [α] -35.6°	282, 438

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TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	Ti (0.03)ᶠ, (+)-DIPT, -20 to -15°, 9 h	" (76) 98% ee	138
	TI (1), (+)-DIPT (1.04), -23°	" (51) 90% ee	222
	(+)-DIPT	" (89) 98% ee	311
	TI (1), (–)-DIPT (1.04), -23°	*n*-C₅H₁₁⋯O⋯OH (51) 80% ee	222
(octadienol)⋯OH	TI (1), (+)-DET (1)	(epoxide)⋯OH (80) >95% ee	59
(methylheptadienol)⋯OH	(+)-DET (0.2), -20°, 5 h	(epoxide)⋯OH (83) >98% ee	543
(geraniol-type)⋯OH	TI (0.05), (–)-DET (0.06), 4 Å, -20°, 4 h	(epoxide)⋯OH (90) [α] +16.27°	227
⋯OH	(+)-DIPT	(epoxide)⋯OH (82)	544
⋯C≡C⋯OH	(+)-DIPT, -20°, 18 h	⋯C≡C⋯O⋯OH (70)	545
	Ti (0.03)ᶠ, (+)-DIPT, -20 to -15°, 8 h	" (82) [α] -17.8°	138

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.9), (+)-DET (1.94), -30°, 5 h	(55) >97% ee	546
	TI (1.9), (–)-DET (1.94), -30°, 5 h	(55) >97% ee	546
NC⌁OH	(+)-DIPT	NC⌁OH (72) 96% ee	107
MPMO⌁OH	(–)-DIPT	MPMO⌁OH (—)	225
THPO⌁OH	(+)-DET, 4 Å	THPO⌁OH (69) 95% ee	129
	TI (0.11), (+)-DIPT (0.14), 3 Å, -40 to -5°	(85) 93% ee	80
	TI (1.13), (+)-DIPT (1.2 5), -30°, 6 h	" (70) 93% ee, [α] -13.4°	80

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

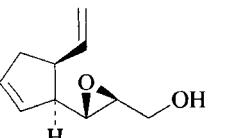| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.11), (–)-DIPT (0.14), 3 Å, -40 to -5°	(73) 93% ee [α] +13.2°	80
	TI (1.13), (–)-DIPT (1.25), -30°, 6 h	" (70) 91% ee, [α] +13.2°	80
NC⌁OH	TI (0.3), (+)-DET (0.3), 4 Å, -8°	NC⌁OH (—) >94% ee	547, 548
Ph-oxazole-Ph⌁OH	(+)-DET, -23°	Ph-oxazole-Ph⌁OH (66) 99% ee, [α] -11.1°	105
BnO⌁OH	(+)-DET (stoichiometric), 3 Å, -20°, 2 h	BnO⌁OH (88) >95% ee [α] -16.5°	549
⌁OH OBn	(+)-DET (stoichiometric), 3 Å, -20°	⌁OH OBn (88) [α] -25.0°	549

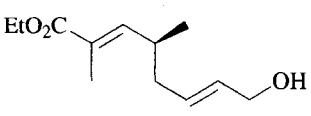TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.1), (+)-DIPT (1.3), -25°, 48 h	(95) 60% de, [α] +108.8°	550
	TI (1.1), (–)-DIPT (1.3), -25°, 48 h	(93), [α] +116.9° *j*	550
	TI (1), (–)-DET (2.0), -20°	(70) 95% de	157, 520
	TI (1.2), (+)-DIPT (1.5), -23°, overnight	(66)*ᵐ* [α] -90°	148

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(–)-DIPT, -23°, 8 d	(68)*q*	148
OTBDMS ... EtO ... OH	TI (1.1), (+)-DET (1.1), -20°, overnight	(72)*ᵐ*	551
BnO ... OMOM ... OH	(+)-DET (stoichiometric), -23°	(—) 50% de	123
	(–)-DET (stoichiometric), -23°	(—) 50% de	123
Ph ... OSiEt₃ ... BnO ... OH	TI (3.6), (+)-DET (5), -20°	(85) >94% de	348

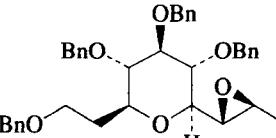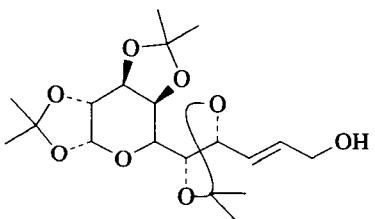TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (3.6), (–)-DET (5), -20°	(74) >94% de	348
	TI (3.6), (+)-DET (5), -20°	(88) >94% de	348
	TI (3.6), (–)-DET (5), -20°	(70) >94% de	348
	TI (1.1), (–)-DET (1.1), -23°		85
	(–)-DET	(—)	164
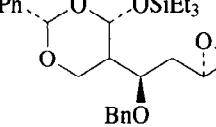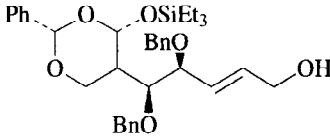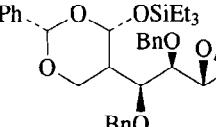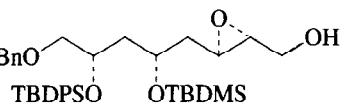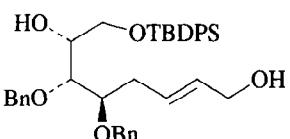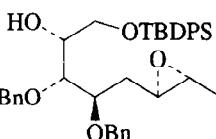
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (+)-DIPT (1.1), -25°, 36 h	(86) 100% de, [α] +62.5°	552
	TI (1), (–)-DIPT (1.1), -25°, 48 h	(80) >92% de, [α] +57.5°	552
n-C$_5$H$_9$ ⁓ OH	TI (0.1), (+)-DET (0.13), 4 Å, -25°, 40 h	(62) 74.6% ee [α] -5.42°	553
	TI (1), (–)-DET (1.1), -20°	(78) 90 ee [α] +4.3°	554
	TI (1), (–)-DET (1.2), -20°	" (78)	555, 556
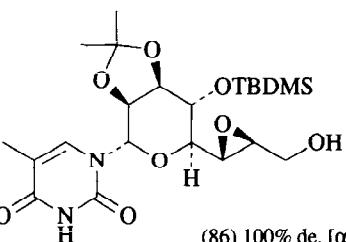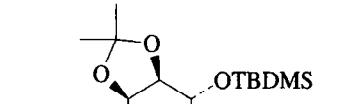
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (+)-DIPT (1.1), -29°, 65 h	(75) 88% ee [α] -6.4° *r*	220
	TI (1), (–)-DIPT (1.1), -29°, 65 h	(77) 88% ee [α] +6.5° *r*	220
	TI (1), (+)-DET (1.2), -20°, 6 d	(78) >94% ee [α] -3.51°	284, 285
	TI (1), (+)-DET (1.1), -20°, 40 h	(76) 92% ee [α] -10.24°	518
	TI (1), (+)-DET (1.1), -25°	(73) 95% ee	116
	TI (1), (–)-DET (1.1), -25°	(82) 95% ee	116
NC~~~~OH	(+)-DIPT	NC~~~~OH (72) 96% ee [α] +12.5°	107

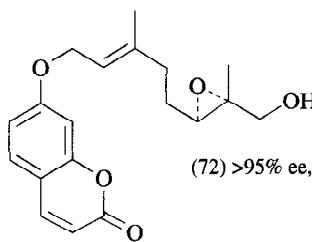TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (+)-DET (1.1), -25°	(30) 95% ee	116
	TI (1), (–)-DET (1.1), -25°	(30) 95% ee	116
	(+)-DET, -20°, 31 d	(60)*m*	557
	(+)-DIPT (stoichiometric), -23°	(0)	148
	(–)-DIPT (stoichiometric), -23°	(0)	148
	(–)-DET, -10°	(70)*m* [α] -143°	558

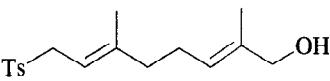TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.10). (+)-DET (1.11), -25°, 3.5 h	(71) 96% ee [α] -18.1°	559-561
	TI (1.4), (–)-DIPT (1.5), -30°, 2.5 h	(84) 96% ee [α] +4.3° *s*	561
	(+)-DET	(—) [α] -10.6° *s*	240
	(–)-DET (stoichiometric)	(92) >95% ee [α] +9° *s*	562
n-C₅H₁₁ TMS OH	(+)-DET	*n*-C₅H₁₁ TMS OH (81)	538
	TI (1), (–)-DET (1), -20°, overnight	(—)	563, 564
	(–)-DET (–) 95% de	(—)	565
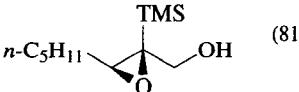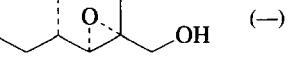
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)
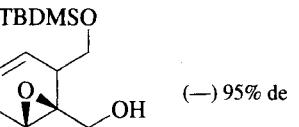
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
TBDMSO OH	(+)-DET	TBDMSO OH (—) 95% de	88
Bu-*t* OH	TIᶜ (1.2), (+)-DET (1.5), -20°	Bu-*t* OH (43) 60% ee	57
OH	(+)-DET (catalytic), 4 Å, -25°, 2 h	OH (80) 82% ee [α] -16.1°	566
TBDPSO OH	(+)-DIPT (catalytic)	TBDPSO OH (—) 86% ee, [α] -2.6°	567
	TI (1.1), (+)-DIPT (1.3), -25°, 5 d	(75) 100% de [α] -5° *g*	568
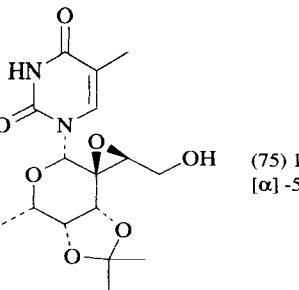
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

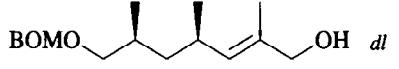| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.1), (–)-DIPT (1.3), -25°, 5 d	" 100% de, [α] -2° [g]	568
	TI (1.1), (+)-DIPT (1.3), -25°, 5 d	(70) 100% de [α] -17.5° [g]	568
	TI (1.1), (–)-DIPT (1.3), -25°, 5 d	" 100% de, [α] -15° [g]	568
	TI (1.1), (+)-DIPT (1.3), -25°	(73) 100% de [α] -62.5° [g]	568
	TI (1.1), (–)-DIPT (1.3), -25°	" 100% de, [α] -67.5° [g]	568

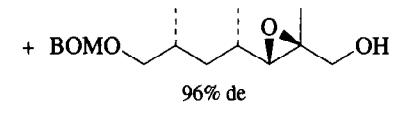TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.1), (+)-DIPT (1.3), -25°	(50) 100% de [α] -50° [g]	568
	TI (1.1), (–)-DIPT (1.3), -25°	" 100% de, [α] -60° [g]	568
	TI (1), (–)-DET (1.2), -50°, 24 h	(70) 93% ee, [α] +36.9°	133
	TI (1), (+)-DET (1.2), -50°, 48 h	(80) 89% ee	134
	TI (1), (–)-DET (1.2), -50°, 48 h	(73) 89% ee, [α] +101.4°	133, 134

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

	Conditions		
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

C$_9$

C_6H_{13}-*n* OH	(+)-Tartrate	C_6H_{13}-*n* OH (87) 97% ee	569
C_6H_{11} OH	TI (1), (+)-DET (1), -23°	C_6H_{11} OH (81) >95% ee	1
$(CH_2)_6OC_6H_4Cl$-*p* OH	TI (0.51), (+)-DET (0.77), 4 Å, -20°, 3 h	$(CH_2)_6OC_6H_4Cl$-*p* OH (49) [α] -30.7°	570
H OH OMPM H	TI (1), (+)-DET (1.2), -23°, 5.5 h	H OH OMPM H (95) <80% de	571
p-MeOC$_6$H$_4$—O H OH racemic	(+)-DET^c, -23°, 5.5 h	*p*-MeOC$_6$H$_4$—O H O OH + (47) [α] -243° ^{d}	572
		p-MeOC$_6$H$_4$—O H O OH (47)	

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

	Conditions		
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

O—O H OH	TI (0.21), (–)-DET (0.38), 4 Å, -20°, 5 h	O—O H O OH (96) 87% de, [α] -10.4°	573
n-C$_6$H$_{13}$ OH	TI (1), (+)-DET (1), -10°, 24 h	*n*-C$_6$H$_{13}$ O OH (—) [α] -38.9°	574
	TI (1), (–)-DET (1), -10°, 24 h	*n*-C$_6$H$_{13}$ O OH (—) [α] +38.7°	574
OH	TI (0.52), (+)-DIPT (0.62), -20°, 3d	O OH (82) 96% ee	575, 576
MeO$_2$C OH	(–)-DET (stoichiometric)	MeO$_2$C O OH (69) [α] -1.5°	577
O—OH	(–)-DIPT, -20°	O—O OH (82) 90% ee	578
TMS OH	TI (0.1), (–)-DIPT, 4 Å, -25°	TMS O OH (96) >93% ee	579
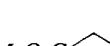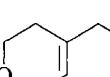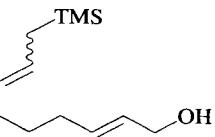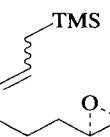
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
Ph⌒⌒OH	(+)-DET (catalytic)	Ph⌒△⌒OH (55) 93% ee	479
	TI (0.05), (+)-DIPT (0.075), 4 Å, -20°, 3h	" (89) >98% ee, [α] -49.6°	224, 438
	Stoichiometric	" (36) >98% ee, [α] -10.7°	282
	TI (1),[p] (+)-DET (1.2), -23°, 0.75 h	" (54) 89% ee, [α] -49.5°	140
	TI (1), (+)-DET (1.2), -23°, 1.2 h	" (44) 95% ee, [α] -51.7°	140
	TI (2), (+)-N,N'-dibenzyl tartramide (1)	Ph⌒△⌒OH (—) 65% ee	130
	TI (1), (–)-DIPT (0.075)	" (—) >98% ee	252
m-MeOC$_6$H$_4$⌒⌒OH	TI (0.05), (+)-DIPT (0.075), 4 Å, -30°, 7 h	m-MeOC$_6$H$_4$⌒△⌒OH (91) 94% ee [α] -66.8°[d]	580
m-BOMOC$_6$H$_4$⌒⌒OH	(–)-DIPT, 4 Å, -30°	m-BOMOC$_6$H$_4$⌒△⌒OH (—) 96% ee	129
p-O$_2$NC$_6$H$_4$⌒⌒OH	TI (0.05), (+)-DIPT (0.075), 4 Å, -20°, 2 h	p-O$_2$NC$_6$H$_4$⌒△⌒OH (89) >98% ee[i] [α] -37.4°	18
p-BrC$_6$H$_4$⌒⌒OH	TI (0.05), (+)-DET (0.075), 4 Å, -20°, 0.75 h	p-BrC$_6$H$_4$⌒△⌒OH (69) >98% ee[i] [α] -35.2	18

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(OMe/Br aryl allylic alcohol)	(+)-DET, -20°, 4 h	(OMe/Br aryl epoxide product) (—)	513
(diene alcohol)	TI (1), (–)-DIPT (1), -20°, 18 h	(epoxide product) (85) [α] +22°	581-583
(diene alcohol)	TI (1), (+)-DET (1), -20°	(epoxide product) (85) 90% ee	584
(diene alcohol)	TI (1), (+)-DIPT (1), -20°, 7 h	(epoxide product) (88) [α] -28.5°	585
(dioxane alcohol)	TI (1.1), (+)-DET (1.1), -23°	(epoxide product) (78) 90% de [α] -44.0°	154
BnO⌒⌒△⌒OH	TI (0.2), (+)-DET (0.26), 4 Å, 0 °, 12 h	BnO⌒⌒△⌒OH (80) >98% de	521
TBDMSO (pyran alcohol)	TI (0.1), (+)-DET (0.15), 4 Å	TBDMSO (pyran epoxide product) (78) 68% de	349

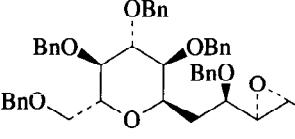TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.1), (–)-DET (0.15)	(92) 90% de	349
	(–)-DET, -20°, 15 h	(—)	586
	TI (0.1), (+)-DET (0.15), 4 Å	(80) 62% de	349
	TI (0.1), (–)-DET (0.15), 4 Å	(87) 89.5% de	349
dl	TI (1), (–)-DET (1.2), 4 Å, -25°	(89) >90% de	587
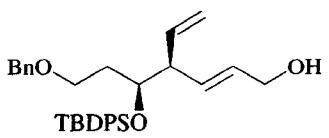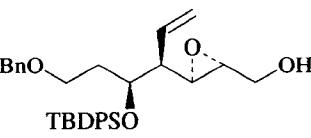
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
dl	TI (1), (–)-DET (1.2), 4 Å, -25°	(92) >90% de	587
	TI (1), (–)-DET (1.2), 4 Å, -25°	(79) 100% de	587
	TI (0.19), (–)-DET (0.3), 4 Å, -25°	(91) 100% de [α] +51°	587
	1. TI (2), (+)-DET (2.1), -20°, 20 h, 2. CSA	(75)	119
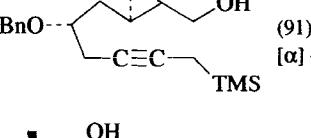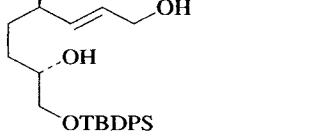
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
TMSO ... Ph ... O ... H (structure)	TI (0.15) (–)-DET (0.2), 4 Å, -20°, 14 h	TMSO ... Ph ... O ... H (epoxide) OH (89)	588
OBn, OBn, O, H (structure)	(+)-DET	OBn, OBn, O, OH, H (structure) (—)	589
	(–)-DET	OBn, OBn, O, OH, H (structure) (—)	589
n-C₆H₁₃ / OH	(–)-DET	*n*-C₆H₁₃ epoxide OH (—)	590
Ph / OH	TI (1), (+)-DET (1.2), 1.2 h	Ph epoxide OH (56) 85% ee, [α] -50°	140-142, 2, 313, 352
	TI (1)ᵖ, (+)-DET (1.2), 48 h	" (50) 85% ee, [α] -30°	140

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
p-O₂NC₆H₄ / OH	(+)-DET , -20°, 7 d	*p*-O₂NC₆H₄ epoxide OH (85) 95% ee [α] -98.3°	591
OH (structure)	TI (1), (+)-DET (1.1), -25°, 40 h	epoxide OH (76)	592
OH (structure)	TI (1), (+)-DET (1), -20°, overnight	epoxide OH (64) >90% ee [α] -12.2°	217
	(+)-DMT	" (90) >95% ee	593
	TI (1), (–)-DET (1), -20°, overnight	epoxide OH (59) >91% ee [α] +12.6°	217
TBDMSO (structure) OH	(–)-DET (1), -23°	TBDMSO epoxide OH (92)	594
BnO, O=, O, H (structure) OH	TI (1.2), (–)-DET (1.9), -20°, 2 d	BnO, O=, O, H epoxide OH (46) 92% de [α] +85.7° ¹	170, 172
TBDMSO, O, O, H (structure) OH	(+)-DET	TBDMSO, O, O, H epoxide OH (—) 68% de	172
	(–)-DET	" (—) 20% de	172

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(structure: OTHP allylic alcohol, OH)	TI (0.1), (+)-DIPT (0.15), 4 Å, -20°, 2.5 h	(structure, OTHP epoxide) (88)	595
	TI (0.1), (–)-DIPT (0.15), 4 Å, -20°, 2.5 h	(structure, OTHP epoxide) (95)	595
TBDMSO (structure, OH)	(+)-DET	TBDMSO (structure) (—) 95% ee + TBDMSO (structure) (—) 95% ee	88
(structure, OH)	TI (2), (+)-DET (2), -20°, overnight	(structure, epoxide OH) (68) 95% ee [α] -0.99°	596
MeC≡C (structure, OH)	(–)-DET, -20°	MeC≡C (structure, epoxide OH) (84) [α] -9.8°	227

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C≡C (structure, OH)	Catalytic (+)-DET, -20°, 4 h	C≡C (structure, epoxide OH) (80) 90-95% ee [α] +3.96°	513
(structure, OH)	(+)-Tartrate	(structure, epoxide OH) (—)	597
(cyclopropylidene structure, OH)	TI (1), (–)-DET (1.2), -50°, 24 h	(cyclobutanone structure, OH) (70) 94% ee, [α] +37.3°	133
(cyclopropylidene structure, OH)	TI (1), (–)-DET (1.2), -50°, 48 h	(cyclobutanone structure, OH) (96) 91% ee, [α] +26.2°	133
MeO₂C (cyclohexane structure, OH) *dl*	TI (1), (+)-DET (1), -20°, 24 h	MeO₂C (epoxide structure, OH) (29) 78% ee + MeO₂C (epoxide structure, OH) (31) 70% ee	598

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(cyclohexanone with 2-methylallyl alcohol substituent)	(+)-DET, -23°	(epoxide product) (—) >90% ee [α] -2.56°	599
C_{10} (2-benzyl allyl alcohol, Ph)	(+)-DAT	(epoxide product, Ph) (60) 80% ee, [α] -26°	600
n-C_7H_{15} ⟋⟍ OH	TI (0.05), (+)-DET (0.075), 4 Å, -23°, 2.5 h	n-C_7H_{15} (epoxide) OH (99) 96% ee [α] -36.5°	18
n-C_7H_{15} (F, F) OH	TI (1), (+)-DIPT (1.2), 4 Å, -38°, 72 h	n-C_7H_{15} (epoxide, F, F) OH (81) 80% ee	601, 602
MeO_2C ⟨ ⟩$_3$ ⟋⟍ OH	(+)-DET	MeO_2C ⟨ ⟩$_3$ (epoxide) OH (69) 93% ee, [α] -15.5°	91
(geraniol-type) OH	TI (1), (+)-DET (1), -23°, 2.5 h	(epoxide) OH (74) 93% ee, [α] -35.4°	603
	TI (0.05), (+)-DET (0.06), -20°, 2.5 h	" (86) [α] -32.2°	227

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(dienol with CO_2Me) + (dienol with CO_2Me)	(−)-DET	(epoxide with CO_2Me) + (epoxide with CO_2Me) + (91)	359
p-MeC_6H_4 ⟋⟍ OH	TI (0.1), (+)-DIPT (0.15), -20°, 34 h	p-MeC_6H_4 (epoxide) OH (62) >98% ee [α] -36.65°	300
p-$MeOC_6H_4O(CH_2)_7$ ⟋⟍ OH	(+)-DET	p-$MeOC_6H_4O(CH_2)_7$ (epoxide) OH (87) >97% ee	604
	(−)-DET	p-$MeOC_6H_4O(CH_2)_7$ (epoxide) OH (74) >97% ee	604
Ph ⟋⟍ OH	(+)-DET	Ph (epoxide) OH (—) >95% ee	605
(5-methylfuran-2-yl chain) OH	(+)-DET	(5-methylfuran-2-yl chain) (epoxide) OH (92) [α] -35.23°	114

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)
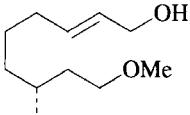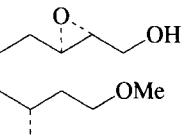
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (–)-DET (1), -20°, 18 h	(68)[m] [α] +28.0°	256
	TI (3), (+)-DET (3.5), -30°, 15 h	(73) 97% de [α] +293.5° [d]	606
	TI (3), (–)-DET (3.5), -30°, 15 h	(71) 96% de [α] +238.3° [d]	606
	(–)-DIPT , 4 Å, -20°	(95)	607
	TI (2), (+)-DIPT (2.4), -20°, 6 h	(70)	118
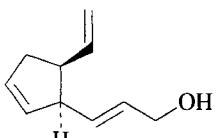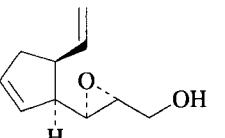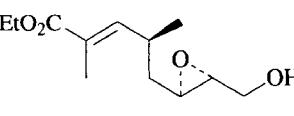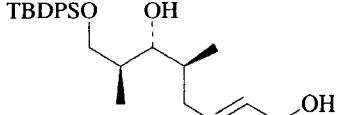
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)
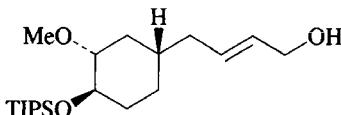
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(+)-DET , 4 Å	(88)	608
	(+)-DET	(—)	164
	TI (1.37), (+)-DIPT (1.52), -23°, 5 d	 (63) 67% de, [α] -58° [j]	147, 149
	TI (1.45), (+)-DIPT (1.6), -23°, 4 d	 (80) 60% de	147, 149
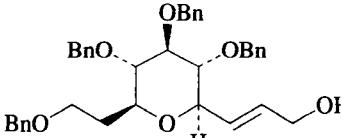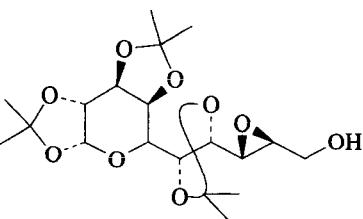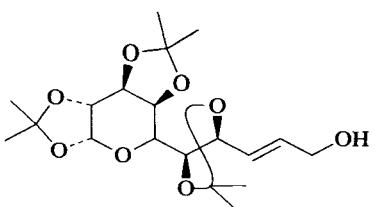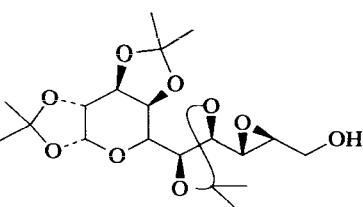
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.45), (–)-DIPT (1.6), -23°, 4 d	(61) [α] -65°	147
BnO, BnO, OBn, OBn	(+)-DET, -30°, 6 h	(90) 96% de, [α] +25.8°	163, 166
OMe	TI (2), (+)-DET (2), -30°, 3 h	(78)	609
n-C₇H₁₅ OH	TI (0.1), (+)-DET (0.14), 4 Å, -10°, 29 h	*n*-C₇H₁₅ OH (74) 86%, ee [α] -4.8°	18
	(+)-DIPT, 4 Å, -20°, 29 h	" (74) 86% ee	610
	TI (0.1), (–)-DET (0.14), 4 Å, -20°, 3 d	*n*-C₇H₁₅ OH (92) 84%, ee	18

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.2), (+)-DET (1.4), -20°, 18 h	OH (81) 84.2% ee	109, 110, 611
Ph OH	(–)-Tartrate	Ph OH (83) 91% ee [α] -8.40° ˢ	145
OBn, OMPM, TBDMSO OH	(+)-DET, -15°	OBn, OMPM, TBDMSO OH (—)	612
	TI (1), (+)-DET (1), -20°, overnight	OH (70)	94
Ph OH	TI (0.05), (+)-DIPT (0.075), 4 Å, -35°, 2 h	Ph OH (79) >98% ee [α] -16.9° ʲ	18
AcO OH	TI (1), (+)-DET (1), -23°	AcO OH (70) 95% ee	1
	TI (1), (–)-DET (1), -15°, overnight	AcO OH (50) [α] +5.86°	94

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (Continued)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (–)-DIPT (1), –20°, 14 h	" (79) [α] +13.2°	83
	(–)-DIPT, 4 Å	" (75) 90% ee	75
	(–)-DMT (catalytic), 3 Å, –23°, 12 h	" (—) 92% ee	76
TBDPSO...OH	(–)-DMT (catalytic), 3 Å, –23°, 18 h	TBDPSO...OH (92)	76
	TI (1), (–)-DET (1), –20°	(72) >95% ee, [α] +15.8°	215, 216
Ts...OH	TI (0.05), (+)-DIPT (0.07), 4 Å, –23°, 3.5 h	Ts...OH (89) >98% ee, [α] –3.56° [d]	613
BzO...OH	TI (0.05), (+)-DIPT (0.073), 3 Å, –10°, 3.5 h	BzO...OH (83) >95% ee, [α] –5.77°	357
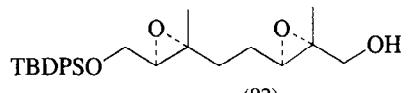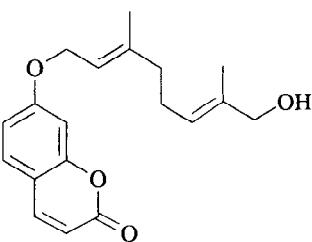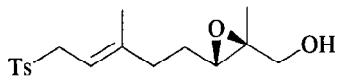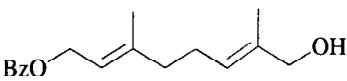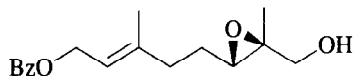
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (Continued)

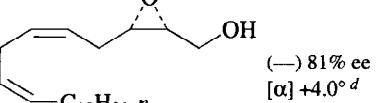| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
...OH	(+)-DET	...OH (—)	614
...OH	(–)-DET, –23°	...OH (—) 80% de	615
BOMO...OH dl	TI (1), (+)-DIPT (1.2), –23°	BOMO...OH (94)[u] 96% de + BOMO...OH 96% de	332
...O₂C...OH	TI (1.1), (+)-DIPT (1.1), –20°, overnight	...O₂C...OH (41)	616
	TI (1.1), (–)-DIPT (1.1), –20°, overnight	...O₂C...OH (36)	616

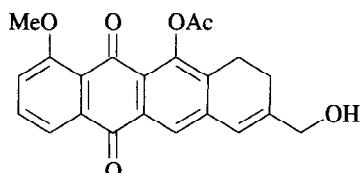TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.05), (+)-DET (0.074), 3 Å, -20°, 0.75 h	(95) 91% ee [α] -5.3°	18, 238
	TI (1), (+)-DET (1), -20°	" (77) 95% ee	1, 234, 617, 618
	TI (0.03)*f*, (+)-DET, -20 to -15°, 7.5 h	" (79) 98% ee	138
	TI (0.03)*f*, (+)-DET, -20 to -15°, 9 h	" (72) 96% ee	138
	TI (1)*p*, (+)-DET, -40°, 1.5 h	" (77) [α] -5.4°	141
	(–)-DIPT, -20°	(98) 88% ee	619
	TI (1), (–)-DET (1.2)	" (79) [α] +5.5°	618
	TI (1), (+)-DET (1), -20°	(79) 94% ee	1, 620
	TI (0.1)), (+)-DET ().15), 3 Å, -23°, 2.5 h	" (88) 72% ee	238
	TI (0.15), (–)-DET (0.2), 3 Å, -20°, 3 h	(99) >70% ee [α] +15.4°	621, 622

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.05), (–)-DET (0.075), 4 Å, -20°, 7 h	(—) 93% ee, [α] +5.0° *c*	623
	TI (1), (–)-DET (1), -15°, overnight	(60) [α] +9.4° *j*	94
TBDPSO	(–)-DMT (catalytic), 3 Å, -23°	TBDPSO (93)	76
Ph	(+)-DIPT (catalytic)	Ph (80) 80-85% ee	624
EtO₂C	(–)-DET, -25°, 20 h	EtO₂C (70) [α] -13.3°	566

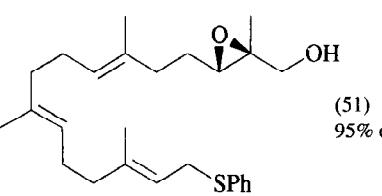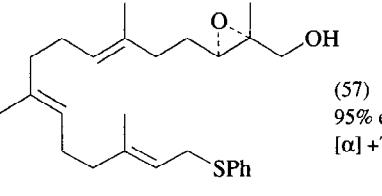TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

	Conditions		
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

TI (1), (+)-DET (1), -20°, overnight — (80) 95% ee [α] -25.8° — 625

TI (1), (–)-DET (1), -20°, overnight — (—) [α] +25° — 625

TI (0.2), (+)-DET, (0.28), 4 Å, -47 to -7° — (95) 94.8% ee [α] -21.9° — 626

TI (0.2), (–)-DET, (0.28), 4 Å, -47 to -7° — (93) 97.4% ee [α] +22.9° — 626

C_{11}

C_8H_{17}-*n* — TI (0.1), (+)-DET (0.13), 4 Å, -20°, overnight — (82) 96% ee — 426

Ph — TI (0.1), (+)-DET (0.13), 4 Å, -20°, overnight — (87) 87% ee — 426

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

	Conditions		
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

(+)-DIPT^a (catalytic) — (81) 92% de — 151, 152

(–)-DIPT^a (catalytic) — (69) 50% de — 150, 152

n-C_8H_{17} — TI (0.05), (+)-DET (0.06), 4 Å, -10°, 1.5 h — *n*-C_8H_{17} (78) 94% ee [α] -35.5° — 18

TI (1.15), (+)-DMT (1.5), -23°, 24 h — " (85) [α] -4.2° — 627

n-$C_5H_{11}C$≡C — TI (1.05), (–)-DMT (1.1), -20°, 24 h — *n*-$C_5H_{11}C$≡C (75) [α] +10.7° — 99

— — (88) [α] -10.0° — 282

(–)-DMT — (76) [α] +8.3° — 100

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
$n\text{-}C_5H_{11}$	TI (1.05), (–)-DMT (1.1)	$n\text{-}C_5H_{11}$ (—) 93% ee, [α] +17.9°	628
	(+)-DET (stoichiometric), –20°, 20 h	(82) >95% ee [α] –10.2°	629
	(+)-DET (stoichiometric), –20°	(85) >95% ee [α] –16.8°	282
	(–)-DET, –20°, 10 h	(85) >95% ee [α] +16.8°	283
Ph	(+)-DET, –23°	Ph (96) 94% ee	630
	TI (1.24), (+)-DET (1.36), 4 Å, –23°, 3 h	" (87) >95% ee, [α] –32.4°	631
OMEM ... OH	(+)-DIPT	OMEM ... OH (—) >95% ee	632

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.15), (+)-DIPT (1.38), –20°, overnight	(75) 83% de	113
	TI (0.3), (+)-DET (0.36), 3 Å, –23°, 6 h	(90) 92% de, [α] +18.3°	356
	TI (0.3), (–)-DET (0.36), 3 Å, –23°, 6 h	(80) 91% de, [α] +54.19°	356
OBn	(+)-DET, 4 Å	OBn (80)	633
MeO BnO MeO OH	(–)-DET	MeO BnO MeO OH (—)	634

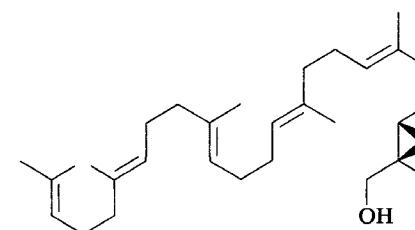TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
dl	(–)-DET, 4 Å	(92)[a] >95% ee + >90% ee	635
dl	(–)-DET, 4 Å	(78)[a] >90% ee + >86% ee	635
	TI (0.05), (+)-DET (0.057), 4 Å, -18°, 15 h	(72) 72% de	636

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.4), (–)-DET (1.4), -20°, 12 h	(99) >98% de	155, 156
	TI (0.15), (–)-DET (0.18), 4 Å, 0°, 7 h	(80) [α] -9.43°	521
	TI (0.15), (–)-DET (0.2), 4 Å, -28°, 14 h	(87)	588
	(+)-DET	(—)	163
	(–)-DET	(—)	163

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.1), (+)-DET (1.1), -20°, overnight	(92)^m [α] -100.8°	637
	(–)-DET	(—)	165
n-C$_8$H$_{17}$	TI (0.05), (+)-DIPT (0.074), 3 Å, -12°, 42 h	(63) >80% ee [α] -3.5°	18
n-C$_5$H$_{11}$	TI (1.1), (+)-DMT (1.1), -25°, 18 h	(71) 94% ee, [α] -10.2°	638
	TI (1), (–)-DIPT (1.2), -25°, 7 d	(90) 85.7% ee, [α] +10.6°	553
	TI (1.2), (+)-DET (1.4), -20°, 26 h	(55) 80.6% ee	109, 110
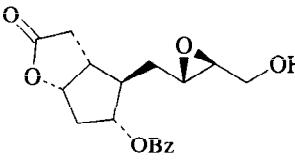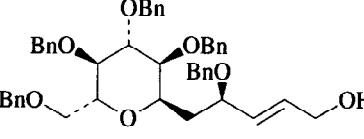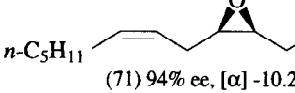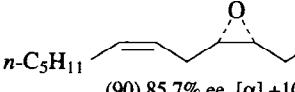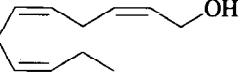
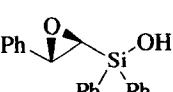TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1)^p, (+)-DET (1.4), -20°, 26 h	" (60) [α] +8.0°	141
	(+)-DET, 4 Å	(—)	639
	TI (1), (–)-DET (1.5), 4 Å, -25°, 15 h	(60) 88% ee [α] +5.53°	640, 641
	(–)-DET, 4 Å	" (60) 87-88% ee	639
Ph	(+)-DET	(80) 95% ee	328
	(–)-DET	(—)	531
p-EtC$_6$H$_4$	TI (1), (+)-DMT (1.1), -20°, overnight	(72) 87% ee, [α] -10.0°	642
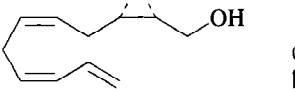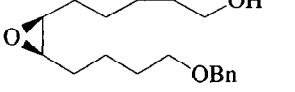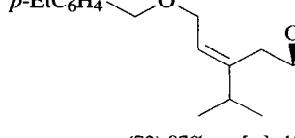
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.2), (+)-DMT (0.2)	(85) 91% ee [α] -103.6°	643
dl	(+)-DIPT, -20°	(84)ᵘ 100% de 86% de	153
	(+)-DET, -20°	(100) 100% de	347
	(–)-DET (stoichiometric), -20°	(90) 91%ee [α] -33.05° ˢ	145

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(+)-DET	>95% ee	644
	(–)-DIPT, -25°, 3 d	(60) >95% ee [α] -4.1° ᵍ,ʲ	645
	(+)-DET (stoichiometric), -20°, 11 h	(—) 84% ee	326
	(–)-DET (stoichiometric), -20°, 11 h	(—) 84% ee	326

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(+)-DET (stoichiometric), -20°, 11 h	(—) 88% ee	326
	(–)-DET (stoichiometric), -20°, 11 h	(—) 88% ee	326
	TI (0.1), (–)-DIPT (0.12), 3 Å, -50°	(83) 82-86% de	646
	TI (1), (–)-DET (1.2), -50°, 24 h	(89) 83% ee, [α] +56.2°	133
	TI (1), (–)-DET (1.2), -50°, 24 h	(82) 73% ee, [α] +47.2°	133

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(–)-DET, -25°	(30) 90-95% de [α] +65.3°	93
C$_{12}$	TI (1), (+)-DET (1.1), -40°, 48 h	(53) >96% ee, [α] +11.9°	647
	TI (1), (+)-DIPT (1), -20°, 20 h	" (55) [α] -13.2°	648
	TI (1), (–)-DIPT (1), -40°, 48 h	(41) >96% ee, [α] -11.0°	647
n-C$_9$H$_{19}$	TI (1), (+)-DET (1.2), -45°, 3 d	n-C$_9$H$_{19}$ (80) 96% ee	1, 649
EEO	(+)-DET	EEO (83) 92% ee [α] -18°	81
	(–)-DET	EEO (82) 92% ee [α] +17°	81

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.05). (+)-DIPT (0.08), -20 to 0°	(76) 79% de	224, 650-652
	TI (0.05). (–)-DIPT (0.08), -20 to 0°	(92) 75% de	224
	(+)-DIPT, 4 Å, -30°	(97) >90% de [α] -30.67°	653
	TI (1.19), (+)-DIPT (1.5), -20°, 5 h	(90)	113
	(–)-DET	(—)	531

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(–)-DMT (stoichiometric), -23°, 12 h	(59)	76
	TI (1.1), (–)-DET (1.1), -23°, 0.7 h	(76) 90% de, [α] -21.0°	154
	TI (0.05). (+)-DIPT (0.075), -20°, 48 h	(92)	654
	TI (1). (–)-DET (1.3), -23°, 16 h	(80)	655

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (–)-DET (1), -20°, 18 h	(57) [α] +5.43°	650, 652
MeO ... OBn	(DET), -20°	(—)	656
dl	(–)-DET	(90)ᵘ >95% de + >95% de	90
MeO ... MeO	TI (0.1), (+) DET, (0.15), 4 Å, -40°, 2.5 h	(97) 93% ee 100% eeⁱ [α] -21.7°	657, 658

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
MeO_2C ... OH	(–)-DIPT, 4 Å, -20°	MeO_2C ... OH (72) 90% de	75
t-BuO_2C ... OH	(+)-DMT (catalytic), 3 Å, -23°, 20 h	t-BuO_2C ... OH (80) 90% de	76
C_6H_4Me-p ... OH	TI (1), (+)-DET (1.2), 3 Å, -50°, 48 h	OH (75) 78% ee, [α] -48.4° C_6H_4Me-p	133
	TI (1), (–)-DET (1.2), 3 Å, -50°, 48 h	OH (76) 79% ee, [α] +53.5° C_6H_4Me-p	133
C_{13}			
n-$C_{10}H_{21}$ ... OH	(+)-DET	n-$C_{10}H_{21}$ ... OH >98% ee	212
	TI (1)ᵖ, (+)-DET (1.2), -40°, 6 h	" (76) 96% ee, [α] +25.9°	141, 649
... OH	TI (1), (–)-DET (1.2), -20°, overnight	... OH (71) 87% ee	659

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (–)-DET (1.3), -20°, 16 h	 (80) [α] -14.3°	655
	TI (3.0), (+)-DET (4.0), -23°	(72)	84
	(+)-Tartrate	(—)	163
	(–)-Tartrate	(—)	163

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(+)-DET	(—)	660
	(–)-DET	(—)	660
	(+)-DET	(—)	660
	(–)-DET	(—)	660
n-C$_{10}$H$_{21}$ ⟍⟍OH	TI (1), (+)-DET (1.2), -45°, 3 d	n-C$_{10}$H$_{21}$ ⟍⟍OH (80) 96% ee	649
	TI (1.03)^p, (+)-DET (1.19), -40°, 10 h	" (43) >95% ee^i, [α] +7.8°^{s}	141, 661

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1)^p, (–)-DET (1.2), –40°, 8 h	n-C$_{10}$H$_{21}$ ... OH (66) >95% ee^i [α] –7.8°^{s}	649
	TI (1), (–)-DET (1.05), –40°, 4 d	" (80) 91% ee	59, 661
(structure with OPr-i)	TI (1), (+)-DET (1.7), –23°, 24 h	(structure with OPr-i) (95) [α] +124.7°	175
(structure with OTMS)	1. TI (1.05), (+)-DIPT (2), 4 Å, –20°, 3 h 2. n-Bu$_4$NF	(structure with OTMS) (85) [α] +26°	83
(structure EtO, EtO, OTBDMS)	(–)-DET	(structure EtO, EtO, OTBDMS) (—)	662

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_{14}$			
n-C$_{11}$H$_{23}$ ... OH	TI (1), (+)-DET (1.2), 4 Å, –20°, 15 h	n-C$_{11}$H$_{23}$ ... OH (78) 94% ee [α] –25.5°	663
n-C$_5$H$_{11}$ ... OH	TI (1), (+)-DET (1), –23°, overnight	n-C$_5$H$_{11}$ ... OH (63) >90% ee, [α] –23.6°	664
	TI (1), (+)-DET (1), –23°, overnight	" (70) >90% ee, [α] –20°	665
(structure with TMS)	TI (1.1), (–)-DET (1.2), –40°	(structure with TMS) (—) 100% ee [α] –20.4°	666
n-C$_{11}$H$_{23}$ ... OH	TI (1.2), (+)-DIPT (1.3), –23°, 36 h	n-C$_{11}$H$_{23}$ ... OH (83.8) [α] +8.3°^{j,s}	667
	TI (1)^p, (+)-DET (1.2), –40°, 8 h	" (75), [α] +7.4°	141
	TI (1.2), (–)-DIPT (1.3), –23°, 36 h	n-C$_{11}$H$_{23}$ ... OH (—) [α] –8.1°^{j,s}	667

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1,1), (+)-DET (1.2), -40°	 (—) >90% ee [α] -1.2°	666
	(+)-DET, -20°, 24 h	 (81) [α] -25.2°	283
	(–)-DET (stoichiometric), -20°	 (87) >95% ee [α] +17.69°	668
	TI (1.2), (+)-DIPT (1.4), -20°	 (79) 96% ee	92

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(–)-DMT, 3 Å, -23°, 4 h	 (—) 88% de	77, 78
	TI (1), (+)-DET (1.3), -23°, 2 h	(59) 94% ee, [α] -9.56°	412, 126
C₁₅	TI (1), (–)-DIPT (1.25), 4 Å, -20°, 16 h	 (60) 90% de	669
n-C₁₂H₂₅	(+)-DET	n-C₁₂H₂₅ (—)	670
	TI (0.05), (–)-DIPT (0.075), 4 Å, -20°, 5 h	(60)	671

C$_{15}$

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.05), (+)-DET (0.075), -20°, 12 h	(92)	654
	TI (1), (+)-DET (1.4), 4 Å, -23°, 40 h	(72) 85.4% ee [α] -7.2°	672
	TI (1), (–)-DET (1.4), 4 Å, -23°, 40 h	(65) 85.4% ee [α] +7.4°	672
	(+)-DET	(—)	531

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.07), (–)-DET (1.12), -50 to -45°, 1 h	(84) 96% ee, [α] +6.53°	213, 214, 179
	(+)-DIPT	(82) 80% ee	673
	TI (0.05), (+)-DET (0.074), 3 Å, -20°, 1.5 h	(—) 91% ee	18
	TI (1), (+)-DET (1), -20°	" (87) >95% ee	1
	TI (1), (+)-DBTA (1.2), -20°	" (—) 96% ee	130
	TI (2), (+)-DET (1)	" (—) 78% ee	130
	TI (2),(+)-DBTA (1), -20°	(—) 82% ee	130
	Ti (1), (+)-DIPT (1), -20°, 15 h	(81) >90% ee [α] +60.9°ˢ	58

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	Ti (1), (+)-DIPT (1), -20°, 15 h	 (81) >90% ee [α] +39.7° [s]	58
	Ti (1), (+)-DIPT (1), -20°, 15 h	 (81) >70% ee [α] +148.2° [s]	58
	TI (1), (+)-DET (1), -20°, 14 h	 (80.6), [α] -6.5° [g]	674
	TI (0.1), (–)-DIPT (1.17), 4 Å, -45°, overnight	 (76) >95% ee	675

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(–)-DET (catalytic), 4 Å, -20°	(92)	179
	TI (1.02), (–)-DET (1.11), -45°, 1 h	" (84) 96% ee, [α] +6.53°	213, 214
C_{16} 	TI (1.07), (–)-DET (1.29), -20°, 15 h	(63) 95% de [α] +21.7°	124
	TI, (+)-DMT	 (—) 95% ee	676
	TI (1), (+)-DET (1.3), -23°, 21 h	(77), [α] -7.13°	412
C_{17} 	TI (0.1), (+)-DET (0.13), 3 Å, -12°, 11 h	(91) 96% ee, [α] -10.9°	18
	(+)-DET (stoichiometric)[c], -20°	" (51)	130

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (+)-DIPT (1), -27°, 18 h	" (26) >94% ee, [α] -9.45°	677
	TI (2)^v, (+)-DET (1), 0°	(73) 68% ee	130
n-C$_{14}$H$_{29}$ ⟍⟍OH	(+)-DIPT (stoichiometric)	n-C$_{14}$H$_{29}$ ⟍⟍OH (77) >95% ee [α] -27.0°^{e}	299, 678
n-C$_{12}$H$_{25}$ ⟍⟍OH	TI (1), (+)-DET (1), -25°, overnight	n-C$_{12}$H$_{25}$ ⟍⟍OH (70) [α] -14°	679
AcO structure OAc	TI (3.6), (+)-DET (5), -20°, overnight	AcO structure OAc (87) [α] -28°	680
⟍⟍OH C$_8$H$_{17}$-n	TI (1), (+)-DIPT (1.2), -30°, 9 d	⟍⟍OH C$_8$H$_{17}$-n (50) 58% ee [α] -2.9°^{d}	681

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
structure OBn / OH	(+)-DET	structure OBn / OH (—)	531
TsNAc structure TBDPSO OH	TI (1), (+)-DET (1.1), -20°, 1.5 h	TsNAc structure TBDPSO OH (98) 90% ee, [α] -14.9°	682
TBDMSO structure OH	(−)-DMT, 3 Å, -23°, 4 h	TBDMSO structure OH (80) 88% de	77, 78

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
Ph, C=C with Me, CH₂OH, Ph (structure)	TI (1.2), (–)-DET (1.5), -20°, 5 h	epoxide product (90) 94% ee	411
$n\text{-}C_{15}H_{31}$ CH=CH-CH₂OH	TI (1.2), (–)-DET (1.6), -20°, 38 h	$n\text{-}C_{15}H_{31}$ epoxide CH₂OH (75) [α] +22.5°	650-652, 321
$n\text{-}C_{13}H_{27}C\equiv C$ CH=CH-CH₂OH	TI (1)[c], (–)-DET (1.2), -25°, 4-5 h[w]	$n\text{-}C_{13}H_{27}C\equiv C$ epoxide CH₂OH (86)[w] >98% ee [α] -2.2°	102, 103
(polyene) CH₂OH with $C_9H_{19}\text{-}n$	TI (1), (+)-DIPT (1.2), -30°, 9 d	epoxide (with $C_9H_{19}\text{-}n$) 71% ee [α] -3.4°[d]	681
	TI (1.2), (+)-DMT (1.4), -23 to -30°, 69 h	" (77) 68% ee	683, 684
	TI (1), (–)-DIPT (1.2), -30°, 9 d	epoxide (with $C_9H_{19}\text{-}n$) 60% ee [α] +3.3°[d]	681
	TI (1), (–)-DMT (1), -20°, 2 d	" (70) 65% ee	683, 684

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(pyran structure) BOMO, H, H, OTMS, CH₂OH	TI (0.05), (–)-DET (0.08), 4 Å, -23°, 16 h	epoxide product BOMO, H, H, OTMS (94) 48% de, [α] +6.8°	685
(macrocycle) CH₂OH	TI (1), (+)-DET (1.3), -23°	epoxide macrocycle CH₂OH (—) >90% ee	686
	TI (1), (+)-DET (1.3), -23°, 16.5 h	" (74), [α] -5.82°	412
C_{19} Ph(CH₂)₁₀ (D, D epoxide) CH₂OH	TI (0.05), (+)-DET (0.05), 4 Å, -22°, 2.5 h	Ph(CH₂)₁₀ (D, D epoxide) CH₂OH (65) >97% ee [α] -19.15°[d]	687
	TI (0.05), (–)-DET (0.05), 4 Å, -22°, 2.5 h	Ph(CH₂)₁₀ (D, D epoxide) CH₂OH (60) >97% ee [α] +19.3°[d]	687

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
MOMO *i*-Pr(CH₂)₉ ⋯ OH	TI (0.4), (–)-DIPT (0.5), 4 Å, -20°, 15 h	MOMO O *i*-Pr(CH₂)₉ ⋯ OH (90) 50% de	688
OH C₁₀H₂₁-*n*	TI (1), (+)-DIPT (1.2), -30°, 9 d	O OH C₁₀H₂₁-*n* (—) 90% ee [α] -3.4° *d*	681
	TI (1), (–)-DIPT (1.2), -30°, 9 d	O OH C₁₀H₂₁-*n* (—) 81% ee [α] +4.0° *d*	681
MeO O OAc OH O	TI (1), (+)-DET (1.2), 4 Å, -20°, 15 h	MeO O OAc O OH O (80) 96% ee	122
C₂₀ OH C₁₁H₂₃-*n*	TI (1), (+)-DIPT (1.2), -30°, 9 d	O OH C₁₁H₂₃-*n* (—) 87% ee [α] -3.4° *d*	681
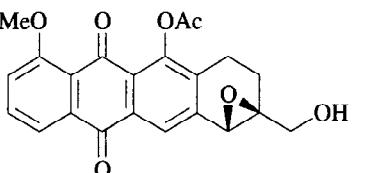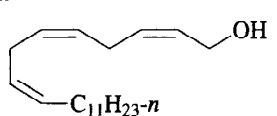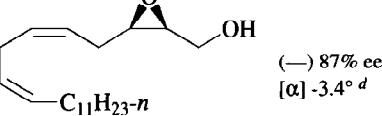
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (–)-DIPT (1.2), -30°, 9 d	O OH C₁₁H₂₃-*n* (—) 81% ee [α] +3.8° *d*	681
OH SPh	TI (0.106), (+)-DET (0.127), -20°, 4 h	O OH SPh (51) 95% ee	689
	TI (0.106), (–)-DET (0.127), -20°, 4 h	O OH SPh (57) 95% ee [α] +7.88°	689
OTMS OH MOMO H H	1. TI (1.1), (+)-DIPT (1.5), 4 Å, -20°, 4 h 2. Bu₄NF	OH O OH MOMO H H (98) [α]+3.0°	82, 83
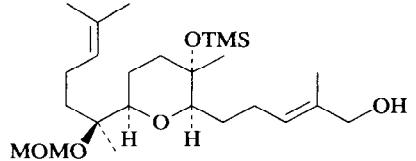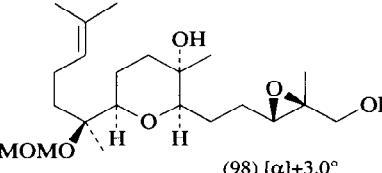
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (+)-DET (1), -20°, 18 h	(57)	690
	TI (1), (–)-DET (1), -20°, 18 h	(36)	690
	TI (0.4), (–)-DET (0.6), 4 Å, -25°, 2 h	(93) 80% de	690
	TI (1), (+)-DET (1), -20°, 18 h	(74)	691

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield (s) (%)	Refs.
	TI (1), (–)-DET (1), -20°, 18 h	(65)	691
	TI (4.6, (–)-DET (4.7), -50°, 2 h	(65) 50% de, [α] +28°	692
	(–)-DMT, -20°	(85) 95% ee [α] +4.39° s	693-695
	TI (1), (–)-DIPT (1), 4 Å, -30°, 16 h	" (95), [α] +4.88°	653, 696

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

| | Conditions | | |
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_{21}$			
	TI (1), (+)-DET (1), -20°, 20 h	(80) [α] -8.90°	650-652
	TI (5.8), (–)-DET (5.8), -10°, 40 h	(85) 53% ee	120, 121
C$_{23}$	(–)-DET	(—)	697
C$_{25}$	(+)-DET (stoichiometric)	(—) >95% ee, [α] -23.8°	438

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

| | Conditions | | |
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_{26}$			
	TI (1), (–)-DET (1), -20°, overnight	(72) >95% de, [α] +42° [g]	698
C$_{27}$			
	TI (0.8), (+)-DET (0.8), -25°, 18 h	(86) >98% de, [α] -38.4°	79

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (0.8), (–)-DET (0.8), -25°, 18 h	(79) >98% de, [α] -4.8°	79
	TI (1), (–)-DET (1), -25°, 24 h	(82) 90% de	699
	TI (2.4), (+)-DET (2.4), 3 Å, -25°, 16 h	(74) >95% ee	700

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (+)-DET (1), -20°, 18 h	(86) 98% de, [α] -38.4°	79
	TI (1), (–)-DET (1), -20°, 18 h	(70) 98% de, [α] -4.8°	79
C_{30}	TI (1), (+)-DET (1), -20°, 1 h	(70) 100% de, [α] +43°	701

TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1), (–)-DET (1), -20°, 1 h	(82) 100% de, [α] +64°	701
	TI (0.2), (+)-DET (0.2), 4 Å, -20°, 1 h	(87) 87% ee, [α] -3.31°	358, 702
	TI (1), (+)-DMT (1), -20°, 3 h	" (70) 80% ee, [α] -3.05°	703
	TI (0.2), (–)-DET (0.2), 4 Å, -20°, 1 h	(93) 78% ee, [α] -5.8°	358
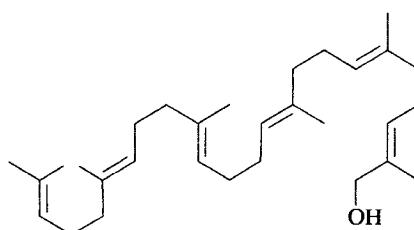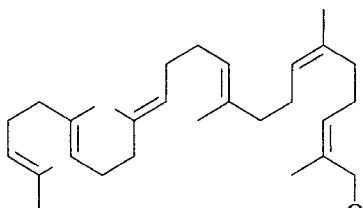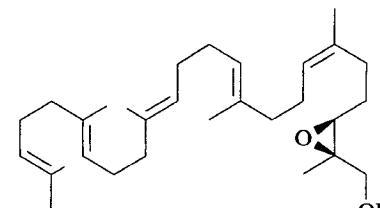
TABLE I. ASYMMETRIC EPOXIDATION OF PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

a The oxidant was cumene hydroperoxide.

b The product was isolated as the mesylate.

c The titanium alkoxide was Ti(OBu-*t*)$_4$.

d The rotation was measured in dichloromethane.

e The rotation was measured in benzene.

f The titanium alkoxide was titanium-pillared montmorillonite.

g The rotation was measured in methanol.

h The reaction was slow.

i The % ee was reported for recrystallized material.

j The rotation was reported for recrystallized material.

k The rotation was measured in diethyl ether.

l The reaction was quenched with triethanolamine.

m A single isomer was obtained.

n The optical purity was enhanced by the sequence: 3,5-dinitrobenzoylation, recrystallization, and hydrolysis.

o The intermediate allylic alcohol produced in situ by the ene reaction of singlet oxygen with 2-*tert*-butylpropene was oxidized with Ti(OBu-*t*)$_4$ and (+)-DET.

p The reaction was conducted in the presence of catalytic amounts of calcium hydride and silica gel.

q The reaction furnished a diastereomeric mixture containing a marginal excess of 2*R*,3*R* isomer.

r The rotation was reported for neat material.

s The rotation was measured in ethanol.

t The rotation was reported for chromatographically purified material.

u The total yield of diastereomeric products was reported.

v The titanium alkoxide was TiCl$_2$(OPr-*i*)$_2$. The resulting 2-chloromethylhexane-1,3-diol was converted into the epoxy alcohol by treatment with base.

w The reaction was carried out in a 1:1 mixture of 2,3-dimethyl-2-butene and dichloromethane.

TABLE II. ASYMMETRIC EPOXIDATION OF BISALLYLIC ALCOHOLS

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C_8 HO ... OH	(+)-DIPT (0.6), 4 Å, -20°, 84 h	HO ... OH (96) 70% ee, $[\alpha]$ -18.4°	53
C_{10} HO ... OH	(+)-Tartrate (catalytic)	HO ... OH (65)	70
C_{11} OH HO ... t-BuO$_2$C O H H O CO$_2$Bu-t	(+)-DET (0.6), 4 Å, -40°, 13 h	OH HO ... t-BuO$_2$C O H H O CO$_2$Bu-t (81)	72
C_{12} OH OH	TI (2.5), (+)-DET (3), -15°, 18 h	OH OH (27) 99.45% ee[a]	68, 69
OH OH	TI (2.5), (+)-DET (3), -15°, 18 h	OH OH (—)	68
C_{13} OH OH	TI (0.6), (+)-DET (0.6), -20°, 4 d	OH OH (58.4) $[\alpha]$ -33.8°	71

[a] The ee was calculated (see text, p. 14).

TABLE III. ASYMMETRIC EPOXIDATION OF ALKENYLSILANOLS
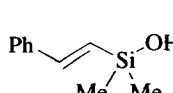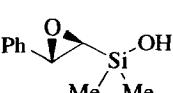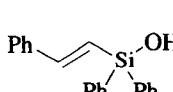
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_8$			
PhSiOH / Me Me	(+)-DET (stoichiometric), -20°, 40 h	PhSiOH / Me Me (50) 85-90% ee	54
PhSiOH / Ph Ph	(+)-DET (catalytic), MS^a, -20°, 40 h	PhSiOH / Ph Ph 20% ee	54
	(+)-DET (stoichiometric), -20°, 40 h	" (70) 7% ee	54

^{a} The type of molecular sieves used was not reported.

TABLE IV. KINETIC RESOLUTION OF RACEMIC PRIMARY ALLYLIC ALCOHOLS

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
C₉	(–)-DIPT, -20°	(55) 40% ee. [α] +1.0°	(—)	146
C₁₀	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20° 50-60% conversion	(—) 48% ee	(—)	145
C₁₁	"	(—) 6% ee	(—)	145
	"	(—) >95% ee	(—)	145
	"	(—) 80% ee	(—)	145
	"	(—) 40% ee	(—)	145
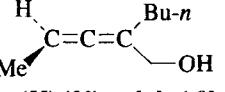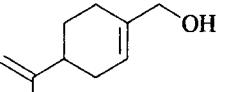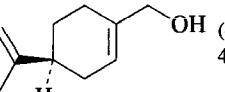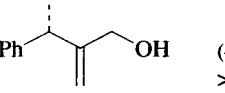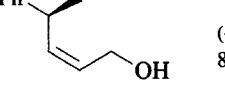
TABLE IV. KINETIC RESOLUTION OF RACEMIC PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
+ enantiomer	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20° 50-60% conversion	(—) 85% ee	(—)	145
+ enantiomer R =	TI (1.5), (+)-DET (1.52), TBHP (3.0), -20°, 12 h	(15) >95% ee	(29) >95% ee + (19) >95% ee	168, 169
C₁₂	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20° 50-60% conversion	(—) 70% ee	(—)	145, 146
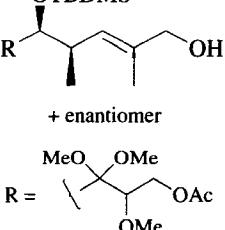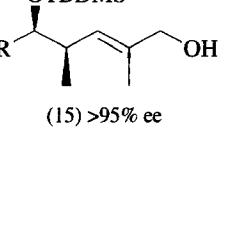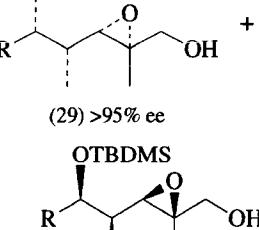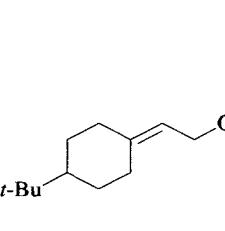
Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
(structure)	(−)-DIPT	(—)	(structures) +	90
			total (90) >95% ee	

C$_{13}$

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
(structure) + enantiomer	TI (1.0), (+)-DET (1.2), TBHP (0.5), -23°, 50 min	(62) >95% ee [α] -64.7°	(30) >95% ee	56

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
(phosphine oxide structure)	TI (0.5), (+)-DIPT (0.6), TBHP (0.5), 4 Å, -16°, 5 d	(allylic alcohol structure)	(epoxy alcohol structure) I + II	449

	R			anti (I)	anti:syn	syn (II)
C$_{17}$	Me	(—) 10% ee		(—)	54:46	(—)
C$_{18}$	Et	(—) 31% ee		(—) 82% ee	65:35	(—)
C$_{19}$	Pr-*i*	(—) 65% ee		(—) 85% ee	93:7	(—)
C$_{21}$	C$_5$H$_{11}$-*n*	(—) 36% ee		(—)	68:32	(—)
C$_{22}$	C$_6$H$_{11}$	(—) 65% ee		(—) 75% ee	90:10	(—)

TABLE IV. KINETIC RESOLUTION OF RACEMIC PRIMARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
C$_{17}$ *i*-Pr$_3$SiC≡C—(CH$_2$)$_{10}$ structure + enantiomer	TI (1.0), (+)-DET (1.2), TBHP (0.58), -23°, 2.5 h	(45) 70% ee, [α] +39.4° [a]	(—)	704
C$_{18}$ (structure) + enantiomer	TI (1.0), (+)-DET (1.2), TBHP (0.6), -23°, 10 min	(89) 95% ee	(—)	705
C$_{18}$ *n*-Bu (CH$_2$)$_n$ structure + enantiomer	TI (1.0), (+)-DIPT (1.2), -20°	(structure)	(structure)	412

	n	TBHP	t		
C$_{18}$	10	0.6	42 min	(35) 98% ee, [α] +67.8°	(58) 56% ee
C$_{20}$	12	0.6	20 min	(40) 99% ee, [α] +133°	(31) 76% ee
	12	1.5	6.8 h	(—)	(62) 0% ee
C$_{21}$	13	0.6	1.5 h	(41) 90% ee, [α] +121.1°	(41) 66% ee
	13	1.5	5 h	(—)	(55) 0% ee
C$_{22}$	14	0.6	16 min	(33) 0% ee	(29) 80% ee
	14	1.5	3.5 h	(—)	(62) 0% ee

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
C$_{25}$ (structure) + enantiomer	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -23°, 10 min	(42) >90% ee, [α] +46.9°	(—)	686

[a] The type of solvent was not reported.
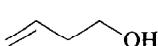
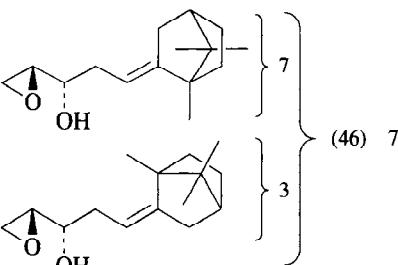| Substrate	Conditions Tl (or ZR^a) (eq), DRT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_4$	(+)-DET^b, 0°, 4 d	(11-25) 55% ee [α] +12.48° ^{c}	176
	Zr (1), (+)-DCTA^d (1.3), 0°,12 d	" (4) 40% ee	178
C$_5$	Zr (1), (+)-DCTA^d (1.3), 0°, 9 d	(25) 77% ee	178
C$_6$	(+)-DET^b, -20°	(35-40) 41% ee [α] +17.69° ^{e}	176
	Zr (1), (+)-DCTA^d (1.3), 0°,14 d	" (38) 43% ee	178
	(+)-DET^b, 0°, 5 d	(50) 36% ee [α] +5.35° ^{e}	176
	(+)-DET^b, -20°	" (30) 50% ee	176
	Zr (1), (+)-DCTA^d (1.3), 0°, 8 d	" (23) 72% ee	178
	(+)-DET^b, -20°	(41) 27% ee	176
	(+)-DET^b, -20°	f (60) 23% ee [α] +1.46° ^{e}	176
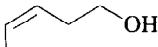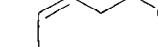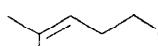
Substrate	Conditions Tl (or ZR^a) (eq), DRT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(+)-DET^b, -20°	(15) [α] +1.63° ^{e}	176
C$_7$	Zr (1), (+)-DCTA^d (1.3), 0°, 8 d	(28) 74% ee	178
	(+)-DET^b, -20°	(62) 48% ee [α] +2.70° ^{e}	176
C$_8$	Tl (1), (+)-DET (1.2), 144 h	(50) 60% ee [α] +4.8°	140
	Tl (1)^g, (+)-DET (1.2), 24 h	" (60) 60% ee, [α] +4.6°	140
C$_9$	Zr (1), (+)-DCTA^d (1.3), 0°, 16 d	(21) 53% ee	178
C$_{10}$	Tl (1), (+)-DET (1.17), 0°, 48 h	f (22) 29% ee	706
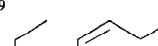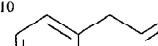
TABLE V. ASYMMETRIC EPOXIDATION OF HOMO-, BISHOMO-, AND TRISHOMOALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (or ZR^a) (eq), DRT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_{11}$	TI (1), (+)-DET (1.17), 0°, 48 h	f (<10)	706
C$_{12}$	TI (1), (+)-DET (1.17), 0°, 48 h	f (49) 56% ee	706
	(−)-DET, (catalytic), 3 Å, −23°, 4 d	(80) 50% de	76
	TI (1.1), (−)-DET (1.3), (MS)^{h,i}, 0-23°, 15 h	(74)^j	179

TABLE V. ASYMMETRIC EPOXIDATION OF HOMO-, BISHOMO-, AND TRISHOMOALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (or ZR^a) (eq), DRT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(+)-DET, (MS)^{h,i}	(—) 14% de	179
(CH$_2$)$_{10}$ ... OH *dl*	TI (1)^k, (+)-DET (1.5)	(CH$_2$)$_{10}$ ... O ... OH (35) [α] −1.3°	126

^{a} ZR represents Zr(OPr-n)$_4$.

^{b} The Ti(OPr-i)$_4$:DRT ratio was 1:1.1-1.2.

^{c} The rotation was measured in dichloromethane.

^{d} DCTA represents (*R,R*)-(+)-*N,N*'-dicyclohexyltartramide.

^{e} The rotation was measured in ethanol.

^{f} The stereochemistry of the product was not reported.

^{g} The reaction was conducted in the presence of catalytic amounts of calcium hydride and silica gel.

^{h} The type of molecular sieves used was not reported.

^{i} The oxidant was trityl hydroperoxide.

^{j} The reaction did not produce an appreciable amount of the diastereomeric 6*R*,7*R*-epoxide.

^{k} The reaction was carried out in dichloroethane.

TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS

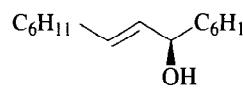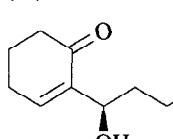| Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	A. Secondary Allylic Alcohols			
C$_4$	TI (0.1), (–)-DIPT (0.12), 41.5 h	(—) 88% ee	(—)	38
	TI^a (0.1), (–)-DIPT (0.12), 51 h	" (—) 72% ee	(—)	38
	(–)-DIPT	(—)	(51) 91% ee [α] -16.3° ^{b}	707, 708
	TI (1.0), (–)-DIPT (1.2), TBHP (0.5), -20°	(—)	" (27) >95% ee	709
	TI (1.0), (–)-DIPT(1.2), TBHP (0.6), -20°, 26 h	OBn (37) 95% ee [α] +5.9°	OBn (41) 94% ee [α] -10.4°	581, 582
	TI (0.1), (–)-DIPT (0.12), 3 Å, TBHP (0.6), -15°, 14 d	(—)	" (41) >95% ee, [α] -11.23°	710, 711
C$_5$	(–)-DIPT, 4 Å, -20°, 30 h	(—)	(31) >95% ee [α] -29.9°	712
	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20°, 6 d	(–) 91% ee [α] -7.7° ^{c}	(—)	10
TMS	—	TMS (—)	(—)	713
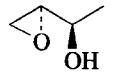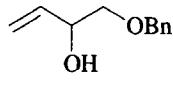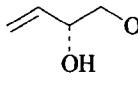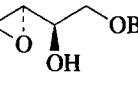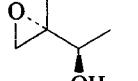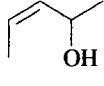
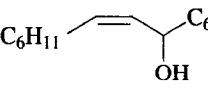# TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS (*Continued*)
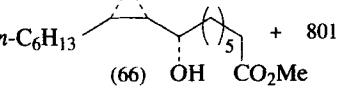
Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°, 15 h	(—)	(24)	714
	TI (1.0), (–)-DIPT (1.2) TBHP (0.6), -20°, 15 h	(—)	(23)	714
	(+)-DIPT, 70% conversion	(—) 100% ee	(—)	715
	TI (0.04), (+)-DIPT (0.06), cumene hydroperoxide (1.95), 4 Å, -5°	" 100% ee, [α] -24°	(—)	716
NHBoc	—	(—)^d	(—)	717
NHCbz	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20°, 8 d	NHCbz (32) 92% ee, [α] -2.60°	NHCbz (24), [α] +5.93°	95, 96
	TI (1.0), (–)-DIPT (1.2), TBHP (0.6), -20°, 8 d	NHCbz (44) 92% ee, [α] +2.64°	NHCbz (34), [α] -5.93°	96
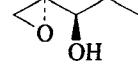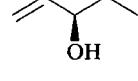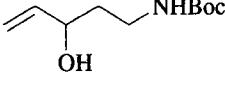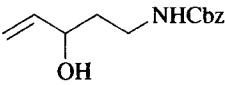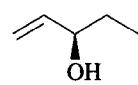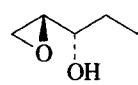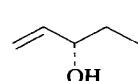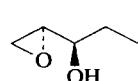
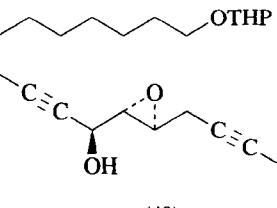| Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	(+)-DIPT	(—) 94% ee [α] -7.9°	(—)	718
	(–)-DIPT, -20°	(—)	(45) 88% ee	719, 720
	(+)-Tartrate	(—)	(—)	721, 722
	TI (0.1), (–)-DIPT (0.12), 10 h	(—) 89% ee	(—)	38
	TI[a] (0.1), (–)-DIPT (0.12), 10 h	" (—) 92% ee	(—)	38
	—	(—) 60% ee	(—)	723
	TI (1.0), (+)-DIPT (1.2), -20°, overnight	(30) 79% ee	(—)	724
	TI (0.5), (+)-DET (0.6), TBHP (0.5), 4 Å, -16°, 5 d	95% ee	>95% ee	449

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	—	(—)	(—) 60% ee	725
C6	TI (1.0). (–)-DIPT (1.1) TBHP (1.5). -20°, 16 h	(—)	(40) 90% ee, [α] +26.2°	112
	TI (1.0), (–)-DMT TBHP (0.5), -20°	(—)	(27) 93% ee	709
	—	(–) 98% ee [α] -4.9241	(—)	726
	(+)-DIPT	(39) [α] +4.8°	(—)	727
	TI (1.2), (+)-DIPT (1.5) TBHP (3.0), -25°, 96 h	(16) >95% ee, [α] +14.6°c	(—)	414

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	(–)-DIPT	96% ee	(—)	728
	TI (0.1), (–)-DIPT (0.12), 12 h	" (—) 92% ee	(—)	38
	TI[a] (0.1), (–)-DIPT (0.12), 20 h	" (—) 82% ee	(—)	38
	TI (1.0), (–)-DIPT (1.2), TBHP (0.4). -20°	(—)	(35) >95% ee	145
	(+)-Tartrate	(—)	(35) >95% ee	729
	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20°, 4 d	(—) 30% ee [α] +37.1°	(—)	10
	TI (1.0), (+)-DIPT, CaH₂ (cat.), SiO₂ (cat.), TBHP (0.6), -20°, 6 h	(25) 94% ee [α] -4.3°	(24) 96% ee [α] -2.6°	140
	TI (0.5), (+)-DET (0.6), 4 Å, TBHP (0.5), -16°, 5 d	91% ee	>95% ee	449

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
Bu-*n*	—	Bu-*n* (—) >95% ee	(—)	730
	TI (1.0), (+)-DET (1.1), TBHP (1.0), -20°, overnight	" (43.5) >90% ee, [α] -6.0°	(—)	731
	TI (1.0), (–)-DIPT (1.17), TBHP (1.39), -20 41, 40 h	(—)	Bu-*n* (37) 94% ee [α] -24.5°	732
	TI (0.5), (+)-DIPT (0.6), TBHP (2), -20°, 4.5 h	(—)	(49) [α] -11.2° [b]	733
	TI (0.5), (–)-DIPT (0.6), TBHP (2), -20°, 4.5 h	(—)	(48) [α] +11° [b]	733
	(–)-DIPT, -10°		" [α] +8.7° [b]	734
Bu-*t*	TI (1.0), (+)-DET (1.0)	(—)	Bu-*t* (60) 10% ee	57
	TI (0.1), (+)-DIPT (0.15)[e], 3 Å, -20°, 12 h	(28) [α] +3.4°	(—)	735, 736
	TI (0.1), (+)-DIPT (0.15)[e], 3 Å, -20°	(36) [α] +2.0°	(—)	735, 736

TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	(+)-DIPT	(55) 48% ee	(—)	737
	TI (0.1), (+)-DCHT (0.15), 3 Å, -20°, 44 h	(35) 98% ee	(—)	738
	TI (1.1), (+)-DIPT (1.2), 4 Å, TBHP (1.5), -20°, 44 h	(46) 95% ee	(44) 98% ee, [α] -11.6°	493
	TI (0.13), (–)-DIPT (0.17), 4 Å, TBHP (0.67), -25°, 20 h	(46) 80% ee [α] +6.7°	(—)	739
	—		(—)	721, 740-742
	TI (0.1), (–)-DIPT (0.12), 18 h	(—) 90% ee	(—)	38
	TI*a* (0.1), (–)-DIPT (0.12), 16 h	" (—) 47% ee	(—)	38

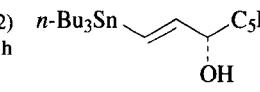TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS (*Continued*)

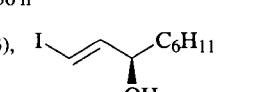| Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (0.13), (+)-DIPT (0.21), TBHP (0.42), -25°	(35) 90% ee	(43.5) 90% ee	743
	TI (0.13), (–)-DIPT (0.21), TBHP (0.45), -20°, 5 d	(39) 90% ee	(40) 90% ee	183
	(–)-DCHT	(—)	(—) >96% ee	744
	TI (1.0), (–)-DIPT (1.5), TBHP (0.4), -20°, 18 h	(30) 72% ee, [α] -8.9°	(27) >95% ee, [α] +3.0°	183, 247
	TI (0.1), (+)-DIPT (0.16), TBHP (0.42), -20°, 43 h	(46) 68% ee	(37) >95% ee	183
	TI (0.1), (–)-DIPT (0.15), 4 Å, TBHP (0.5), -25°, 20 h	(—)	" (43) >96% ee	322
BnO	(+)-DET, -20°	(—)	(46)	745
I, CO₂Me	TI (0.31), (–)-DIPT (0.37), 4 Å, TBHP (1.5), -20°, 48 h	(38) >98% ee	(—)	746

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (1.0), (+)-DIPT (1.1), TBHP (0.6), -20°, 4 d	(—) 80% ee [α] +25° [b]	(—)	10
	(+)-DIPT	(31) 69% ee	(41) 50% ee	747
69% ee	(−)-DIPT	(10) 38% ee	(59) 86% ee	747
C$_8$	TI (1.0), (−)-DIPT (1.2) TBHP (2.0), -20°, 14.5 h	(—)	(42) 93% ee [α] -22.3°	748,749
	TI (0.56), (+)-DIPT (0.67) TBHP (1.13), -20°, 16 h	(—)	(41) [α] +24.7°	749
	(−)-DIPT, -20°, 6 d	(—) >98% ee [α] +14.9^{ob}	(—)	750
	—	(—) 78% ee, [α] +7.3°	(—)	751

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
C≡CTMS	TI (0.1), (+)-DCHT (0.15), 3 Å, -20°, 44 h	(—)	(—)	738
C≡CH OTBDPS	(−)-DCHT, -20°	(46) 98% ee	(—)	752
Bu-*n*	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20°, 15 h	(—) >96% ee [α] +3.2° [c]	(—)	10
	TI(0.1), (+)-DIPT (0.15) TBHP (0.7), -20°, 27 h	" (44) 94% ee, [α] +3.6^{cf}	(—)	18
	TI(0.1), (+)-DCHT (0.15) TBHP (0.7), -20°, 29 h	" (44) 97% ee, [α] +3.8^{cf}	(—)	18
	TI(0.1), (+)-DCDT (0.15) TBHP (0.7), -20°, 24 h	" (42) >98% ee, [α] +4.2^{cf}	(—)	18
C≡CTMS	(−)-DIPT, TBHP (0.6), -22°	C≡CTMS (—)	C≡CTMS (—) 93% ee	753
Bu-*t*	TI (1.2)^a, (+)-DIPT (1.5)	(—)	Bu-*t* (60) 30% ee	57

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
TMS / C₅H₁₁-n / OH	Tl (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°, 24 h	TMS C₅H₁₁-n OH (44) 87% ee [α] +6.8°	TMS C₅H₁₁-n OH (8) 79% ee [α] -7.0°	191, 13
(structure) O–C(=O)–N(Pr-i)₂ OH *dl*	Tl (1), (+)-DIPT (1.2), TBHP (0.55), -16°, 24 h	O–C(=O)–N(Pr-i)₂ OH (59) 41% ee, [α] +8.6° *f*	O–C(=O)–N(Pr-i)₂ OH (26) 57% ee, [α] -14.6° *d*	754
n-Bu / OH	—	n-Bu / OH (—)	(—)	730
OBn / OH + enantiomer	(+)-DET	(—)	OBn OH (35)	755
	(−)-DET	(—)	OBn OH (35)	755

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
Bu-n / OH	—	Bu-n / OH (—)	(—)	721, 722
Bu-t / OH	Tl (1.2), (+)-DMT (1.5)	(—)	Bu-t OH (—)	57
Pr-i / OH	(+)-DIPT	Pr-i OH (—) 67% ee (—) [α] +7.2°		756
	—	" (—) 78% ee	(—)	757
OH (diene)	(+)-DIPT	OH (—)	OH (—) 96% ee, [α] -28.3°*c*	758
CO₂Et / OH	Tl (1.0), (−)-DET (1.5) TBHP (0.7), -25°, 25 min	(—)	CO₂Et OH (—), [α] +17.6°	414

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
(enyne-OBn allylic alcohol, OH)	TI (1.0), (−)-DET (1.0), TBHP (0.6), -20°	(—)	(epoxy-OBn structure) (—)	157
Ph₂P=O structure + enantiomer	TI (0.5), (+)-DET (0.6), 4 Å, TBHP (0.5) -16°, 5 d	Ph₂P=O structure 89% ee	Ph₂P=O structure >98% ee	449
Ph₂P=O structure + enantiomer	TI (0.5), (+)-DET (0.6), 4 Å, TBHP (0.5) -16°, 5 d	Ph₂P=O structure 37% ee	Ph₂P=O structure 52% de	449
(1-(cyclohexen-1-yl)ethanol, OH)	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20°, 15 h	(—) >96% ee	(—)	10
	TI (0.1), (+)-DIPT (0.15), 3 Å, TBHP (0.7), -20°, 3.5 h	" (46) >98% ee, [α] +3.29° *c*	(—)	18
	TI (0.1), (+)-DCHT (0.15), 3 Å, TBHP (0.7), -20°, 3.5 h	" (43) >98% ee, [α] +3.59° *c*	(—)	18

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (0.1), (+)-DCDT (0.15), 3 Å, TBHP (0.7), -20°, 4 h	" (43) >98% ee, [α] +3.16° *c*	(—)	18
Ph₂P(O) structure Pr-*n*, OH	TI (0.5), (+)-DET (0.6), 4 Å, TBHP (0.5), -16°, 5 d	Ph₂P(O) structure Pr-*n*, OH 80% ee	Ph₂P(O) structures Pr-*n*, OH (+) 1:1	449
(cyclohexenone structure, O, OH)	(−)-DET, -15°, 50% conversion	(—) 50% ee	(—) 78% ee	759
	(−)-DET, -15°, 75% conversion	" (—) 88% ee	" (—) 19% ee	759
TMS n-Bu structure, OH	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°, 1 h	TMS n-Bu structure, OH (41) >99% ee, [α] +17.5°	TMS n-Bu epoxy structure, OH (42) >99% ee, [α] -4.86°	191, 13

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
C_9				
	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20°, 12 d	(—) >96% ee $[\alpha]$ -19.1°c	(—) $[\alpha]$ -4.0°	10, 408
	TI (0.1), (+)-DIPT (0.15), 3 Å, TBHP (0.6), -20°, 13 d	" (45) 86% ee, $[\alpha]$ -14.9°c	(—)	18
	TI (0.1), (+)-DCHT (0.15), 3 Å, TBHP (0.7), -20°, 7.5 d	" (41) >98% ee, $[\alpha]$ -17°c	(—)	18
	TI (0.1), (+)-DCHT (0.15), 3 Å, TBHP (1.5), -20°, 63 h	" (28) 95% ee	(—)	18
	TI (0.1), (+)-DCDT (0.15), 3 Å, TBHP (0.7), -20°, 11 d	" (34) >98% ee	(—)	18
	—	(—)	(—)	760
	(+)-DIPT	(31) 95% ee $[\alpha]$ -7.8° g	(—)	761, 762
	TI (1.0), (–)-DMT (1.5) TBHP (0.5), -20°	(—)	(23) 90% ee	709

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (0.1), (+)-DIPT (0.16), TBHP (0.68), 4 Å, -20°, 27 d	(47) 97% ee	(45) 97% ee	763
	TI (1.0), (+)-DET (1.1), TBHP (1.0), -20°, overnight	(—) >90% ee $[\alpha]$ -9.5°	(—)	731
	TI (1), (+)-DIPT (1.2), TBHP (0.6), -10°, 2 d	" (42) >99% ee, $[\alpha]$ -92° b	(—)	764
	TI (1.1), (–)-DIPT (1.2), TBHP (1.6), -20°, 3 d	(32) >98% ee $[\alpha]$ +26° c	(—)	765
	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°, 15 h	(42) 63% ee, $[\alpha]$ +26.9° h	(—)	766, 727
	TI (0.1), (+)-DIPT (0.12) TBHP (0.4), -20°, 3 d	(50)	(30) >96% ee	186
	TI (0.4), (–)-DIPT (0.45) TBHP (0.45), -20°, 24 h	(—)	(40) 92% ee, $[\alpha]$ +8.6°f	184

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
$n\text{-}C_5H_{11}$ ... CF_2H OH	TI (1.0), (+)-DIPT (1.2), TBHP (0.55), -20°, 4 d	$n\text{-}C_5H_{11}$ ... CF_2H OH (31) 97% ee, [α] -11.7° [b]	$n\text{-}C_5H_{11}$ ... CF_2H OH (59)	767
	TI (0.13), (+)-DIPT (0.19), TBHP (0.55), -20°, 7 d	" (39) 98% ee, [α] -11.76° [b]	" (52)	767
$n\text{-}C_5H_{11}$ ... CH_2F OH	TI (1.0), (+)-DIPT (1.2), TBHP (0.55), -20°, 24 h	$n\text{-}C_5H_{11}$ ... CH_2F OH (43) 98% ee, [α] -0.39° [b]	$n\text{-}C_5H_{11}$ ... CH_2F OH (56)	767
	TI (0.13), (+)-DIPT (0.19), TBHP (0.55), -20°, 5 d	" (41) 93% ee, [α] -0.35° [b]	" (46)	767
$n\text{-}C_5H_{11}$ ... OH	TI (1.0), (+)-DIPT (1.2) TBHP (0.55), -20°, 24 h	$n\text{-}C_5H_{11}$ ... OH (40) 98% ee	$n\text{-}C_5H_{11}$ ... OH (—)	767
	TI (0.13), (+)-DIPT (0.19) TBHP (0.55), -20°, 5 d	" (34) 97% ee	" (—)	767
NC ... $C_5H_{11}\text{-}n$ OH	TI (1.0), (+)-DIPT (1.2), 5°, 3d	NC ... $C_5H_{11}\text{-}n$ OH (40) 95% ee	NC ... $C_5H_{11}\text{-}n$ OH (—)	106

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
HO (cyclononadiene structure)	TI (1.0), (+)-DAT (1.2), -20°	HO (cyclononadiene structure)	O⟨ HO (epoxy cyclononene structure)	768

DAT	TBHP	Time	Allylic Alcohol	Epoxy Alcohol
DCHT	0.7	24 h	(—)	(33) 32% ee
DCHT	0.4	24 h	(—)	(25) 67% ee
DET	0.4	24 h	(—)	(17) 78% ee
DET	0.7	7 d	(30) 69% ee	(—)
DCHT	0.7	2 d	(24) 84% ee	(—)
DIPT	2.0	36 h	(15) 90% ee	(—)
DCHT	1.5	10 h	(13) >99% ee, [α] -145.6°	(—)

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (0.2), (+)-DET (0.24), TBHP (0.7), -20°, 14 d	(—)	(—)	
	—	(—)	O⟨ HO (epoxy cyclononene structure) (—) 90% ee	769
(methyl cyclohexadiene ethanol) OH	TI (0.1), (+)-DIPT (0.12), TBHP (0.45), -30°, 15 h	(structure) OH (50) 65% ee, [α] +10.8° [c]	(epoxy structure) O OH (37) 95% ee, [α] -50.0° [c]	770

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (0.1), (–)-DIPT (0.12), TBHP (0.45), -30°, 15 h	(38) 60% ee, [α] -9.0° *c*	(45) >99% ee, [α] +53° *c*	770
	(–)-DET, -15°	75% ee	20% ee	759
	(+)-DET	(—) 52% ee [α] +49.8°	(—)	771
C₁₀ NHBoc / OH CO₂Me	(+)-DIPT	(—)	NHBoc, CO₂Me, OH (20) 95% de	772
NHCbz / OH CO₂Me	(–)-DIPT	(—)	NHCbz, CO₂Me, OH (—) 94% de, [α] -15.8°	773

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
X = Aib-L-Phe-D-Pro	TI (1.1), (–)-DIPT (1.3), TBHP (0.6)	(48)	(27) 95% de	774
X = D-Pro-L-Ala-D-Ala	TI (1.0), (–)-DIPT (1.2), 4 Å, TBHP (2.0), -20°, 5 d	(38)	(20)	775
OH OTBDMS	(+)-DIPT	(—)	OH OTBDMS (25) 92% de, [α] +2.7°	776
C₆H₁₁ OH	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°	C₆H₁₁ (—) 93% ee [α] +6.2°	(—)	777
C₆H₁₁ OH	TI (1.0), (+) DIPT (1.2) TBHP (0.6), -20°, 15 h	C₆H₁₁ (—) >96% ee, [α] -14.6° *c*	C₆H₁₁ (—)	10
	TI (0.1), (+)-DIPT (0.15) TBHP (0.7), -20°, 15 h	" (44.2) 94% ee, [α] -13.3° *c*	(—)	18

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (0.1), (+)-DCHT (0.15) TBHP (0.55), -20°, 16 h	" (44.2) 95% ee, [α] -13.2°^{c}	(—)	18
	TI (0.1), (+)-DCDT (0.15) TBHP (0.55), -20°, 16 h	" (44.2) >98% ee, [α] -13.6°^{c}	(—)	18
	TI (0.1), (–)-DIPT (0.12), 17 h	C_6H_{11} alkene with OH, (—) 97% ee	(—)	38
	TI^a (0.1), (–)-DIPT (0.12), 17 h	" (—) 20% ee	(—)	38
Ph-CH=CH-CH(OH)-CH₃	(+)-DIPT	Ph alkene OH (—) 72% ee	(—)	730
	(+)-DIPT	" (37) >99% ee, [α] +24.5°	(—)	778, 779
	TI (1), (+)-DIPT (1.2), TBHP (0.5)	(—)	Ph epoxide OH (—) >98% ee	340, 343
m-MeOC$_6$H$_4$ alkene OH	TI (0.1), (+)-DIPT (0.15), TBHP (0.7), -20°, 3 h	(—)	m-MeOC$_6$H$_4$ epoxide OH (48) [α] -40.4°^{f}	580
t-Bu alkene, OH, cyclopropyl	(–)-DIPT, TBHP, -20°, 48 h	t-Bu alkene OH cyclopropyl (42) 95% ee, [α] +31.1°	(—)	780

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
n-C$_6$H$_{13}$ alkene CF$_3$ OH	TI (1.0), (+)-DIPT (1.2) TBHP (0.55), -20°, 5 d	n-C$_6$H$_{13}$ alkene CF$_3$ OH (46) 60% ee, [α] -1.9°^{b}	n-C$_6$H$_{13}$ epoxide CF$_3$ OH (50)	767
	TI (0.13), (+)-DIPT (0.19) TBHP (0.55), -20°, 21 d	" (51) 47% ee, [α] -1.51°^{b}	" (47)	767
tricyclic HO H structure + enantiomer	TI (1.0), (+)-DIPT (1.15) TBHP (0.6), -20°, 4 h	tricyclic (34) 68% ee [α] +78°	tricyclic epoxide (38) 39% ee [α] -32.6°	781
bicyclic OH + enantiomer	(+)-DIPT	bicyclic OH (—)	(—)	145
diene OH	(+)-DIPT, 90% conversion	diene OH (—) >99% ee	(—)	145
	(–)-DIPT, 90% conversion	diene OH (—) >99% ee	(—)	145

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°	(—) 95% ee	(—)	777
C_{11}	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°	(—) 98% ee [α] -0.6°	(—)	777, 727
	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°	(35) 95% ee [α] +26°	(—) [α] +22°	782
	TI (1.2), (+)-DIPT (1.2), -20°, 48 h	" (35)	" (33)	783
NHBoc / C_6H_{11}	(–)-DIPT, -25°	(—)[b]	(—)	55
	TI (0.1), (–)-DIPT (0.15), 3 Å, -20°	(—)	(29) [α] +13.6°[c]	784, 785

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (0.1), (–)-DIPT (0.15), 3 Å, -20°	(—)	(57) [α] +72.0°[c]	784, 785
	TI (0.1), (–)-DIPT (0.15), 3 Å, -20°	(—)	(29) [α] +51.1°[c]	784, 785
C_6H_{11}	TI (1), (+)-DIPT (1.2), TBHP (0.6), -25°, 15 h	(34) 87% ee [α] -5.8°	(36) 75% ee [α] -24.7°	786
Ph	(+)-DIPT, TBHP (0.6)	(40) 94% ee	(—)	787
TBDPSO ... Ph	(–)-DIPT	(30) 98% ee	(—)	788

TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	Tl (1), (+)-DIPT (1.2) TBHP (0.55), -20°, 4 d	(45) 14% ee, [α] -2.77° [b]	(—)	767
	Tl (1), (+)-DIPT (1.2) TBHP (0.6), -20°, 2 d	(—) 82% ee, [α] -17.1° [c]	(—)	10
+ enantiomer 7 + enantiomer 3	Tl (0.3), (+)-DET (0.36) TBHP (0.6), -35°, 7.5 h	(<43) 55% ee (4)	(52) 61% ee [α] -0.7° [c]	56
C₁₂	Tl (1.4), (+)-DET (1.4) TBHP (2.0), -20°, 12 h	(47) [α] +35.5° [f]	(42) [α] +20.5° [f]	789

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	Tl (1), (+)-DIPT (1.2), TBHP (0.6), -25°, 3 h	(45) 61% ee [α] +26.5°	(34) 89% ee [α] -74.0°	786
	Tl (1), (+)-DIPT (1.2), TBHP (0.6), -25°, 14 h	" (35) 97% ee [α] +42.4°	" (33) 83% ee [α] -69.5°	786
	(–)-DIPT	(—) 99% ee	(—)	728
	(+)-DIPT	(—)	(—)	790
	Tl (1.0), (+)-DIPT (1.2) TBHP (0.6), -23°	(—) 95% ee, [α] +38.7°	(—) 84% ee, [α] +2.5°	782
	Tl (1.0), (+)-DIPT (1.0) TBHP (0.6), -50°, 10 h	(39) [α] +20.8° [c]	(—)	791, 792

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
OMe (tetralin allylic alcohol)	TI (1.0), (–)-DIPT (1.0) TBHP (0.6), -50°, 7 h	(47) [α] -128.3°	(46) 98% ee [α] +81.6°	793
	(+)-DIPT	(—)	(41) 98% ee [α] -81.9°	793
OMe / OMe (dimethoxy tetralin allylic alcohol)	TI (1.0), (–)-DIPT (1.0) TBHP (0.53), -75°, 1 h	(48) >95% ee, [α] -19.2°	(43) >95% ee, [α] +51.6°	794
C13				
CH2=CH–CH(OH)–C10H21-n	TI (1.0), (+)-DIPT (1.2) TBHP (2.0), -28°, 15 d	(—)	C10H21-n (40) 91% ee [α] +16.2°	141
	TI (1.0), (+)-DIPT (1.2), CaH2, SiO2, TBHP (2.0), -40°, 25 h	(—)	" (42) 85% ee, [α] +15.2°	141
	TI (1.0), (+)-DIPT (1.2), TBHP (2.0), -20°, 17 h	(—)	" (50) 86-94% ee, [α] +16.2°	795

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (1.0), (–)-DIPT (1.2) TBHP (2.0), -20°, 17 h	(—)	C10H21-n (40) 91% ee [α] -16.6°	795
(vinyl cyclopropyl alkynyl alcohol) C≡CC5H11-n	—	(—)	(—)	796
CH2=C(...)–Ph allylic alcohol	TI (1), (+)-DIPT (1.2), TBHP (0.6), -25°, 11 h	Ph (37) 94% ee [α] +48.2°	Ph (33) 82% ee [α] -45.2°	786
HC≡C–...–C5H11-n (enyne alcohol)	TI (0.2), (–)-DIPT (0.24), 4 Å, TBHP (0.6), -20°, 20 h	HC≡C–...–C5H11-n (42) 98.6% ee	(—)	746
C14				
(vinyl pinene allylic alcohol)	TI (0.05), (+)-DIPT (0.06), 3 Å, CUHP (0.55), -8°, 12 h	(35)	(—)	736
	TI (0.05), (–)-DIPT (0.06), 3 Å, CUHP (0.55), -8°, 12 h	(35)	(—)	736

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
(cyclohexenone with CH(OH)CH₂Ph side chain)	TI (0.1), (+)-DIPT (0.15), 3 Å, TBHP (0.7), -20°, 9 h	(35)	(39) 75% ee	797
C₁₅ (two terpene allylic alcohols, ratio 7 : 3)	TI (1.0), (+)-DIPT (1.2) TBHP (2.8), -18°, 3 wks	(—)	(46)	798
(bis-dichlorophenyl allylic alcohol)	TI (1.0), (+)-DIPT (1.0) TBHP (0.5), -20°, 15 h	(42) 90% ee, [α] -8.2°	(38) 84% ee, [α] -76.3°	799
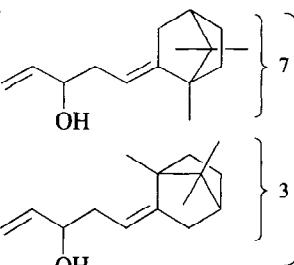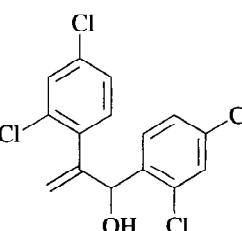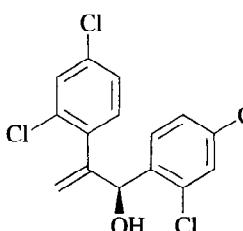
Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
	TI (1.0), (–)-DIPT (1.0) TBHP (0.5), -20°, 15 h	(—)	(41) 84% ee, [α] +69.7°	799
C_6H_{11} ... C_6H_{11} (allylic alcohol)	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°, 15 h	(—) >96% ee, [α] -19.8° *c*	(—)	10
	(+)-DIPT	(—)	" (27) 91% ee	800
(cyclohexenone with CH(OH)CH₂CH₂Ph side chain)	TI (0.1), (+)-DIPT (0.15), 3 Å, TBHP (0.7), -20°, 9 h	(31)	(20) 60% ee	797
C₁₆ n-C₆H₁₃ ... CO₂R ... OH, R= p-[n-C₁₀H₂₁O]C₆H₄	TI (1.0), (+)-DIPT (1.2) TBHP (0.45), -25°, 18 h	(—)	n-C₆H₁₃ ... CO₂R (30-49)	415
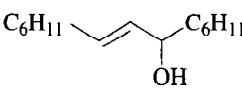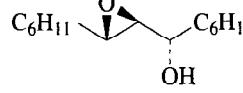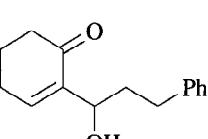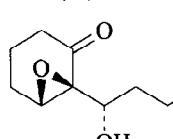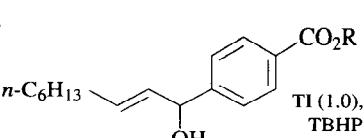
Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
(structure) $C_{12}H_{15}$-n, OH	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°, 15 h	(structure) $C_{12}H_{15}$-n, OH (44) >96% ee, [α] +3.6°	(structure) $C_{12}H_{15}$-n, OH (49)	124
C_6H_{11} (structure) C_6H_{11}, OH	TI (1.0), (+)-DIPT (1.2) TBHP (0.6), -20°, 15 h	C_6H_{11} (structure) C_6H_{11}, OH (—) 10% ee, [α] -0.7° [c]	(—)	10
n-C_6H_{13} (structure) OH CO$_2$Me	(+)-DET, 3 Å, 0°	n-C_6H_{13} (structure) OH CO$_2$Me (10) 93-94% ee	n-C_6H_{13} (structure) OH CO$_2$Me (66) + n-C_6H_{13} (structure) OH CO$_2$Me (23)	801
C$_{17}$ (structure) OH)$_8$	TI (1.1), (+)-DET (1.4), TBHP (0.66)	(structure) OH)$_8$ (26) 15% ee, [α] +2.9°	(structure) OH O)$_8$ (35), [α] -1.3°	126

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.
C$_{18}$ (structure) OTHP, C≡C, C≡C, OH	TI (1.2), (+)-DIPT (1.2), TBHP (0.6), -10°, 48 h	(structure) OTHP, C≡C, C≡C, OH (37)	(structure) OTHP, C≡C, O, C≡C, OH (40)	783
C$_{20}$ (structure) O OAc, O OAc, OH	TI (1.0), (+)-DIPT (1.2), TBHP (0.6), -20°, 15 h	(structure) O OAc, O OAc, OH (32)	(structure) O OAc, O OAc, OH (47)	802

TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS *(Continued)*

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.

B. Secondary E-Trimethylsilylvinyl Carbinols

C_4

TMS, OH (E-alkene, methyl) — (−)-DIPT, TBHP (0.6) — TMS (—) >95% ee — (—) — 803

TMS, R, OH — TI (1.0), (+)-DIPT (1.2) TBHP (1.5), -20° — TMS R OH — TMS (epoxide) R OH

	R	Time (h)			
C_4	CH_2OPh	13	(47) >99% ee, [α] +8.0°	(46) >99% ee, [α] -17.0°	13
	CH_2OBn	9.5	(43) >99% ee, [α] -1.9°	(48) >99% ee, [α] -2.2°	13, 194
	CH_2OTBS	-	(46) >99% ee	(48) >99% ee	194
C_5	$(CH_2)_2OBn$	9	(43) >99% ee, [α] -3.2°	(45) >99% ee, [α] -10.1°	13, 194
C_6	Pr-i	6	(40) >99% ee, [α] -21.8°	(41) >99% ee, [α] -1.07°	13
C_7	$(CH_2)_3CO_2Me$	20	(43) >99% ee, [α] +6.78°	(45) >99% ee, [α] +6.7°	13, 193

C_7

TMS, OH, CO_2Me — TI (1.0), (−)-DIPT (1.2), TBHP (1.5), -21°, 21 h — TMS OH CO_2Me (43) >99% ee — TMS (epoxide) OH CO_2Me (45) >99% ee — 193

TMS, R, OH — TI (0.2), (+)-DIPT (0.24), 3 Å, TBHP (1.5), -20° — TMS R OH — TMS (epoxide) R OH

	R	Time (h)			
C_7	Bu-t	40	(34) 13% ee	(64)	13
C_8	C_5H_{11}-n	2	(42) >99% ee	(44) 94.9% ee	13

TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS *(Continued)*

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.

TMS, R, OH — TI (1.0), (+)-DIPT (1.2) TBHP (1.5), -20° — TMS R OH — TMS (epoxide) R OH

	R	Time (h)			
C_8	C_5H_{11}-n	7	(42) >99% ee, [α] -9.8°	(42) >99% ee, [α] -7.5°	13, 194
	"	18	(—) >99% ee	(—) >97.6% ee	13, 194
	"	2	(42) >99% ee	(—) >94.9% ee	13
	(alkenyl)	2	(44) >99% ee	(42) 97.3% ee	804
C_9	Ph	13.5	(44) >99% ee, [α] -10.8°	(42) 97.3% ee, [α] +25.7°	13
C_{11}	(alkenyl)-C_5H_{11}	3.5	(44) >99% ee, [α] +7.59°	(43) >99% ee, [α] +4.23°	13, 194 805
	$CH_2C\equiv CC_5H_{11}$-n	4	(41) >99% ee, [α] -55.3°	(47) >99% ee, [α] +16.1°	805

C_{11}

TBDMSO, TMS, OH — TI (1.0), (−)-DIPT (1.2) TBHP (1.5), -20°, 16 h — TBDMSO, TMS, OH (43) >99% ee, [α] -4.7° — TBDMSO, TMS (epoxide) OH (42) >99% ee, [α] +6.2° *j* — 805

C. Secondary E-Tributylstannylvinyl Carbinols

n-Bu$_3$Sn, R, OH — TI (0.3), (+)-DIPT (0.36) TBHP (1.5), -21° — n-Bu$_3$Sn R OH — n-Bu$_3$Sn (epoxide) R OH

TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.

	R	Time (h)			
C_4	CH_2OPh	4	(40) >99% ee	(—)	11
C_7	$(CH_2)_3CO_2Me$	—	(>44) >99% ee	(—)	803
C_8	C_5H_{11}-n	40	(—) >99% ee	(—) 80% ee	11
C_9	C_6H_{11}	4	(41) >99% ee	(—)	11
C_{11}	$(CH_2)_7CO_2Me$	36	(>40) >99% ee	(—)	803

C_7
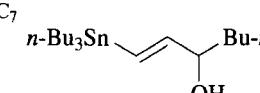
n-Bu$_3$Sn ⟶ Bu-n / OH TI (0.1), (+)-DIPT (0.18), 3 Å, TBHP (0.7), -20° (—) n-Bu$_3$Sn ⟶ Bu-n (epoxide) / OH (45) >90% ee, [α] -24.3°   198

C_8
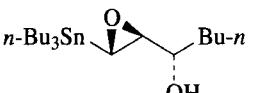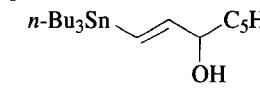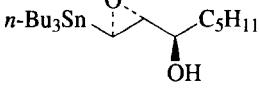
n-Bu$_3$Sn ⟶ C_5H_{11}-n / OH TI (1.0), (–)-DIPT (1.2) TBHP (1.5), -20°, 4 h n-Bu$_3$Sn ⟶ C_5H_{11}-n / OH (38-42) 95% ee, [α] +3.1° n-Bu$_3$Sn ⟶ C_5H_{11}-n (epoxide) / OH (—) 92% ee   11

D. Secondary E-Iodovinyl Carbinols

C_8
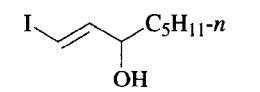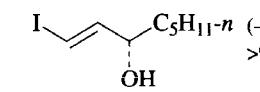
I ⟶ C_5H_{11}-n / OH (–)-DIPT   I ⟶ C_5H_{11}-n (—) >99% ee / OH   (—)   197

TI (1.0), (–)-DIPT (1.2), TBHP (1.5), -20°, 42 h   " (>49) >99% ee, [α] +9.87° [b]   I ⟶ C_5H_{11}-n (epoxide) (—) >99% ee / OH   12
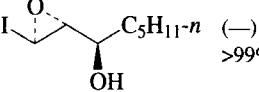
TI (1.0), (–)-DIPT (1.2), TBHP (1.5), -20°, 36 h   " (—) 96.2% ee   " (—) >98% ee   12

TABLE VI. KINETIC RESOLUTION OF RACEMIC SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions	Allylic Alcohol(s) and Yield(s) (%)	Epoxy Alcohol(s) and Yield(s) (%)	Refs.

| | TI (0.2), (–)-DIPT (0.24), TBHP (1.5), 4 Å, -20°, 36 h | " (45) >99% ee | " (—) 96.9% ee | 12 |

| | TI (0.2), (–)-DIPT (0.24), TBHP (1.5), 4 Å, 20°, 36 h | " (—) 98% ee | (—) | 12 |

C_9
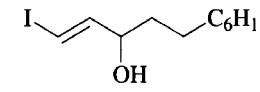
I ⟶ C_6H_{11} / OH   TI (0.23), (+)-DIPT (0.33), TBHP, (1.5), 4 Å, -21°   I ⟶ C_6H_{11} / OH (42) >99% ee, [α] -11.4°   (—)   198, 805

C_{11}

I ⟶ C_6H_{11} / OH   TI (0.3), (+)-DIPT (0.36), TBHP (1.5), 4 Å, -21°, 40 h   I ⟶ C_6H_{11} / OH (41) >99% ee, [α] -6.1°   (—)   805
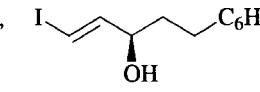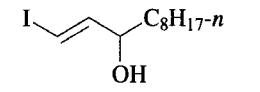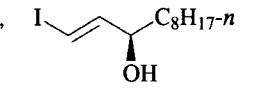
I ⟶ C_8H_{17}-n / OH   TI (0.3), (+)-DIPT (0.36), TBHP (1.5), 4 Å, -21°, 40 h   I ⟶ C_8H_{17}-n / OH (44) >99% ee, [α] -7.8°   (—)   198, 805

[a] Ti(OBu-t)$_4$ was used instead of Ti(OPr-t)$_4$.
[b] The rotation was measured in methanol.
[c] The rotation was measured in ethanol.
[d] The reaction was too slow to be practical.
[e] 2-Phenyl-2-propyl hydroperoxide was used instead of *tert*-butyl hydroperoxide.
[f] The rotation was measured in dichloromethane.
[g] The rotation was measured in benzene.
[h] The rotation was measured in n-hexane.
[i] The configuration was not determined.
[j] The rotation was measured in acetone.

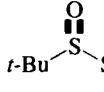TABLE VII. ASYMMETRIC EPOXIDATION OF CHIRAL SECONDARY ALLYLIC ALCOHOLS
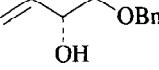
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_4$	TI (1.05), (+)-DIPT (1.05), TBHP (2), -20°, 18 h	(86), [α] +9.2°	582
C$_5$	TI (1.05), (+)-DIPT (1.2), 4 Å, TBHP (2), -20°, 72 h	(92) [α] -11.0°	177
	TI (1.05), (+)-DIPT (1.2), 4 Å, TBHP (2), -20°, 72 h	(88) [α] -22.6°	177
C$_6$	(+)-DIPT	(60) >95% de	145
	TI (1), (–)-DIPT (1.2), 4 Å, TBHP (1.2), 10 h	(42) ~100% de	187
	(+)-DET (1.2)	(—)	806
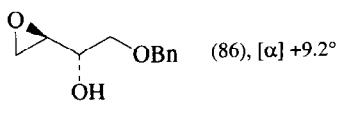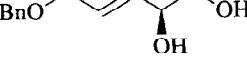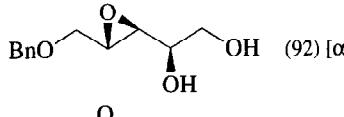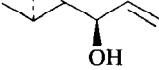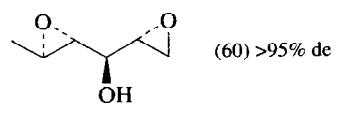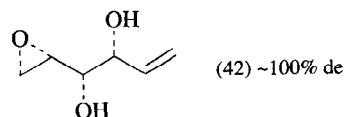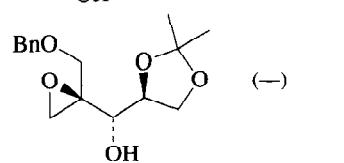
TABLE VII. ASYMMETRIC EPOXIDATION OF CHIRAL SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_7$	(+)-DIPT (0.13), TBHP (0.5)	(76) 90% ee	807
	TI (1.1), (+)-DIPT (1.2), 4 Å, TBHP (1.5), -20°	(82)	188
	TI (1.1), (–)-DIPT (1.2), 4 Å, TBHP (1.5), -20°	(54) 13% de	188
	TI (1.1), (+)-DIPT (1.2), 4 Å, TBHP (1.5), -20°	(89)	188
	TI (1.1), (–)-DIPT (1.2), 4 Å, TBHP (1.5), -20°	(54) 13% de	188
	TI (1.1), (+)-DIPT (1.2), 4 Å, TBHP (1.5), -20°	(70)	188

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	TI (1.1), (–)-DIPT (1.2), 4 Å, TBHP (1.5), -20°	(70)	188
(BnO...OH ... OBn / OH substrate)	TI (1.1), (+)-DIPT (1.2), 4 Å, TBHP (1.5), -20°	(29) 23% de	188
	TI (1.1), (–)-DIPT (1.2), 4 Å, TBHP (1.5), -20°	(28) 51% de	188
C_8 BnO...OTBDPS / OH	(+)-DIPT, -20°	(90)	808
OTBDPS / C≡C / OH ... OBn	TI (2), (–)-DET (2), TBHP (1.5), -20°	(80)	157

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
84% ee (OH)	(+)-DET, 4 Å, -20°, 60 h	(50) 98% ee + (5)	809
C_9 TMS...C_5H_{11}-n / OH	TI (0.2), (+)-DET (0.24), TBHP (2), -20°, 20 h	TMS epoxide...C_5H_{11}-n / OH (75), [α] +6.7° + TMS...C_5H_{11}-n / OH (8)	197
n-C_5H_{11}...OH / OH	TI (1.05), (+)-DIPT (1.2), 4 Å, TBHP (1.1), -20°, 72 h	n-C_5H_{11} epoxide...OH / OH (73) [α] -37.9°	177
NC...C_5H_{11}-n / OH	TI (1), (+)-DIPT (1.2), 5°, 6 d	NC epoxide...C_5H_{11}-n / OH (85)	106
64-72% ee (OH)	TI (1), (–)-DIPT (1.2), TBHP (0.8), -20°	(71) 88% ee [α] +9.5° [a]	810
BnO...OBn / OH	(–)-DIPT, 4 Å, -20°	BnO...OBn / OH (85) >97% de	811

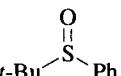| Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(+)-DIPT, 4 Å, -20°	BnO〜〜⟨O⟩〜OBn OH (83) >97% de	811
BnO〜〜⟨O⟩〜OBn OH	(–)-DIPT, 4 Å, -20°	BnO〜⟨O⟩〜⟨O⟩〜OBn OH (97) >97% de	811
HO〜(cyclononene)	(–)-DET	O〜(epoxide) HO (83)	768
C₁₀ TBDMSO MPMO *t*-BuCO₂〜〜〜〜OH Br	(–)-DIPT, 4 Å, -20°, 3 d	TBDMSO MPMO *t*-BuCO₂〜〜⟨O⟩〜OH Br (97)	812
〜〜〜〜OH OH	TI (1.05), (+)-DIPT (1.2), 4 Å, TBHP (1.1), -20°, 72 h	〜〜〜⟨O⟩〜OH OH (56) [α] -32.7°	177
TBDMSO〜〜〜OBn OH	(+)-DET	TBDMSO〜〜⟨O⟩〜OBn OH (—) 40% de	512

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	(–)-DET	TBDMSO〜〜⟨O⟩〜OBn OH (—) 100% de	512
C₁₁ OH 〜〜Ph	(+)-DET (catalytic), MS	OH 〜〜⟨O⟩Ph (—)	44
	(–)-DET (catalytic), MS	OH 〜〜⟨O⟩Ph (—) 6% de	44
TMS〜〜〜C₅H₁₁-*n* OH	TI (0.3), (–)-DIPT (0.37), 4 Å, -21°, 4 h	TMS〜⟨O⟩〜〜C₅H₁₁-*n* OH (86)	198
TDMSO TMS〜〜〜〜 OH	TI (1), (+)-DIPT (1.2), -21°	TDMSO TMS〜⟨O⟩〜〜 OH (89)	198
Ph〜〜OH OH	TI (1.05), (+)-DIPT (1.2), TBHP (1.1), 4 Å, -20°, 72 h	Ph〜⟨O⟩〜OH OH (87) [α] -33.4°	177

TABLE VII. ASYMMETRIC EPOXIDATION OF CHIRAL SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C₁₂ 	(+)-DET, -23°	 (—) 100% de	512
	(–)-DET, -23°	 (—) 100% de	512
	TI (1), (+)-DET (1), TBHP (0.6), -50°, 10 h	 (>74)	791, 792
C₁₃ 	(+)-DET, 0°	 (—) 99% de	813
	(–)-DET, 0°	" (—) 20% de	813

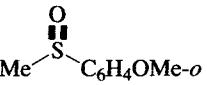TABLE VII. ASYMMETRIC EPOXIDATION OF CHIRAL SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C₁₄ 	TI (1), (+)-DIPT (1.2), -20°, 22 h	 (96) 90% de	814
C₁₉ n-C₁₅H₃₁	TI (1.05), (+)-DIPT (1.2), 4 Å, TBHP (1.1), -20°, 72 h	n-C₁₅H₃₁ (63) [α] -22.5°	177
	TI (2.1), (+)-DIPT (2.5), CaH₂ (0.4), SiO₂ (0.5), -20°, 96 h	 (71) 75% de	140
	TI (2.1), (+)-DIPT (2.5) TBHP (1.0), -20°, 30 d	" (0)	140
	TI (2.1), (–)-DIPT (2.5), CaH₂ (0.4), SiO₂ (0.5), -20°, 30 h	" (81) 80% de	140
	TI (2.1), (–)-DIPT (2.5) TBHP (1.0), -20°, 30 d	" (5)	140

TABLE VII. ASYMMETRIC EPOXIDATION OF CHIRAL SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

C$_{25}$

| | (+)-DET | I + II (95) | I:II = 70:30 | 815 |
| | (−)-DET | I + II (96) | I:II = 44:56 | 815 |

I   II

C$_{27}$

| | (+)-DET | I:II = 33:67 | 816 |
| | (−)-DET | I:II = 96:4 | 816 |

I   II

TABLE VII. ASYMMETRIC EPOXIDATION OF CHIRAL SECONDARY ALLYLIC ALCOHOLS (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

| | (+)-DET | I:II = 98:2 | 816 |
| | (−)-DET | I:II = 50:50 | 816 |

I   II

C$_{28}$

| | (+)-DET (100% conversion) | (—) | 817 |
| | (−)-DET (40% conversion) | (—) | 817 |

^{a} The rotation was measured in dichloromethane.

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_5$	TI (1.36), (+)-DIPT (1.8), 4 Å TBHP (4.8), -25°		274
	$\dfrac{t\,(h)}{3}$ 24 140	(40-48) 84% ee, 92% de (40-48) 93% ee, 99.7% de (40-48) >97% ee, >99.7% de	
	TI (0.07), (+)-DIPT (0.09), 4 Å, TBHP (2.0), -15°, 118 h	" (55) >99% ee, [α] +48.8°	279
	TI (0.1), (+)-DIPT (0.12), 4 Å, TBHP (1.5), -20°, 90 h	" (60) 99% ee, 97% de	274
	TI (1.0), (+)-DET (1.2), TBHP (1.2), -20°, 3 d	" (50-60) >90% ee, [α] +46.7°	274, 275
	(–)-DET	(50), [α] -50.0°	274
	(–)-DIPT	" (—) >97% ee, 99% de	275
TMS TMS OH	TI (0.2), (–)-DIPT (0.24), 4 Å, TBHP (1.5), -21°, 35 h	TMS TMS (92) >98% ee, >99% de [α] -24.0°	276
	TI (0.2), (+)-DIPT (0.24), 4 Å, TBHP (1.5), -21°, 35 h	TMS TMS (92) >98% ee, >99% de	276
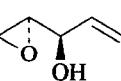
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C$_6$	TI (0.4), (–)-DIPT (0.8), TBHP (10), 114 h	(60) 90% ee, 75% de	187
C$_7$	TI (1.1), (–)-DIPT (1.3), TBHP (2), -25°		274, 277
	$\dfrac{t\,(h)}{0.5}$ 1.0 1.5	(80-85) 88% ee, >99% de (80-85) 94% ee, >99% de (80-85) >99.3% ee, >99% de	
BnO OBn OH	TI (1.15), (+)-DIPT (1.5), TBHP (2.6), -25°	BnO OBn OH	274
	$\dfrac{t\,(h)}{1}$ 3 44	(70-78) 93% ee, 97% de (70-78) 95% ee, 97% de (70-78) 93% ee, 97% de	
TBDMSO TBDMSO OH	(+)-DET	TBDMSO TBDMSO OH (71) [α] +6.8°	529

	Conditions		
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

C_{11}

(–)-DET

TBDMSO, TBDMSO (93) [α] -8.2°   529

TI (1.36),
(+)-DIPT (1.8), 4 Å,
TBHP (4.8), -25°   (68)   278

TI (1.36),
(–)-DIPT (1.8), 4 Å,
TBHP (4.8), -25°   (72)   278

(+)-DIPT, 4 Å, -20°   (82)   280

C_{13}

OBn

TI (1.36),
(+)-DIPT (1.8), 4 Å,
TBHP (4.8), -25°   (89)   278

	Conditions		
Substrate	TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.

C_{15}

TI (1.36),
(+)-DIPT (1.8), 4 Å,
TBHP (4.8), -25°   278

(81)

TABLE IX. KINETIC RESOLUTION OF α-HYDROXY-FURANS, -THIOPHENES, AND -PYRROLES

Substrate	Conditions TI (eq), DAT (eq), MS	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.

TI (1), (+)-DIPT (1.2), TBHP (0.6), -20°

Structure I

Structure II

	R^1	R^2	R^3	R^4	t (h)	**I**	**II**	
C_6	H	H	H	Me	24	(32) >95% ee, [α] +20.8°	(53)	413
C_7	H	H	H	$CH=CH_2$	24	(32) >95% ee, [α] -1.74°	(—)	14, 413
	H	H	H	$C≡CTMS$	20	(38) 88% ee, [α] -16.5°	(—)	14, 413
C_8	H	H	H	$CH_2CH=CH_2$	36	(42) >95% ee, [α] +39.9°	(—)	413
	H	H	H	Pr-i	25	(39) >95% ee, [α] +18.1°	(55)	14, 413
C_9	H	H	H	Bu-t	40	(41) 6% ee	(55)	14, 413
C_{10}	H	H	H	C_5H_{11}-n	25	(42) >95% ee, [α] +13.8°	(53)	14, 413
C_{11}	Me	H	H	$C_5H_{11}n$	6	(40) >95% ee, [α] +7.8°	(55)	14, 413
	H	H	Me	C_5H_{11}-n	4	(39) >95% ee, [α] +8.9°	(—)	14, 413
	H	H	H	Ph	40	(42) 99% ee, [α] +6.9°	(44)	413

TI (0.2), (+)-DIPT (0.24), 4 Å, TBHP (1.5), -20°

	R^1	R^2	R^3	R^4	t (h)	**I**	**II**	
C_6	H	H	H	Me	12	(33) >95% ee	(—)	413
C_7	H	H	H	CH_2CO_2Et	22	(40) >95% ee	(—)	413
C_9	H	H	H	Bu-n	50	(38) 99% ee, [α] +16.2°	(—)	413
C_{10}	H	H	H	C_5H_{11}-n	14	(38) >95% ee	(—)	413
			H	Me	45	(43) >99% ee, [α] +19.9°	(—)	413
C_{11}	Me	H	H	C_5H_{11}-n	6	(40) >95% ee	(—)	413
	H	H	H	Ph	48	(38) >95% ee	(—)	413

TABLE IX. KINETIC RESOLUTION OF α-HYDROXY-FURANS, -THIOPHENES, AND -PYRROLES (*Continued*)

Substrate	Conditions TI (eq), DAT (eq), MS	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.

TI (0.1), (+)-DIPT (0.15), TBHP (0.7), 3 Å

	R	Temp	Time (h)			818
C_6	Me	-20°	5	(36) 80% ee, [α] +17.4°	(38)	
C_7	Et	-20°	3.5	(32) 95% ee, [α] +12.6°	(42)	
C_8	CH=CHMe	-30°	7	(32) 82% ee, [α] -40.4°	(52)	
C_9	Bu-n	-35°	6	(43) 94% ee, [α] +9.2°	(46)	
C_{11}	C_6H_{11}	-25°	7	(44) >98% ee, [α] +20.0°	(52)	
C_{15}	$C_{10}H_{21}$-n	-25°	4	(44) >98% ee, [α] -9.6°	(51)	

C_8

TI (0.11), (+)-DIPT (0.16), 3 Å, TBHP (0.5), -20°, 6 h

(—)

(—)   819

TI (0.22), (+)-DIPT (0.24), 3 Å, TBHP (0.6), -21°, 30 min

+ enantiomer

(45) >99% ee, [α] +14.7°

(48)   820

TI (0.22), (+)-DIPT (0.24), 3 Å, TBHP (0.6), -21°, 30 min

+ enantiomer

(49) >99% ee, [α] +9.52°

(—)   820

TABLE IX. KINETIC RESOLUTION OF α-HYDROXY-FURANS, -THIOPHENES, AND -PYRROLES (*Continued*)

	Substrate	Conditions TI (eq), DAT (eq), MS	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
C₈		TI (0.22), (+)-DIPT (0.24), TBHP (0.6), -25°	 (41) >95% ee	(—)	821
		TI (1), (+)-DIPT (1.2), TBHP (3), 0°		Polymer	822
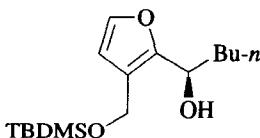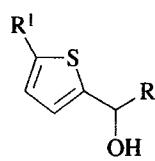
	R¹	R²	h
C₈	H	Pr-*i*	18
C₉	H	Bu-*n*	18
	H	Bu-*t*	18
C₁₁	Me	C₅H₁₁-*n*	20
	H	Ph	45

	Remaining Alcohol	Oxidation
	(30) 91% ee, [α] +14.2°	(—)
	(39) >95% ee	(—)
	(25) 47% ee	(—)
	(35) >95% ee, [α] +14.9°	(—)
	(30) >95% ee, [α] -9.8°	(—)

	Substrate	Conditions	Remaining Alcohol	Oxidation Product	Refs.
		TI (1), (–)-DIPT (1.2), TBHP (1.5), CaH₂, SiO₂, -10°, 16 h			823

	R		
C₇	Et	(40) 90% ee, [α] -36.2°	(—)
C₁₁	C₆H₁₃-*n*	(36) >95% ee, [α] -45.5°	(—)

TABLE IX. KINETIC RESOLUTION OF α-HYDROXY-FURANS, -THIOPHENES, AND -PYRROLES (*Continued*)

	Substrate	Conditions TI (eq), DAT (eq), MS	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
		TI (1), (+)-DIPT (1.2), TBHP (1.5), CaH₂, SiO₂, -10°, 16 h			823

	R		
C₆	Me	(43) >95% ee, [α] +21.5°	(—)
C₇	Et	(38) 92% ee, [α] +37.1°	(—)
C₈	CH₂CH=CH₂	(38) >95% ee, [α] +65.6°	(—)
C₉	Bu-*n*	(35) 90% ee, [α] +42.6°	(—)
C₁₁	C₆H₁₃-*n*	(33) 94% ee, [α] +42.9°	(—)
C₁₅	C₁₀H₂₁-*n*	(30) 90% ee, [α] +38.0°	(—)

TABLE X. KINETIC RESOLUTION OF α-TOSYLAMINOFURANS

	Substrate	Conditions TI (eq), DAT (eq), MS	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
		TI (1.0), (+)-DIPT (1.2) TBHP (2.5), CaH$_2$, SiO$_2$, rt			200
	R	Time (h)			
C$_6$	Me	2	(50) 90% ee, [α] -7.6° [a]	(8)	
C$_7$	Et	2	(47) 93.3% ee, [α] -5.0° [a]	(45)	
C$_8$	Pr-n	2	(46) 94.7% ee, [α] -5.3° [a]	(47)	
C$_9$	Bu-n	2	(46) 90% ee, [α] -5.0° [a]	(41)	
	Bu-i	2	(47) 90.7% ee, [α] -7.4° [a]	(43)	
C$_{11}$	C$_6$H$_{13}$-n	3	(45) 100% ee, [α] -4.3° [a]	(46)	
		TI (1.0), (–)-DIPT (1.2) TBHP (2.5), CaH$_2$, SiO$_2$, rt			200
C$_7$	Et	3	(50) 93.5% ee, [α] +5.0° [a]	(46)	
C$_{11}$	C$_6$H$_{13}$-n	3.5	(49.5) 100% ee, [α] +4.4° [a]	(48)	

[a] The rotation was measured in ethanol.

TABLE XI. EPOXIDATION OF ALLYLIC ALCOHOLS WITH IN SITU HYDROXY DERIVATIZATION

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C_3			
allyl-OH	1. TI (0.05), (–)-DIPT, (0.06), 3 Å[a], 0°, 6 h 2. P(OMe)$_3$, -20° 3. TsCl, Et$_3$N, -20°, 10 h	epoxide-OTs (40) 94% ee[b], [α] +17.5° 97% ee[c], [α] +18.1°	18, 135, 66, 824
	1. TI (0.05), (+)-DIPT, (0.06), 3 Å[a], -5°, 5 h 2. P(OMe)$_3$, -20° 3. PNBCl, Et$_3$N, 0°, 1 h	epoxide-OPNB (61) 92-94% ee[b], [α] -38.7°	18
	1. TI (0.05), (–)-DIPT, (0.06), 3 Å[a], 0°, 6 h 2. P(OMe)$_3$, -20° 3. TBDPSCl, DMAP, -20°, 10 h 10b, 86a	epoxide-OTBDPS (45) 91% ee, [α] -2.28°	18
	1. TI (0.05), (+)-DIPT, (0.06), 3 Å[a] 43, 584a 2. P(OMe)$_3$, -20° 3. m-O$_2$NC$_6$H$_4$SO$_2$Cl, Et$_3$N	epoxide-OSO$_2$C$_6$H$_4$NO$_2$-m (57) 96% ee,[b] 99% ee, [α] +23°[c]	66
	1. TI (0.05), (+)-DIPT, (0.06), 3Å[a] 2. P(OMe)$_3$ 3. p-ClC$_6$H$_4$SO$_2$Cl	epoxide-OSO$_2$C$_6$H$_4$Cl-p (38) 95% ee,[b] [α] +22.6°	66
	1. TI (0.05), (–)-DIPT, (0.06), 3 Å[a], -3° 2. P(OMe)$_3$, -30° 3. TrCl, Et$_3$N	epoxide-OTr (53)	67
C_4			
methallyl-OH	1. TI (0.05), (–)-DIPT, (0.06), 3 Å, -20°, 4.5 h 2. P(OMe)$_3$, -20° 3. TsCl, DMAP, -10°	epoxide-OTs (69) 95% ee, [α] +4.84°	18
	1. TI (0.05), (+)-DIPT, (0.06), 3 Å, -20°, 4.5 h 2. P(OMe)$_3$, -20° 3. PNBCl, Et$_3$N, 0°	epoxide-OPNB (78) 98% ee[b], [α] -5.87°	18

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
(2E)-2-buten-1-ol structure drawn as CH₃CH=CHCH₂OH	1. TI (0.05), (–)-DIPT, (0.06), 3 Å, -20°, 5 h 2. P(OMe)₃, -20° 3. 2-C₁₀H₇SO₂Cl, Et₃N, -10°	epoxide–CH₂OSO₂C₁₀H₇-2 (60) 92% ee[b], $[\alpha]$ +5.94°	18
	1. TI (0.05), (–)-DIPT, (0.06), 3 Å, -20°, 2 h 2. P(OMe)₃, -20° 3. TsCl, Et₃N, -20°, 10 h	epoxide–CH₂OTs (70) 98% ee[b], $[\alpha]$ +34.22°	18
	1. TI (0.05), (+)-DIPT, (0.06), 3 Å, -20°, 2 h 2. P(OMe)₃, -20° 3. PNBCl, Et₃N, 0°, 1 h	epoxide–CH₂OPNB (65) 98% ee[b], $[\alpha]$ -48.5°	18
	1. TI (0.05), (–)-DIPT, (0.06), 3 Å, -20°, 2 h 2. P(OMe)₃, -20° 3. TBDMSCl, DMAP	epoxide–CH₂OTBDMS (68) 92% ee, $[\alpha]$ +13.12°	18
	1. (–)-DET 2. P(OMe)₃, -20° 3. TBDPSCl, DMAP	epoxide–CH₂OTBDPS (76)	825
	1. TI (0.05), (–)-DIPT, (0.06), 3 Å[a], -3°, 8 h 2. P(OMc)₃, -20° 3. TrCl, Et₃N, 2°, overnight	epoxide–CH₂OTr (53)	67
	1. (+)-DET 2. in situ tosylation	epoxide–CH₂OTs (—) 98% ee, $[\alpha]$ -33.6° [b]	826
(2Z)-2-buten-1-ol structure	1. TI (0.05), (+)-DIPT, (0.06), 3 Å, -20°, 20 h 2. P(OMe)₃, -20° 3. PNBCl, Et₃N, 0°, 1 h	epoxide–CH₂OPNB (68) 92% ee[b], $[\alpha]$ -28.4°	18

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C₅			
(2Z)-2-penten-1-ol structure	1. TI (0.1), (+)-DIPT (0.12), 4 Å 2. 3,5-(O₂N)₂C₆H₃COCl, Et₃N	epoxide–CH₂O₂C–C₆H₃(NO₂)₂-3,5 (52) 98% ee[b] $[\alpha]$ -31.3°	827
prenol / 3-methyl-2-buten-1-ol structure	1. TI (0.05), (+)-DIPT (0.06), 3 Å, -40°, 2 h 2. P(OMe)₃, -20° 3. PNBCl, Et₃N, 0°, 1 h	epoxide–CH₂OPNB (70) 98% ee[b], $[\alpha]$ -36.09°	18
	1. TI (0.05), (–)-DIPT (0.06), 3 Å, -40°, 2 h 2. P(OMe)₃, -20° 3. 2-C₁₀H₇SO₂Cl, DMAP, -10°, 5 h	epoxide–CH₂OSO₂C₁₀H₇-2 (40) $[\alpha]$ +22.43°	18
	1. TI (0.05), (–)-DIPT (0.06), 3 Å, -40°, 2 h 2. P(OMc)₃, -20° 3. TsCl, Et₃N, -20°, 10 h	epoxide–CH₂OTs (55) 93% ee, $[\alpha]$ +20.15°	18
C₁₀ — OTBDPS...geranyl-type substrate ...OH	1. TI (0.05), (–)-DET (0.075), 4 Å, -40 to -20°, 4 h 2. P(OMe)₃, -20° 3. TsCl, Et₃N, -20°	OTBDPS...epoxide...OTs (57) $[\alpha]$ +6.85° [d]	623
geraniol structure ...OH	1. TI (0.05), (+)-DIPT (0.06), 3 Å, -10°, 15 min 2. P(OMe)₃, -20° 3. Ac₂O, Et₃N, rt	epoxide...OAc (98) 86% ee, $[\alpha]$ -26.9°	18

TABLE XI. EPOXIDATION OF ALLYLIC ALCOHOLS WITH IN SITU HYDROXY DERIVATIZATION (*Continued*)
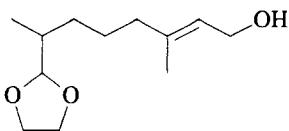
Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
	1. TI (0.05), (–)-DET (0.075), 4 Å, -20°, 7 h 2. TsCl, Et₃N, 0-5°, 36 h	 (67)[e] 93% ee, [α] +17.1° [d]	623
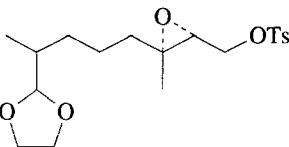
[a] The oxidant was cumene hydroperoxide.

[b] The ee and rotation were reported for the recrystallized material.

[c] The rotation was reported for twice recrystallized material.

[d] The rotation was measured in dichloromethane.

[e] The corresponding epoxy alcohol (11%) was also obtained.

TABLE XII. EPOXIDATION OF ALLYLIC ALCOHOLS WITH IN SITU EPOXIDE OPENING

Substrate	Conditions TI (eq), DAT (eq), MS	Product(s) and Yield(s) (%)	Refs.
C_3 (allyl alcohol)	1. TI (0.05), (+)-DIPT[a], (0.06), 3 Å, 0°, 5 h 2. P(OMe)$_3$, -30 to -25° 3. PhSH, Ti(OPr-i)$_4$, rt	PhS—CH$_2$—CH(OH)—CH$_2$OH (88) 90% ee [α] +21.3°[b]	136
	1. TI (0.05), (+)-DIPT[a], (0.06), 3 Å, 0°, 5 h 2. P(OMe)$_3$, -30 to -25° 3. 1-C$_{10}$H$_7$ONa, Ti(OPr-i)$_4$, rt, overnight	(1-naphthyl-O)—CH$_2$—CH(OH)—CH$_2$OH (54) 90% ee [α] +7.3°[b]	135
C_4 (methallyl alcohol)	1. TI (0.05), (+)-DIPT[a], (0.06), 3 Å, 0°, 5 h 2. P(OMe)$_3$, -30 to -25° 3. BnNHPr-i, Ti(OPr-i)$_4$, rt, overnight	(i-Pr)BnN—CH$_2$—CH(OH)—CH$_2$OH (68) 90% ee [α] -39.8°[b]	136
	1. TI (0.05), (+)-DIPT[a], (0.06), 3 Å, -20°, 4 h 2. P(OMe)$_3$, -30 to -25°, 0.5 h 3. PhSH, Ti(OPr-i)$_4$, rt	PhS—CH$_2$—C(CH$_3$)(OH)—CH$_2$OH (100) 92% ee [α] +2.27°[c]	136

[a] The oxidant was cumene hydroperoxide.

[b] The rotation was measured in ethanol.

[c] The rotation was measured in methanol.

TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
C₁			
Me–S–S–Me	TI (1), (+)-DET (2), H₂O (1), -20°, 16 d	Me–S(O)–S–Me (60) 41% ee, [α] -4.8°	204
Me–S–CH₂–S–Me	TI (1), (+)-DET (2), H₂O (1), -20°, 24 h	Me–S(O)–CH₂–S–Me (89) 40% ee, [α] -29.7°[a]	202
2-(methylthio)benzimidazole	TI (1), (+)-DET (2), H₂O (1), -20°, 24 h	benzimidazole sulfoxide (42) 61% ee, [α] -20.8°	202
C₂			
Me–S–CH₂CO₂Et	TI (1), (+)-DET (2), H₂O (1), -20°, 5.5 h	Me–S(O)–CH₂CO₂Et (84) 63% ee, [α] -31.3°[a]	202
C₃			
Me–S–CH₂CH₂CO₂Me	TI (1), (+)-DET (2), H₂O (1), -20°, 5 h	Me–S(O)–CH₂CH₂CO₂Me (85) 64% ee, [α] -50.2°	202
i-Pr–S–S–i-Pr	TI (1), (+)-DET (2), H₂O (1), -20°, 6 h	i-Pr–S(O)–S–i-Pr (43) 52% ee, [α] -58.4°	204
Me–S–CH₂CH(NHCOCF₃)CO₂Me	TI (1), (+)-DET (2), H₂O (1), -20°, 24 h	Me–S(O)–CH₂CH(NHCOCF₃)CO₂Me (73) 92% de[b], [α] -13.6°[a]	203

TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (*Continued*)

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
C₄			
Me–S–Bu-t	TI (1), (+)-DET (2), H₂O (1), -20°, 22 h	Me–S(O)–Bu-t (72) 53% ee, [α] -2.1°[a]	23. 205
n-Bu–S–S–Bu-n	TI (1), (+)-DET (2), H₂O (1), -20°, 3 d	n-Bu–S(O)–S–Bu-n (62), [α] +0.7°	204
t-Bu–S–S–Bu-t	TI (1), (+)-DET (2), H₂O (1), -20°, 5 d	t-Bu–S(O)–S–Bu-t (34) 41% ee, [α] -63.5°	204
C₅			
Me–S–CH₂CH(CH₃)CH₂CH₃	TI (1), (+)-DET (2), H₂O (1), -21°, 24 h	Me–S(O)–CH₂CH(CH₃)CH₂CH₃ (93)[b,c]	23
Me–S–(2-pyridyl)	TI (1), (+)-DET (2), H₂O (1), -20°, 16 h	Me–S(O)–(2-pyridyl) (63) 77% ee	202
Me–S–(3-pyridyl)	TI (1), (+)-DET (2), H₂O (1), -50°, 72 h	Me–S(O)–(3-pyridyl) (55)	207
Me–S–(5-chloro-3-pyridyl)	TI (1), (+)-DET (2), H₂O (1), -40°, 20 h	Me–S(O)–(5-chloro-3-pyridyl) (75)	207

TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (*Continued*)

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
	TI (1), (+)-DET (2), H$_2$O (1), -40°, 20 h	(70)	207
C$_6$	TI (1), (+)-DET (2), H$_2$O (1), -20°	(83) 75% ee, [α] -59.1° [a]	201
	TI[d] (1), (+)-DET (2), H$_2$O (1), -40°	(86) 29% de	482
	TI[d] (1), (+)-DET (2), H$_2$O (1), -40°	(90) 17% de	482
	TI[d] (1), (+)-DET (2), H$_2$O (1), -40°	(61) 67% de	482
	TI[d] (1), (−)-DET (2), H$_2$O (1), -40°	(72) 64% de	482
Me$^{\diagdown S}$C$_6$H$_{11}$	TI (1), (+)-DET (2), H$_2$O (1), -20°, 18 h	(67) 54% ee, [α] -44.3° [a]	23, 204
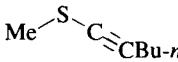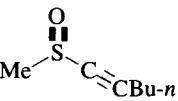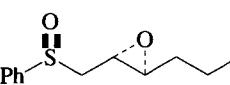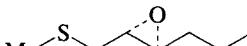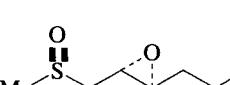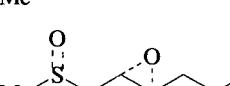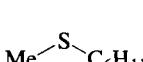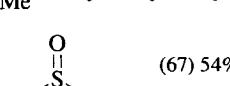
TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (*Continued*)
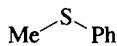
Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
Me$^{\diagdown S\diagdown}$Ph	TI (1), (+)-DET (2), H$_2$O (1), -20°, 12 h	(81) 89% ee	22
	TI[d] (1), (+)-DET (2), H$_2$O (1), -23°, 20 h	" (93) 93% ee, [α] +135.4° [a]	201
Me$^{\diagdown S\diagdown}$C$_6$H$_4$Cl-p	TI (1), (+)-DET (2), H$_2$O (1), -23°	(85) 78% ee	201
	TI[d] (1), (+)-DET (2), H$_2$O (1), -23°, 20 h	" (85) 91% ee, [α] +114° [a]	201
Cl$\diagdown\diagup^{S\diagdown}$Ph	TI (1), (+)-DET (2), H$_2$O (1), -20°, 16 h	(60) 47% ee, [α] +88.1° [a]	203
MeO$^{\diagdown S\diagdown}$Ph	TI (1), (+)-DET (2), H$_2$O (1), -20°, 3 d	(86) 29% ee	204
$\diagup\!\!=\!\!\diagdown^{S\diagdown}$Ph	TI (1), (+)-DET (2), H$_2$O (1), -20°, 16 h	(80) 70% ee, [α] +215° [a]	203
NC$\diagdown\diagup^{S\diagdown}$Ph	TI (1), (+)-DET (2), H$_2$O (1), -20°, 24 h	(85) 34% ee, [α] +59° [a]	203
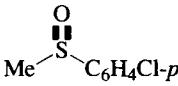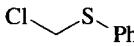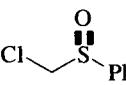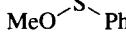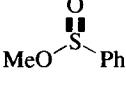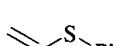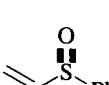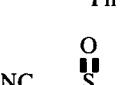
TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (*Continued*)
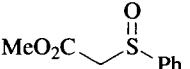
Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
MeO₂C∼S∼Ph	TI (1), (+)-DET (2), H₂O (1), -20°, 16 h	MeO₂C∼S(=O)∼Ph (81) 64% ee, [α] +98° [a]	203
CH₃C(=O)CH₂∼S∼Ph	TI (1), (+)-DET (2), H₂O (1), -20°, 24 h	CH₃C(=O)CH₂∼S(=O)∼Ph (68) 60% ee, [α] +131.3° [a]	203
cyclopropyl∼S∼Ph	TI (1), (+)-DET (2), H₂O (1), -20°, 24 h	cyclopropyl∼S(=O)∼Ph (73) 95% ee, [α] +136.7° [a]	204
t-Bu∼S∼Ph	TI[e] (1), (+)-DET (4), -20°, 30 h	*t*-Bu∼S(=O)∼Ph (99) 34.5% ee[b], [α] +62.1° [a]	24
Ph∼S∼S∼Ph	TI (1), (+)-DET (2), H₂O (1), -20°, 1.7 d	Ph∼S(=O)∼S∼Ph (20)[b], [α] +20.2°	204
HO∼∼S∼C₆H₄Cl-*p*	TI[e] (1), (+)-DET (4), -20°, 24 h	HO∼∼S(=O)∼C₆H₄Cl-*p* (41) 14% ee[b] [α] -23.4° [a]	24
Me∼S∼C₆H₄OMe-*p*	TI (1), (+)-DET (2), H₂O (1), -20°, 65 h	Me∼S(=O)∼C₆H₄OMe-*p* (70) 84% ee	202
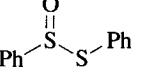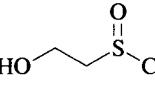
Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
Me∼S∼C₆H₄OMe-*o*	TI[d] (1), (+)-DET (2), H₂O (1), -23°, 20 h	Me∼S(=O)∼C₆H₄OMe-*o* (97) 93% ee, [α] +313° [a]	201
	TI (1), (+)-DET (2), H₂O (1), -20°, 4 h	" (77) 89.4% ee, [α] +18.3° [a]	203
i-PrO∼S∼Ph	TI (1), (+)-DET (2), H₂O (1), -20°, 3 d	*i*-PrO∼S(=O)∼Ph (91) 8.5% ee, [α] -16° [a]	204
MeO∼S∼(2-NO₂,4-NO₂-C₆H₃)	TI (1), (+)-DET (2), H₂O (1), -20°, 8 d	MeO∼S(=O)∼(2-NO₂,4-NO₂-C₆H₃) (0)	204
C₇ Me∼S∼CH₂Ph	TI[e] (1), (+)-DET (4), -77°, 24 h	Me∼S(=O)∼CH₂Ph (70) 46% ee, [α] +25.3° [a]	24
	TI (1), (+)-DET (2), H₂O (1), -20°	" (88) 35% ee, [α] -33.6° [f,g]	201
	TI (1), (+)-DET (2), H₂O (1), -20°	" (84) 62% ee, [α] -59°	201
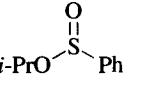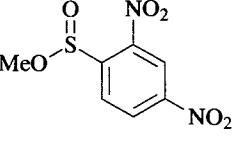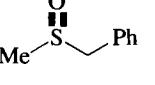
TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (Continued)

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
Me–S–C$_6$H$_4$Me-p	TI (1), (+)-DET (2), H$_2$O (1), -40°, 12 h	Me–S(=O)–C$_6$H$_4$Me-p (95) 93% ee, [α] +132° [a]	22, 23
	TI[d] (1), (+)-DET (2), H$_2$O (1), -23°	" (93) 96% ee, [α] +139° [a]	201
	TI[e] (1), (+)-DET (4), -20°, 14 h	" (60) 88.3% ee, [α] +128.5° [a]	24
Me–S–C$_6$H$_4$Me-o	TI (1), (+)-DET (2), H$_2$O (1), -20°	Me–S(=O)–C$_6$H$_4$Me-o (77) 89% ee, [α] +183° [a]	202
Et–S–C$_6$H$_4$Me-p	TI (1), (+)-DET (2), H$_2$O (1), -20°, 3 h	Et–S(=O)–C$_6$H$_4$Me-p (71) 74% ee, [α] +139.4° [a]	22, 23
i-Pr–S–C$_6$H$_4$Me-p	TI (1), (+)-DET (2), H$_2$O (1), -20°, 3 h	i-Pr–S(=O)–C$_6$H$_4$Me-p (56) 63% ee[b], [α] +111° [a]	22
n-Bu–S–C$_6$H$_4$Me-p	TI (1), (+)-DET (2), H$_2$O (1), -20°, 3 h	n-Bu–S(=O)–C$_6$H$_4$Me-p (28) 20% ee[b], [α] +38° [a]	22, 23
	TI (1), (+)-DET (2), H$_2$O (1), -20°	n-Bu–S(=O)–C$_6$H$_4$Me-p (75) 20% ee	202

TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (Continued)

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
t-BuO$_2$C–CH$_2$–S–C$_6$H$_4$Me-p	TI (1), (+)-DET (2), H$_2$O (1), -30°, 60 h	t-BuO$_2$C–CH$_2$–S(=O)–C$_6$H$_4$Me-p (50) 9% ee [α] +15.1° [a]	202, 22
n-BuC≡C–S–C$_6$H$_4$Me-p	TI (1), (+)-DET (2), H$_2$O (1), -20°, 18 h	n-BuC≡C–S(=O)–C$_6$H$_4$Me-p (97) 29% ee [α] +22.2°	201
Ph–CH$_2$–S–C$_6$H$_4$Me-p	TI (1), (+)-DET (2), H$_2$O (1), -20°, 12 h	Ph–CH$_2$–S(=O)–C$_6$H$_4$Me-p (41) 7% ee	22
Me–S–C$_6$H$_4$–CH$_2$OH	TI (1), (+)-DET (2), H$_2$O (1), -20°, 48 h	Me–S(=O)–C$_6$H$_4$–CH$_2$OH (71) 76% ee	201
Me–S–C$_6$H$_4$CO$_2$Me-p	TI (1), (+)-DET (2), H$_2$O (1), 60 h	Me–S(=O)–C$_6$H$_4$CO$_2$Me-p (50) 91% ee[b]	205
Me–S–C$_6$H$_4$CO$_2$Me-o	TI (1), (+)-DET (2), H$_2$O (1), 7 h	Me–S(=O)–C$_6$H$_4$CO$_2$Me-o (50) 60% ee[b]	205
i-PrNH–S–C$_6$H$_4$Me-p	TI (1), (+)-DET (2), H$_2$O (1), -20°, 3 d	i-PrNH–S(=O)–C$_6$H$_4$Me-p (28) 24% ee [α] +42.7°	203

TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (*Continued*)

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
$Et_2N \diagup^S \diagdown C_6H_4Me\text{-}p$	TI (1), (+)-DET (2), H$_2$O (1), -20°, 7 d	(60) 35% ee [α] +42.4°	203
$MeO \diagup^S \diagdown C_6H_4Me\text{-}p$	TI (1), (+)-DET (2), H$_2$O (1), -20°, 1 d	(88) 36% ee [α] +79.7°	203
$p\text{-}MeC_6H_4 \diagdown S \diagdown S \diagdown C_6H_4Me\text{-}p$	TI (1), (+)-DET (2), H$_2$O (1), -20°, 5 d	$p\text{-}MeC_6H_4 \diagdown S \diagdown \overset{O}{\underset{}{S}} \diagdown C_6H_4Me\text{-}p$ (10) 13% ee [α] +70.0°	203
C$_8$ $Me \diagup^S \diagdown C_8H_{17}\text{-}n$	TI (1), (+)-DET (2), H$_2$O (1), -20°, 64 h	(77) 71% ee	23, 205
	TI (1)^d, (+)-DET (2), H$_2$O (1), -23°	" (71) 80% ee, [α] -66.6° ^{a}	201
C$_9$	TI (1), (+)-DET (2), H$_2$O (1), -20°, 24 h	(0)	22
	TI (1), (+)-DET (2), H$_2$O (1), -45°, 48 h	(80)	207
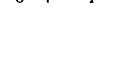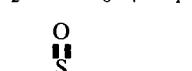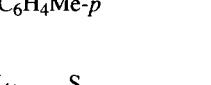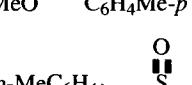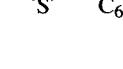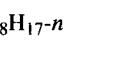
TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (*Continued*)

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
C$_{10}$	TI (1), (+)-DET (2), H$_2$O (1), -20°, 5 h	(98) 89% ee [α] +402° ^{a}	205
	TI (1), (+)-DET (2), H$_2$O (1), -20°, 4 h	(88) 90% ee^b [α] +120° ^{a}	23, 205
	TI (1), (+)-DET (2), H$_2$O (1), -21°, 12 h	(78) 24% ee^b [α] +39° ^{a}	23, 205
C$_{12}$	TI (1)^e, (+)-DET (2), H$_2$O (0.5), -15°, 1 h	(52) 78.1% ee [α] +40.4° ^{g}	828
	TI (1)^d, (–)-DET (2), H$_2$O (0.5), -15°, 1 h	(47) [α] -40.5° ^{g}	828
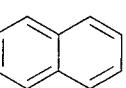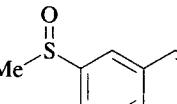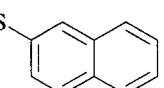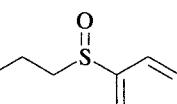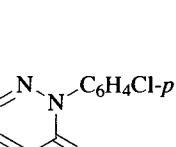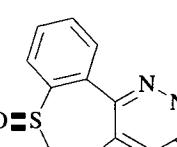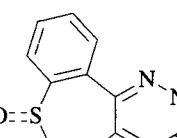
TABLE XIII. ASYMMETRIC OXIDATION OF SULFIDES AND DISULFIDES (*Continued*)

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
C₁₄			

C_{14}

TI (1), (+)-DET (2),
H₂O (1), -20°, 4 h

(33) 86% ee
[α] +97° *a*

205

TI (1), (+)-DET (2),
H₂O (1)

30% ee, [α] +185.4° *g,h*

829

a The rotation was measured in acetone.

b The configuration of sulfoxide moiety was not determined.

c The product contained two diastereomers of 42 and 38% ee, respectively.

d Cumene hydroperoxide was used instead of TBHP.

e The reaction was carried out in 1,2-dichloroethane.

f The rotation was measured in EtOH.

g The rotation was reported for recrystallized material.

h The rotation was measured in MeCN-MeOH (1:1).

TABLE XIV. ASYMMETRIC OXIDATION OF β–HYDROXY SULFIDES

Substrate	Conditions[a] TI (eq), DAT (eq)	Diastereomeric Product(s)[b] and Yield(s) (%)[c]	Refs.
C_6			
$O_2CC_6H_4NO_2$-o Me—S Et *dl*	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	O=S $O_2CC_6H_4NO_2$-o Me Et **a**: (58) 68% ee **b**: (22) 65% ee	830
$O_2CC_6H_4NO_2$-p Me—S Et *dl*	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	O=S $O_2CC_6H_4NO_2$-p Me Et **a**: (46) 60% ee **b**: (13) 38% ee	830
$O_2CC_6H_3(NO_2)_2$-3,5 Me—S Et *dl*	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	O=S $O_2CC_6H_3(NO_2)_2$-3,5 Me Et **a**: (52) 75% ee **b**: (25) 50% ee	830
$OSiPh_3$ Me—S Et *dl*	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	O=S $OSiPh_3$ Me Et **a**: (67) 65% ee **b**: (20)	830
C_8			
OH Me—S Ph *dl*	TI (0.25), (+)-DET (1), -20°, 14-16 h	O=S OH Me Ph **a**: (13.6) 3% ee **b**: (6.4) 5% ee	830, 831
$O_2CC_6H_4NO_2$-o Me—S Ph *dl*	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	O=S $O_2CC_6H_4NO_2$-o Me Ph **a**: (38) 54% ee **b**: (33) 50% ee	830, 831

TABLE XIV. ASYMMETRIC OXIDATION OF β–HYDROXY SULFIDES (*Continued*)

Substrate	Conditions[a] TI (eq), DAT (eq)	Diastereomeric Product(s)[b] and Yield(s) (%)[c]	Refs.
OTBDPS Me–S–...–Ph *dl*	TI (0.25), (+)-DET (1), -20°, 14-16 h	O OTBDPS Me–S–...–Ph a: (50) 75% ee b: (41) 71% ee	830, 831
OSiPh₃ Me–S–...–Ph *dl*	TI (0.25), (+)-DET (1), -20°, 14-16 h	O OSiPh₃ Me–S–...–Ph a: (44) 70% ee b: (34) 64% ee	830, 831
	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	" a: (43) 80% ee; b: (43) 75% ee	830, 831
C₉ OH Me–S–...–Ph *dl*	TI (0.25), (+)-DET (1), -20°, 14-16 h	O OH Me–S–...–Ph a: (22) 18% ee b: (<0.2)	830, 831
OAc Me–S–...–Ph *dl*	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	O OAc Me–S–...–Ph a: (74) 71% ee b: (12)	830
OTMS Me–S–...–Ph *dl*	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	O OTMS Me–S–...–Ph a: (73) 66% ee b: (11)	830
OSiPh₃ Me–S–...–Ph *dl*	TI (0.25), (+)-DET (1), -20°, 14-16 h	O OSiPh₃ Me–S–...–Ph a: (79) 70% ee b: (11)	830, 831

TABLE XIV. ASYMMETRIC OXIDATION OF β–HYDROXY SULFIDES (*Continued*)

Substrate	Conditions[a] TI (eq), DAT (eq)	Diastereomeric Product(s)[b] and Yield(s) (%)[c]	Refs.
	TI (0.25), (+)-DET (1)[d], -20°, 14-16 h	O OSiPh₃ Me–S–...–Ph a: (83) 78% ee b: (8) 70% ee	830, 831

[a] The ratio of *tert*-butyl hydroperoxide to sulfide was 0.5.

[b] The absolute and relative configurations of the two diastereomeric products a and b were not determined.

[c] The yield was based on the oxidant.

[d] Cumene hydroperoxide was used instead of *tert*-butyl hydroperoxide.

TABLE XV. ASYMMETRIC OXIDATION OF DITHIOACETALS

	Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)[a]	Refs.
C_1		TI (1), (+)-DET (2), H_2O (1) -20°, 16 h	(78) 20% ee, [α] +41.7°[b]	203
C_2	EtO_2C	TI (1), (+)-DET (2), H_2O (1) -40°, 50 h	EtO_2C (65) 60:40[c], 80% ee[d]	206
C_3	EtO_2C	TI (1), (+)-DET (2), H_2O (1) -38°, 50 h	EtO_2C (65) 100:0[c], 80% ee[d] [α] +18.9°[e]	206

TABLE XV. ASYMMETRIC OXIDATION OF DITHIOACETALS (*Continued*)

	Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)[a]	Refs.
C_5	t-Bu	TI (1), (+)-DET (4), -20°, 8 h[f]	t-Bu (82) 99:1[c], 70% ee[d]	832
	t-Bu	TI (1), (+)-DET (2), H_2O (1) -78°, 50 h	t-Bu (49) 90:10[c], 0% ee[d]	206
C_6	t-Bu	TI (1), (+)-DET (4), -20°, 14 h[f]	t-Bu (61) 99:1[c], 68% ee[d]	832
C_7	Ph	TI (0.19), (+)-DET (0.77), -20°, 15 h[f]	Ph (76) 94:6[c], 76% ee[d]	832
	Ph	TI (0.19), (+)-DET (0.77), -20°, 15 h[f]	Ph (88) 90:10[c], 14% ee[d]	832
C_8	Ph	TI (0.19), (+)-DET (0.77), -20°, 15 h[f]	Ph (66) 97:3[c], 83% ee[d]	832

TABLE XV. ASYMMETRIC OXIDATION OF DITHIOACETALS (*Continued*)

	Conditions		
Substrate	TI (eq), DAT (eq)	Product(s) and Yield(s) (%)[a]	Refs.
	TI (0.19), (+)-DET (0.77), -20°, 15 h[f]	(87) 85:15[c], 39% ee[d]	832
	TI (1), (+)-DET (2), H$_2$O (1), -40°, 50 h	" (65) 100:0[d], 78% ee, [α] +18.9°[g]	206
	(+)-DET	(—) 100:0, 76% ee	833

[a] The absolute configurations of the sulfoxides were not determined.

[b] The rotation was measured in acetone.

[c] The ratio is that of the diastereomers (*trans:cis*).

[d] The value refers to the major *trans* isomer.

[e] The rotation was measured in dichloromethane.

[f] The reaction was carried out in 1,2-dichloroethane.

[g] The rotation was measured in ethanol.

TABLE XVI. KINETIC RESOLUTION OF A RACEMIC SULFIDE

Substrate	Conditions TI (eq), DAT (eq)	Sulfide and Yield (%)	Sulfoxide and Yield (%)	Refs.
C$_{17}$	TI (0.6), (+)-DIPT (1.2 H$_2$O (0.6), TBHP (0.6) 4 Å, -20°, 6 h	 (36) 67% ee[a], [α] -56.99° [b]	 (—)	834
	TI (0.6), (–)-DIPT (1.2 H$_2$O (0.6), TBHP (0.7) 4 Å, -20°, 6 h	 (—) 84% ee[a], [α] +70.41° [b]	(—)	834
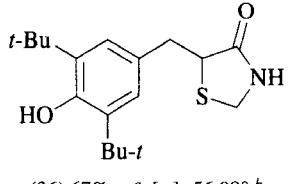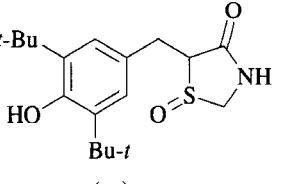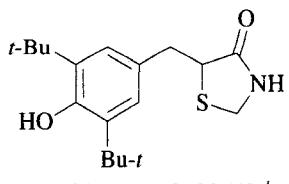
[a] The absolute configuration was not determined.

[b] The rotation was measured in methanol.

TABLE XVII. ASYMMETRIC OXIDATION OF SELENIDES

Substrate	Conditions TI (eq), DAT (eq)	Product(s) and Yield(s) (%)	Refs.
C₁₄	TI (1), (+)-DIPT (4), -5°	(82) 18% ee, [α] -16°	26
	TI (1), (−)-DIPT (4), -5°	(75) 20% ee, [α] +14°	26
	TI (1), (+)-DIPT (4), -5°	(72) 40% ee, [α] -101°	26
	TI (1), (−)-DIPT (4), -5°	(70) 28% ee, [α] +85°	26

TABLE XVIII. KINETIC RESOLUTION OF β-HYDROXYAMINES[a]

	Substrate			Conditions TI (eq), DAT (eq)	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
				1. TI(2), (+)-DIPT (1.2), rt, 30 min 2. TBHP (0.6), - 20°, 2 h			21
	R^1	R^2	R^3				
C_3	CH_2OBn	Me	Me		(34) 91% ee, [α] -9.75°	(—)	
	$CH_2OC_{10}H_7$-1	Me	Me		(40) 92% ee, [α] -2.6°	(56)	
	$CH_2OC_{10}H_7$-1	Bn	i-Pr		(36) 32% ee, [α] +9.2°	(56)	
	$CH_2OC_6H_4Me$-m	Bn			(35) 85% ee, [α] +13.7°	(—)	
C_8	Ph	Me	Me		(35) 95% ee, [α] -47.7°	(50)	
	C_6H_{11}	$(CH_2)_2$	$(CH_2)_2$		(36) 92% ee, [α] -20.7°	(50)	
	Ph	Bn	i-Pr		(35) 15% ee, [α] -0.74°	(61)	
	Ph	$(CH_2)_2$	$(CH_2)_2$		(37) 95% ee, [α] -40.3°	(59)	
	Ph	Bn	Bn		(19) 10% ee, [α] -0.06°	(—)	
	Ph	Me	Bn		(33) 86% ee, [α] -49.2°	(62)	
	Ph	$(CH_2)_2$	$(CH_2)_3$		(37) 97% ee, [α] -51.2°	(54)	
C_{10}	n-C_8H_{17}	Me	Me		(36) 91% ee, [α] -3.58°	(53)	
	n-C_8H_{17}	$(CH_2)_2$	$(CH_2)_2$		(37) 94% ee, [α] -1.20°	(54)	
	n-C_8H_{17}	Bn	Bn		(34) 0% ee	(60)	

TABLE XVIII. KINETIC RESOLUTION OF β-HYDROXYAMINES[a] (*Continued*)

Substrate	Conditions TI (eq), DAT (eq)	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
+ enantiomer	1. TI(2), (+)-DIPT (1.2), rt, 30 min 2. TBHP (0.6), -20°, 2 h			21

	R^1	R^2			
C_6	$(CH_2)_4$		(25) 95% ee, [α] -2.95°	(55)	
C_9	Ph	Me	(40) 95% ee, [α] +26.3°	(53)	

Substrate	Conditions TI (eq), DAT (eq)	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
+ enantiomer	1. TI(2), (+)-DIPT (1.2), rt, 30 min 2. TBHP (0.6), -20°, 2 h			21

	R^1	R^2	R^3	R^4		
C_6	$(CH_2)_4$		Me	Me	(40) 92% ee, [α] -25.4°	(55)
	$(CH_2)_4$		Bn	Bn	(36) 0% ee	(50)
C_9	Ph	Me	Me	Me	(42) 93% ee, [α] -40.2°	(53)

Substrate	Conditions TI (eq), DAT (eq)	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
+ enantiomer	1. TI(2), (+)-DIPT (1.4), rt, 30 min 2. TBHP (0.6), -15°, 4 h			139

	R		
C_6	$(CH_2)_4$	(39) 93% ee, [α] -62.3°	(46) 59% ee, [α] +36.7°
	$(CH_2)_5$	(38) 96% ee, [α] -66.5°	(60) 46.4% ee, [α] +13.0°

TABLE XVIII. KINETIC RESOLUTION OF β-HYDROXYAMINES[a] (*Continued*)

Substrate	Conditions TI (eq), DAT (eq)	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
C_8	1. TI (2), (+)-DIPT, rt, 30 min 2. TBHP (0.6), -20°, 2 h			21
	(+)-DIPT (1.2) (+)-DIPT (2.4)	(37) 95% ee, [α] -40.3° (—) 71% ee	(59) (—)	
	1. TI (2), (+)-DIPT (1), rt, 0.5 h 2. TBHP (0.6), -20°, 2 h	(37) 97% ee	(54)	21
C_9 + enantiomer	1. TI (2), (+)-DIPT, rt, 30 min 2. TBHP (0.6), -20°, 2 h			21
	(+)-DIPT (1.2) (+)-DIPT (1.3) (+)-DIPT (1.4) (+)-DIPT (1.5) (+)-DIPT (2.4)	(36-39) 58% ee (36-39) 85% ee (36-39) 96% ee (36-39) 95% ee (36-39) 50% ee	(—) (—) (—) (—) (—)	
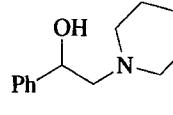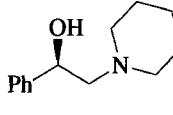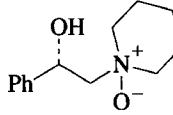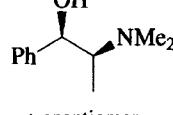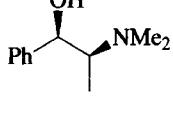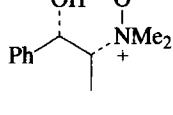
TABLE XVIII. KINETIC RESOLUTION OF β-HYDROXYAMINES[a] (*Continued*)

Substrate	Conditions TI (eq), DAT (eq)	Remaining Alcohol(s) and Yield(s) (%)	Oxidation Product(s) and Yield(s) (%)	Refs.
OH NMe₂ Ph + enantiomer	1. (+)-DIPT (1.2), H₂O 2. TI (2), rt, 30 min 3. TBHP (0.6), -20°, 2 h	OH NMe₂ Ph	OH O⁻ NMe₂ Ph +	21
	H₂O (0.5)	(—) 71% ee, 60% conversion	(—)	
	H₂O (1.0)	(—) 53% ee, 58% conversion	(—)	
	H₂O (2.0)	(—) 0% ee, 32% conversion	(—)	
OH Ph NMe₂	1. TI (2), (+)-DIPT (1.2), rt, 30 min 2. TBHP (0.6), -20°, 2 h	OH Ph NMe₂ (52) 0% ee	OH Ph +NMe₂ O⁻ (37)	21
C₁₀ OH n-C₈H₁₇ N	1. TI (2), (+)-DIPT, rt, 30 min 2. TBHP (0.6), -20°, 2 h	OH n-C₈H₁₇ N	OH n-C₈H₁₇ N+ O⁻	21
	(+)-DIPT (1.2)	(27) 94% ee, [α] -1.2°	(54)	
	(+)-DIPT (2.4)	(—) 0% ee	(—)	
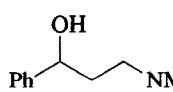
[a] All optical rotations in this table were measured in ethanol.

9. Acknowledgment

References

1. Katsuki, T.; Sharpless, K. B. J. Am. Chem. Soc., 1980, **102**, 5974.
2. Finn, M. G.; Sharpless, K. B. in *Asymmetric Synthesis*, Morrison, J. D., Ed., Academic Press, Orlando, FL, 1985, **Vol.5**, pp. 247–348.
3. Pfenninger, A. Synthesis, 1986, 89.
4. Rossiter, B. E. in *Asymmetric Synthesis*, Morrison, J. D., Ed., Academic Press, Orlando, FL, 1985, Vol. **5**, pp. 193–246.
5. Katsuki, T. J. Syn. Org. Chem. Jpn., 1987, **45**, 90; Chem. Abstr., 1986, **107**, 134136k.
6. Johnson, R.; Sharpless, K. B. in *Comprehensive Organic Synthesis*, Trost, B. M., Ed., Pergamon, Oxford, 1991, Vol. **7**, Ch. "3, 2".
7. Behrens, C. H.; Sharpless, K. B. Aldrichim. Acta, 1983, **16**, 67.
8. Wood, R. D.; Ganem, B. Tetrahedron Lett., 1982, **23**, 707.
9. Erickson, T. J. J. Org. Chem., 1986, **51**, 934.
10. Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. J. Am. Chem. Soc., 1981, **103**, 6237.
11. Kitano, Y.; Matsumoto, T.; Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F. Chem. Lett., 1987, 1523.
12. Kitano, Y.; Matsumoto, T.; Wakasa, T.; Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F. Tetrahedron Lett., 1987, **28**, 6351.
13. Kitano, Y.; Matsumoto, T.; Sato, F. Tetrahedron, 1988, **44**, 4073.
14. Kobayashi, Y.; Kusakabe, M.; Kitano, Y.; Sato, F. J. Org. Chem., 1988, **53**, 1586.
15. Kitano, Y.; Kusakabe, M.; Kobayashi, Y.; Sato, F. J. Org. Chem., 1989, **54**, 994.
16. Carlier, P. R.; Mungall, W. S.; Schroder, G.; Sharpless, K. B. J. Am. Chem. Soc., 1988, **110**, 2978.
17. Hanson, R. M.; Sharpless, K. B. J. Org. Chem., 1986, **51**, 1922.
18. Gao, Y.; Hanson, R. M.; Kluder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. J. Am. Chem. Soc., 1987, **109**, 5765.
19. Sharpless, K. B. Janssen Chim. Acta, 1988, **6**, 3; Chem. Abstr., 1988, **109**, 128034a.
20. Miyano, S.; Lu, L. D.-L.; Viti, S. M.; Sharpless, K. B. J. Org. Chem., 1983, **48**, 3608.
21. Miyano, S.; Lu, L. D.-L.; Viti, S. M.; Sharpless, K. B. J. Org. Chem., 1985, **50**, 4350.
22. Pitchen, P.; Kagan, H. B. Tetrahedron Lett., 1984, **25**, 1049.
23. Pitchen, P.; Dunach, E.; Deshmukh, M. N.; Kagan, H. B. J. Am. Chem. Soc., 1984, **106**, 8188.

24. Di Furia, F.; Modena, G.; Seraglia, R. Synthesis, 1984, 325.

25. Kagan, H. B.; Rebiere, F. Synlett, 1990, 643.

26. Tiecco, M.; Tingoli, M.; Testaferri, L.; Bartoli, D. Tetrahedron Lett., 1987, **28**, 3849.

27. Parker, R. E.; Isaacs, N. S. Chem. Rev., 1959, **59**, 737.

28. Swern, D. in *Organic Peroxides*, D. Swern, Ed., Wiley-Interscience, New York, 1971, Vol.**2**, Ch. "5".

29. Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. Tetrahedron, 1983, **39**, 2323.

30. Sharpless, K. B.; Verhoeven, T. R. Aldrichim. Acta, 1979, **12**, 63.

31. Sharpless, K. B. *Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research XXVII, Houston, Texas, 1983*, pp. 59–89.

32. Chaumette, P.; Mimoun, H.; Saussine, L.; Fischer, J.; Mitschler, A. J. Organomet. Chem., 1983, **250**, 291.

33. Mimoun, H.; Charpentier, R.; Mitschler, A.; Fisher, J.; Weiss, R. J. Am. Chem. Soc., 1980, **102**, 1047.

34. Mimoun, H. Angew. Chem. Int. Ed. Engl., 1982, **21**, 734.

35. Sharpless, K. B.; Woodard, S. S.; and Finn, M. G. Pure & Appl. Chem., 1983 **55**, 1823.

36. Woodard, S. S.; Finn, M. G.; Sharpless, K. B. J. Am. Chem. Soc., 1991, **113**, 106.

37. Finn, M. G.; Sharpless, K. B. J. Am. Chem. Soc., 1991, **113**, 113.

38. McKee, B. H.; Kalantar, T. H.; Sharpless, K. B. J. Org. Chem., 1991, **56**, 6966.

39. Narula, A. S. Tetrahedron Lett., 1982, **23**, 5579.

40. Bach, R. D.; Wolber, G. J.; Coddens, B. A. J. Am. Chem. Soc., 1984, **106**, 6098.

41. Rossiter, B. E.; Sharpless, K. B. The Scripps Research Institute, La Jolla, CA, unpublished results.

42. Puchot, C.; Samuel, O.; Dunach, E.; Zhao, S.; Agami, C.; Kagan, H. B. J. Am. Chem. Soc., 1986, **108**, 2353.

43. Woodard, S. S. Ph.D Dissertation, Stanford University, Stanford, California, 1981.

44. Burgess, K.; Jennings, L. D. J. Am. Chem. Soc., 1990, **112**, 7434.

45. Carlier, P. R.; Sharpless, K. B. J. Org. Chem., 1989, **54**, 4016.

46. Williams, I. D.; Pedersen, S. F.; Sharpless, K. B.; Lippard, S. J. J. Am. Chem. Soc., 1984, **106**, 6430.

47. Sharpless, K. B. Chem. Scripta, 1987, **27**, 521.

48. Pedersen, S. F.; Dewan, J. C.; Eckman, R. R.; Sharpless, K. B. J. Am.

Chem. Soc., 1987, **109**, 1279.

49. Katsuki, T.; Sharpless, K. B.; Kyushu University, unpublished result.

50. Chamberlin, A. R.; Mulholland, Jr., R. L.; Kahn, S. D.; Hehre, W. J. J. Am. Chem. Soc., 1987, **109**, 672.

51. Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. Angew. Chem., Int. Ed. Engl., 1985, **24**, 1.

52. Corey, E. J. J. Org. Chem., 1990, **55**, 1693.

53. Takano, S.; Iwabuchi, Y.; Ogasawara, K. Tetrahedron Lett., 1991, **32**, 3527.

54. Chan, T. H.; Chen, L. M.; Wang, D. J. Chem. Soc., Chem. Commun., 1988, 1280.

55. Luly, J. R.; Hsiao, C.-N.; BaMaung. N.; Plattner, J. J. J. Org. Chem., 1988, **53**, 6109.

56. Marshall, J. A.; Flynn, K. E. J. Am. Chem. Soc., 1982, **104**, 7430.

57. Schweiter, M. J.; Sharpless, K. B. Tetrahedron Lett., 1985, **26**, 2543.

58. Takahashi, K.; Ogata, M. J. Org. Chem, 1987, **52**, 1877.

59. Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. J. Am. Chem. Soc., 1981, **103**, 464.

60. Baker, R.; Swain, C. J.; Head, J. C. J. Chem. Soc., Chem. Commun., 1986, 874.

61. Rossiter, B. E.; Verhoeven, T. R.; Sharpless, K. B. Tetrahedron Lett., 1979, 4733.

62. Chong, J. M.; Wong, S. J. Org. Chem., 1987, **52**, 2596.

63. Mori, K.; Seu, Y.-B. Tetrahedron, 1988, **44**, 1035.

64. Mori, K.; Nakazono, Y. Tetrahedron, 1986, **42**, 6459.

65. Hoagland, S.; Morita, Y.; Bai, D.-L.; Marki, H.-P.; Kees, K.; Brown, L.; Heathcock, C. H. J. Org. Chem., 1988, **53**, 4730.

66. Klunder, J. M.; Onami, T.; Sharpless, K. B. J. Org. Chem., 1989, **54**, 1295.

67. Hendrickson, H. S.; Hendrickson, E. K. Chem. & Phys. Lipids, 1990, **53**, 115.

68. Hoye, T. R.; Suhadolnik, J. C. J. Am. Chem. Soc., 1985, **107**, 5312.

69. Hoye, T. R.; Suhadolnik, J. C. Tetrahedron, 1986, **42**, 2855.

70. Hoye, T. R.; Jenkins, S. A. J. Am. Chem. Soc., 1987, **109**, 6196.

71. Nakahara, Y.; Fujita, A.; Ogawa, T. Agric. Biol. Chem., 1987, **51**, 1009.

72. Burke, S. D.; Buchanan, J. L.; Rovin, J. D. Tetrahedron Lett., 1991, **32**, 3961.

73. Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Tuddenham, D.; Walker, F. J. J. Org. Chem, 1982, **47**,

1373.

74. Lee, A. W. M.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Walker, F. J. J. Am. Chem. Soc., 1982, **104**, 3515.

75. Russell, S. T.; Robinson, J. A.; Williams, D. J. J. Chem. Soc., Chem. Commun., 1987, 351.

76. Paterson, I.; Boddy, I.; Mason, I. Tetrahedron Lett., 1987, **28**, 5205.

77. Paterson, I.; Boddy, I. Tetrahedron Lett., 1988, **29**, 5301.

78. Paterson I.; Craw, P. A. Tetrahedron Lett., 1989, **30**, 5799.

79. Koizumi, N.; Ishiguro, M.; Yasuda, M.; Ikekawa, N. J. Chem. Soc., Perkin Trans. 1, 1983, 1401.

80. Oehlschlager, A. C.; Johnston, B. D. J. Org. Chem., 1987, **52**, 940.

81. Shibuya, H.; Kawashima, K.; Baek, N. I.; Narita, N.; Yoshikawa, M.; Kitagawa, I. Chem. Pharm. Bull., 1989, **37**, 260.

82. Hashimoto, M.; Kan, T.; Yanagiya, M.; Shirahama, H.; Matsumoto, T. Tetrahedron Lett., 1987, **28**, 5665.

83. Hashimoto, M.; Kan, T.; Nozaki, K.; Yanagiya, M.; Shirahama, H.; Matsumoto, T. J. Org. Chem., 1990, **55**, 5088.

84. Nicolaou, K. C.; Duggan, M. E.; Hwang, C.-K.; Somers, P. K. J. Chem. Soc., Chem. Commun., 1985, 1359.

85. Nicolaou, K. C.; Uenishi, J. J. Chem. Soc., Chem. Commun., 1982, 1292.

86. Nicolaou, K. C.; Daines, R. A.; Uenishi, J.; Li, W. S.; Papahatjis, D. P.; Chakraborty, T. K. J. Am. Chem. Soc., 1987, **109**, 2205.

87. Nicolaou, K. C.; Daines, R. A.; Uenishi, J.; Li, W. S.; Papahatjis, D. P.; Chakraborty, T. K. J. Am. Chem. Soc., 1988, **110**, 4672.

88. Crimmins, M. T.; Lever, J. G. Tetrahedron Lett., 1986, **27**, 291.

89. Bonadies, F.; Fabio, R. D.; Gubiotti, A.; Mecozzi, S.; Bonini, C. Tetrahedron Lett., 1987, **28**, 703.

90. Rastetter, W. H.; Adams, J.; Bordner, J. Tetrahedron Lett., 1982, **23**, 1319.

91. Baker, S. R.; Boot, J. R.; Morgan, S. E.; Osborne, D. J.; Ross, W. J.; Schrubsall, P. R. Tetrahedron Lett., 1983, **24**, 4469.

92. Prestwich, G. D.; Wawrzénczyk, C. Proc. Natl. Acad. Sci. USA, 1985, **82**, 5290.

93. Petterson, L.; Frejd, T.; Magnusson, G. Tetrahedron Lett., 1987, **28**, 2753.

94. Wuts, P. G. M.; D'Costa, R.; Butler, W. J. Org. Chem., 1984, **49**, 2582.

95. Takahata, H.; Banba, Y.; Momose, T. Tetrahedron: Asymmetry, 1991, **2**, 445.

96. Takahata, H.; Banba, Y.; Momose, T. Tetrahedron, 1991, **47**, 7635.

97. Takahata, H.; Banba, Y.; Tajima, M.; Momose, T. J. Org. Chem., 1991, **56**, 240.

98. Adams, C. E.; Walker, F. J.; Sharpless, K. B. J. Org. Chem., 1985, **50**, 420.

99. Corey, E. J.; Hopkins, P. B.; Munroe, J. E.; Marfat, A., Hashimoto, S. J. Am. Chem. Soc., 1980, **102**, 7986.

100. Corey, E. J.; Pyne, S. G.; Su, W.-G. Tetrahedron Lett., 1983, **24**, 4883.

101. Oehlschlager, A. C.; Czyzewska, E. Tetrahedron Lett., 1983, **24**, 5587.

102. Bernet, B.; Vasella, A. Tetrahedron Lett., 1983, **24**, 5491.

103. Julina, R.; Herzig, T.; Bernet, B.; Vasella, A. Helv. Chim. Acta, 1986, **69**, 368.

104. Pale, P.; Chuche, J. Tetrahedron Lett., 1987, **28**, 6447.

105. Pridgen, L. N.; Shilcrat, S. C.; Lantos, I. Tetrahedron Lett., 1984, **25**, 2835.

106. Yamakawa, I.; Urabe, H.; Kobayashi, Y., Sato, F. Tetrahedron Lett., 1991, **32**, 2045.

107. Levine, S. G.; Bonner, M. P. Tetrahedron Lett., 1989, **30**, 4767.

108. Urabe, H.; Aoyama, Y.; Sato, F. J. Org. Chem., 1992, **57**, 5056.

109. Mori, K.; Ebata, T. Tetrahedron Lett., 1981, **22**, 4281.

110. Mori, K.; Ebata, T. Tetrahedron, 1986, **42**, 3471.

111. Overman, L. E.; Thompson, A. S. J. Am. Chem. Soc., 1988, **110**, 2248.

112. Corey, E. J.; Tramontano, A. J. Am. Chem. Soc., 1984, **106**, 462.

113. Ireland, R. E.; Smith, M. G. J. Am. Chem. Soc., 1988, **110**, 854.

114. Takano, S.; Otaki, S.; Ogasawara, K. J. Chem. Soc., Chem. Commun., 1983, 1172.

115. Schollkopf, U.; Tiller, T.; and Bardenhagen, J. Tetrahedron, 1988, **44**, 5293.

116. Johnston, B. D.; Oehlschlager, A. C. J. Org. Chem., 1982, **47**, 5384.

117. Abad, A.; Agullo, C.; Arno, M.; Cunat, A. C.; Zaragoza, R. J. J. Org. Chem, 1992, **57**, 50.

118. Doherty, A. M.; Ley, S. V. Tetrahedron Lett., 1986, **27**, 105.

119. de Laszlo, S. E.; Ford, M. J.; Ley, S. V.; Maw, G. N. Tetrahedron Lett., 1990, **31**, 5525.

120. Kende, A. S.; Rizzi, J. P. J. Am. Chem. Soc., 1981, **103**, 4247.

121. Rizzi, J. P.; Kende, A. S. Tetrahedron, 1984, **40**, 4693.

122. Naruta, Y.; Nishigaichi, Y.; Maruyama, K. Tetrahedron Lett., 1989, **30**, 3319.

123. Finan, J. M.; Kishi, Y. Tetrahedron Lett., 1982, **23**, 2719.

124. Sugiyama, S.; Honda, M.; Komori, T. Justus Liebigs Ann. Chem., 1988,

619.

125. Kanemoto, S.; Nonaka, T.; Oshima, K.; Utimoto, K.; Nozaki, H. Tetrahedron Lett., 1986, **27**, 3387.

126. Marshall, J. A.; Jenson, T. M. J. Org. Chem., 1984, **49**, 1707.

127. Falck, J. R.; Manna, S.; Siddhanta, A. K.; Capdevila, J; Buynak, J. D. Tetrahedron Lett., 1983, **24**, 5715.

128. Martin, V. S.; Katsuki, T.; Tuddenham, D.; Sharpless, K. B. Kyushu University, unpublished results.

129. Okamura, H.; Kuroda, S.; Tomita, K.; Ikegami, S.; Sugimoto, Y.; Sakaguchi, S.; Katsuki, T.; Yamaguchi, M. Tetrahedron Lett., 1991, **32**, 5137.

130. Lu, L. D.-L.; Johnson, R. A.; Finn, M. G.; Sharpless, K. B. J. Org. Chem., 1984, **49**, 728.

131. Tanner, D.; Somfai, P. Tetrahedron, 1986, **42**, 5985.

132. Tanner, D.; Somfai, P. Tetrahedron, 1987, **43**, 4395.

133. Nemoto, H.; Ishibashi, H.; Nagamochi, M.; Fukumoto, K. J. Org. Chem., 1992, **57**, 1707.

134. Nemoto, H.; Ishibashi, H.; Fukumoto, K. Heterocycles, 1992, **33**, 549.

135. Klunder, J. M.; Ko, S. Y.; Sharpless, K. B. J. Org. Chem., 1986, **51**, 3710.

136. Ko, S. Y.; Sharpless, K. B. J. Org. Chem., 1986, **51**, 5413.

137. Ko, S. Y.; Masamune, H.; Sharpless, K. B. J. Org. Chem., 1987, **52**, 667.

138. Choudary, B. M; Valli, V. L. K.; Prasad, A. D. J. Chem. Soc., Chem. Commun., 1990, 1186.

139. Hayashi, M.; Okamura, F.; Toba, T.; Oguni, N.; Sharpless, K. B. Chem. Lett., 1990, 547.

140. Wang, Z. M.; Zhou, W. S. Tetrahedron, 1987, **43**, 2935.

141. Wang, Z. M.; Zhou, W. S.; Lin, G. Q. Tetrahedron Lett., 1985, **26**, 6221.

142. Wang, Z. M.; Zhou, W. S. Synth. Commun., 1989, **19**, 2627.

143. Yamamoto, K.; Ando, H.; Shuetake, T.; Chikamatsu, H. J. Chem. Soc., Chem. Commun., 1989, 754.

144. Farrall, M. J.; Alexis, M.; Trecarten, M. Nouv. J. Chim., 1983, **7**, 449.

145. Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. Pure & Appl. Chem., 1983, **55**, 589.

146. Marshall, J. A.; Robinson, E. D.; Zapata, A. J. Org. Chem., 1989, **54**, 5854.

147. Brimacombe, J. S.; Hanna, R.; Kabir, A. K. M. S. J. Chem. Soc., Perkin Trans. 1, 1987, 2421.

148. Brimacombe, J. S.; Kabir, A. K. M. S.; Bennett, F. J. Chem. Soc., Perkin

Trans. 1, 1986, 1677.

149. Brimacombe, J. S.; Roderick, H.; Kabir, A. K. M. S. Carbohydr. Res., 1986, **153**, C7.

150. White, J. D.; Jayasinghe, L. R. Tetrahedron Lett., 1988, **29**, 2139.

151. White, J. D.; Amedio, Jr., J. C.; Gut, S.; Jayasinghe, L. J. Org. Chem., 1989, **54**, 4268.

152. White, J. D.; Amedio, Jr., J. C.; Gut, S.; Ohira, S.; Jayasinghe, L. R. J. Org. Chem., 1992, **57**, 2270.

153. Levine, S. G.; Heard, N. E. Synth. Commun., 1991, **21**, 549.

154. Nagaoka, H.; Kishi, Y. Tetrahedron, 1981, **37**, 3873.

155. Nishiyama, S.; Toshima, H.; Kanai, H.; Yamamura, S. Tetrahedron Lett., 1986, **27**, 3643.

156. Nishiyama, S.; Toshima, H.; Kanai, H.; Yamamura, S. Tetrahedron, 1988, **44**, 6315.

157. Dolle, R. E.; Nicolaou, K. C. J. Am. Chem. Soc., 1985, **107**, 1691.

158. Mori, K.; Itou, M. Justus Liebigs Ann. Chem., 1992, 87.

159. Smith, III, A. B.; Sarvatore, B. A.; Hull, K. G.; Duan, J. J.-W. Tetrahedron Lett., 1991, **32**, 4859.

160. Minami, N.; Ko, S. S.; Kishi, Y. J. Am. Chem. Soc., 1982, **104**, 1109.

161. Ko, S. Y.; Lee, A. W. M.; Masamune, S.; Reed, III, L. A.; Sharpless, K. B.; Walker, F. J. Science, 1983, **220**, 949.

162. Ko, S. Y.; Lee, A. W. M.; Masamune, S.; Reed, III, L. A.; Sharpless, K. B.; Walker, F. J. Tetrahedron, 1990, **46**, 245.

163. Klein, L. L.; McWhorter Jr., W. W.; Ko, S. S.; Pfaff, K.-P.; Kishi, Y.; Uemura, D.; Hirata, Y. J. Am. Chem. Soc., 1982, **104**, 7362.

164. Ko, S. S.; Finan, J. M.; Yonaga, M.; Kishi, Y.; Uemura, D.; Hirata, Y. J. Am. Chem. Soc., 1982, **104**, 7364.

165. Fujioka, H.; Christ, W. J.; Cha, J. K.; Leder, J.; Kishi, Y.; Uemura, D.; Hirata, Y. J. Am. Chem. Soc., 1982, **104**, 7367.

166. McWhorter, Jr., W. W.; Kang, S. H.; Kishi, Y. Tetrahedron Lett., 1983, **24**, 2243.

167. Clayden, J.; Collington, E. W.; Warren, S. Tetrahedron Lett., 1992, **33**, 7043.

168. Isobe, M.; Kitamura, M.; Mio, S.; Goto, T. Tetrahedron Lett., 1982, **23**, 221.

169. Kitamura, M.; Isobe, M.; Ichikawa, Y.; Goto, T. J. Org. Chem., 1984, **49**, 3517.

170. Ichikawa, Y.; Isobe, M.; Bai, D.-L.; Goto, T. Tetrahedron, 1987, **43**, 4737.

171. Ichikawa, Y.; Isobe, M.; Goto, T. Tetrahedron, 1987, **43**, 4749.

172. Isobe, M.; Ichikawa, Y.; Goto, T. Tetrahedron Lett., 1985, **26**, 5199.

173. Meyers, A. I.; Hudspeth, J. P. Tetrahedron Lett., 1981, **22**, 3925.

174. Meyers, A. I.; Babiak, K. A.; Campbell, A. L.; Comins, D. L.; Fleming, M. P.; Henning, R.; Heuschmann, M.; Hudspeth, J. P.; Kane, J. M.; Reider, P. J.; Roland, D. M.; Shimizu, K.; Tomioka, K.; Walkup, R. D. J. Am. Chem. Soc., 1983, **105**, 5015.

175. Nakajima, N.; Tanaka, T.; Hamada, T.; Oikawa, Y.; Yonemitsu, O. Chem. Pharm. Bull., 1987, **35**, 2228.

176. Rossiter, B. E.; Sharpless, K. B. J. Org. Chem., 1984, **49**, 3707.

177. Takano, S.; Iwabuchi, Y.; Ogasawara, K. Synlett, 1991, 548.

178. Ikegami, S.; Katsuki, T.; Yamaguchi, M. Chem. Lett., 1987, 83.

179. Corey, E. J.; Ha, D.-C. Tetrahedron Lett., 1988, **29**, 3171.

180. Adam, W.; Griesbeck, A.; Staab, E. Tetrahedron Lett., 1986, **27**, 2839.

181. Adam, W.; Griesbeck, A.; Staab, E. Angew. Chem., Int. Ed. Engl., 1986, **25**, 269.

182. Adam, W.; Braun, M.; Griesbeck, A.; Lucchini, V.; Staab, E.; Will, B. J. Am. Chem. Soc., 1989, **111**, 203

183. Roush, W. R.; Brown, R. J. J. Org. Chem., 1983, **48**, 5093.

184. Roush, W. R.; Spada, A. P. Tetrahedron Lett., 1983, **24**, 3693.

185. Page, P. C. B.; Rayner, C. M.; Sutherland, I. O. Tetrahedron Lett., 1986, **27**, 3535.

186. Page, P. C. B.; Rayner, C. M.; Sutherland, I. O. J. Chem. Soc., Perkin Trans. 1, 1990, 2403.

187. Takano, S.; Iwabuchi, Y.; Ogasawara, K. J. Am. Chem. Soc., 1991, **113**, 2786.

188. Takano, S.; Setoh, M.; Takahashi, M.; Ogasawara, K. Tetrahedron Lett., 1992, **33**, 5365.

189. For precedents to this equation, see footnote 7 in ref. 10.

190. Kitano, Y.; Matsumoto, T.; Sato, F. J. Chem. Soc., Chem. Commun., 1986, 1323.

191. Kitano, Y.; Matsumoto, T.; Takeda, Y.; Sato, F. J. Chem. Soc., Chem. Commun., 1986, 1732.

192. Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F. Tetrahedron Lett., 1987, **28**, 2033.

193. Kobayashi, Y.; Shimazaki, T.; Sato. F. Tetrahedron Lett., 1987, **28**, 5849.

194. Kusakabe, M.; Kato, H.; Sato, F. Chem. Lett., 1987, 2163.

195. Shimazaki, T.; Kobayashi, Y.; Sato, F. Chem. Lett., 1988, 1785.

196. Kobayashi, Y.; Kusakaba, M.; Kitano, Y.; Sato, F. J. Org. Chem., 1988, **53**, 1587.

197. Matsumoto, T.; Kitano, Y.; Sato, F. Tetrahedron Lett., 1988, **29**, 5685.

198. Lohse, P.; Loner, H.; Acklin, P.; Sternfeld, F.; Pfaltz, A. Tetrahedron Lett., 1991, **32**, 615.

199. Discordia, R. P.; Dittmer, D. C. J. Org. Chem., 1990, **55**, 1414.

200. Zhou, W.-S.; Lu, Z.-H.; Wang, Z.-M. Tetrahedron Lett., 1991, **32**, 1467.

201. Zhao, S. H.; Samuel, O.; Kagan, H. B. Tetrahedron, 1987, **43**, 5135.

202. Kagan, H. B.; Dunach, E.; Nemecek, C.; Pitchen, P.; Samuel, O.; Zhao, S. H. Pure & Appl. Chem., 1985, **57**, 1911.

203. Dunach, E.; Kagan, H. B. Nouv. J. Chem., 1985, **9**, 1.

204. Nemecek, C.; Dunach, E.; Kagan, H. B. Nouv. J. Chem., 1986, **10**, 761.

205. Kagan, H. B.; Dunach, E.; Deshmukh, M.; Pitchen, P. Chem. Scripta, 1985, **25**, 101.

206. Samuel, O.; Ronan, B.; Kagan, H. B. J. Organomet. Chem., 1989, **53**, 1587.

207. Boussad, N.; Trefouel, T.; Dupas, G.; Bourguignon, J.; Queguiner, G. Phosphorus, Sulfur, Silicon, 1992, **66**, 127.

208. Mitsunobu, O. Synthesis, 1981, 1.

209. Walba, D. M.; Vohra, R. T; Clark, N. A.; Handschy, M. A.; Xue, J.; Parmar, D. S.; Langerwall, S. T.; Skarp, K. J. Am. Chem. Soc., 1986, **108**, 7424.

210. Wasserman, H. H.; Oku, T. Tetrahedron Lett., 1986, **27**, 4913.

211. Discordia, R. P.; Murphy, C. K.; Dittmer, D. C. Tetrahedron Lett., 1990, **31**, 5603.

212. Chong, J. M. Tetrahedron Lett., 1992, **33**, 33.

213. Kigoshi, H.; Ojika, M.; Shizuri, Y.; Niwa, H.; Yamada, K. Tetrahedron Lett., 1982, **23**, 5413.

214. Kigoshi, H.; Ojika, M.; Shizuri, Y.; Niwa, H.; Yamada, K. Tetrahedron, 1986, **42**, 3789.

215. Aziz, M.; Rouessac, F. Tetrahedron Lett., 1987, **28**, 2579.

216. Aziz, M.; Rouessac, F. Tetrahedron, 1988, **44**, 101.

217. Mori, K.; Ueda, H. Tetrahedron, 1981, **37**, 2581.

218. Tius, M. A.; Fauq, A. J. Am. Chem. Soc., 1986, **108**, 6389.

219. Nicolaou, K. C.; Duggan, M. E.; Ladduwahetty, T. Tetrahedron Lett., 1984, **25**, 2069.

220. Millar, J. G.; Underhill, E. W. J. Org. Chem., 1986, **51**, 4726.

221. Williams, D. R.; Jass, P. A.; Tse, H.-L. A.; Gaston, R. D. J. Am. Chem. Soc., 1990, **112**, 4552.

222. Corey, L. D.; Singh, S. M.; Oehlschlager, A. C. Can. J. Chem., 1987, **65**, 1821.

223. Yadav, J. S.; Shekharam, T.; Gadgil, V. R. J. Chem. Soc., Chem.

Commun., 1990, 843.

224. Takano, S.; Samizu, K.; Sugihara, T.; Ogasawara, K. J. Chem. Soc., Chem. Commun., 1989, 1344.

225. Mhaskar, S. Y.; Lakshminarayana, G. Tetrahedron Lett., 1990, **31**, 7227.

226. Yadav, J. S.; Deshpande, P. K.; Sharma, G. V. M. Pure & Appl. Chem., 1990, **62**, 1333.

227. Yadav, J. S.; Deshpande, P. K.; Sharma, G. V. M. Tetrahedron, 1990, **46**, 7033.

228. Marshall, J. A.; Luke, G. P. Synlett, 1992, 1007.

229. Omura, K.; Swern, D. Tetrahedron, 1977, **33**, 1651.

230. Collins, J. C.; Hess, W. W.; Frank, F. J. Tetrahedron Lett., 1968, 3363.

231. Collins, J. C.; Hess, W. W. Org. Synth., 1972, **52**, 5.

232. Narasaka, K.; Morikawa, A.; Saigo, K.; Mukaiyama, T. Bull. Chem. Soc. Jpn., 1977, **50**, 2773.

233. Noyori, R. in *Organic Synthesis, Today and Tomorrow*, Trost, B. M.; Hutchinson, C. R., Eds., Pergamon Press, Oxford, 1980, pp. 273–284.

234. Marshall, J. A.; Trometer, J. D. Tetrahedron Lett., 1987, **28**, 4985.

235. Marshall, J. A.; Trometer, J. D.; Blough, B. E.; Crute, T. D. J. Org. Chem., 1988, **53**, 4274.

236. Marshall, J. A.; Blough, B. E. J. Org. Chem., 1991, **56**, 2225.

237. Marshall, J. A.; Trometer, J. D.; Blough, B. E.; Crute, T. D. Tetrahedron Lett., 1988, **29**, 913.

238. Marshall, J. A.; Trometer, J. D.; Cleary, D. G. Tetrahedron, 1989, **45**, 391.

239. Molander, G. A.; La Belle, B. E.; Hahn, G. J. Org. Chem., 1986, **51**, 5259.

240. Oshima, M.; Yamazaki, H.; Shimizu, I.; Nisar, M.; Tsuji, J. J. Am. Chem. Soc., 1989, **111**, 6280.

241. Trost, B. M.; Angle, S. R. J. Am. Chem. Soc., 1985, **107**, 6123.

242. Trost, B. M.; Lynch, J. K.; Angle, S. R. Tetrahedron Lett., 1987, **28**, 375.

243. Trost, B. M.; Sudhakar, A. R. J. Am. Chem. Soc., 1987, **109**, 3792.

244. Wershofen, S.; Scharf, H.-D. Synthesis, 1988, 854.

245. Molander G. A.; Shubert, D. C. J. Am. Chem. Soc., 1987, **109**, 576.

246. Okamoto, S.; Tsujiyama, H.; Yoshio, T.; Sato, F. Tetrahedron Lett., 1991, **32**, 5789.

247. Roush, W. R.; Straub, J. A.; VanNiuewenhze, M. S. J. Org. Chem., 1991, **56**, 1636.

248. Miyashita, M.; Suzuki, T.; Yoshikoshi, A. Tetrahedron Lett., 1987, **28**, 4293.

249. Miyashita, M.; Hoshino, H.; Yoshikoshi, A. Tetrahedron Lett., 1988, **29**, 347.

250. Molander, G. A.; Hahn, G. J. Org. Chem., 1986, **51**, 2596.

251. Molander, G. A.; Belle, B. E. L.; Hahn, G. J. Org. Chem., 1986, **51**, 5259.

252. Evans, D. A.; Williams, J. M. Tetrahedron Lett., 1988, **29**, 5065.

253. Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. J. Org. Chem., 1981, **46**, 3936.

254. Chong, J. M.; Sharpless, K. B. J. Org. Chem., 1985, **50**, 1560.

255. Roush, W. R; Blizzard, T. A. J. Org. Chem., 1984, **49**, 4332.

256. Thijs, L.; Stokkingreef, E. H. M.; Lemmens, J. M.; Zwanenburg, B. Tetrahedron, 1985, **41**, 2949.

257. Waanders, P. P.; Thijs, L.; Zwanenburg, B. Tetrahedron Lett., 1987, **28**, 2409.

258. Payne, G. B. J. Org. Chem., 1962, **27**, 3819.

259. Behrens, C. H.; Ko, S. Y.; Sharpless, K. B.; Walker, F. J. J. Org. Chem., 1985, **50**, 5687.

260. Wrobel, J. E.; Ganem, B. J. Org. Chem., 1983, **48**, 3761.

261. Behrens, C. H.; Sharpless, K. B. J. Org. Chem., 1985, **50**, 5696.

262. Takano, S.; Morimoto, M.; Ogasawara, K. Synthesis, 1984, 834.

263. Garner, P.; Park, J. M.; Rotello, V. Tetrahedron Lett., 1985, **26**, 3299.

264. Hatakeyama, S.; Sakurai, K.; Takano, S. J. Chem. Soc., Chem. Commun., 1985, 1759.

265. Hatakeyama, S.; Sakurai, K.; Takano, S. Tetrahedron Lett., 1986, **27**, 4485.

266. Hafele, B.; Schroter, D.; Jager, V. Angew. Chem., Int. Ed. Engl., 1986, **25**, 87.

267. Koppenhoefer, B.; Walser, M.; Schroter, D.; Hafele, B.; Jager, V. Tetrahedron, 1987, **43**, 2059.

268. Jager, V.; Hurnmer, W.; Stahl, U.; Gracza, T. Synthesis, 1991, 769.

269. Jager, V.; Schroter, D.; Koppenhoefer, B. Tetrahedron, 1991, **47**, 2195.

270. Babine, R. E. Tetrahedron Lett., 1986, **27**, 5791.

271. Askin, D.; Volante, R. P.; Remer, R. A.; Ryan, K. M.; Shinkai, I. Tetrahedron Lett., 1988, **29**, 277.

272. Hummer, W.; Gracza, T.; Jager, V. Tetrahedron Lett., 1989, **30**, 1517.

273. Schmidt, R. R.; Frische, K. Justus Liebigs Ann. Chem., 1988, 209.

274. Schreiber, S. L.; Schreiber, T. S.; Smith, D. B. J. Am. Chem. Soc., 1987, **109**, 1525.

275. Nakatsuka, M.; Ragan, J. A.; Sammakia, T.; Smith, D. B.; Uehling, D. E.; Schreiber, S. L. J. Am. Chem. Soc., 1990, **112**, 5583.

276. Kobayashi, Y.; Kato, N.; Shimazaki, T.; Sato, F. Tetrahedron Lett., 1988, **29**, 6297.

277. Schreiber, S. L.; Smith, D. B. J. Org. Chem., 1989, **54**, 9.

278. Schreiber, S. L.; Goulet, M. T.; Schulte, G. J. Am. Chem. Soc., 1987, **109**, 4718.

279. Nakatsuka, M.; Ragan, J. A.; Sammakia, T.; Smith, D. B.; Uehling, D. E.; Schreiber, S. L. J. Am. Chem. Soc., 1990, **112**, 5583.

280. Schreiber, S. L.; Goulet, M. T. J. Am. Chem. Soc., 1987, **109**, 8120.

281. Soulie, J.; Lampilas, M.; Lallemand, J. Y. Tetrahedron, 1987, **43**, 2701.

282. Palazon, J. M.; Anorbe, B.; Martin, V. S. Tetrahedron Lett., 1986, **27**, 4987.

283. Palazon, J. M.; Martin, V. S. Tetrahedron Lett., 1988, **29**, 681.

284. Page, P. C. B.; Rayner, C. M.; Sutherland, I. O. J. Chem. Soc., Chem. Commun., 1988, 356.

285. Page, P. C. B.; Rayner, C. M.; Sutherland, I. O. J. Chem. Soc., Perkin Trans. 1, 1990, 1375.

286. Soulie, J.; Ta, C.; Lallemand, J.-Y. Tetrahedron, 1992, **48**, 443.

287. Yamaguchi, M.; Hirao, I. J. Chem. Soc., Chem. Commun., 1984, 202.

288. Schneider, J. A.; Yoshihara, K. J. Org. Chem., 1986, **51**, 1077.

289. Sundararaman, P.; Barth, G.; Djerassi, C. J. Am. Chem. Soc., 1981, **103**, 5004.

290. Hanson, R. M. Tetrahedron Lett., 1984, **25**, 3783.

291. Tucker, H. J. Org. Chem., 1979, **44**, 2943.

292. Suzuki, T.; Saimoto, H.; Tomioka, H.; Oshima, K.; Nozaki, H. Tetrahedron Lett., 1982, **23**, 3597.

293. Roush, W. R.; Adam, M. A.; Peseckis, S. M. Tetrahedron Lett., 1983, **24**, 1377.

294. Herold, P.; Mohr, P.; Tamm, C. Helv. Chim. Acta, 1983, **66**, 744.

295. Ahn, K. H.; Kim, J. S.; Jin, C. S.; Kang, D. H.; Han, D. S.; Shin, Y. S.; Kim, D. H. Synlett, 1992, 306.

296. Maruoka, K.; Sano, H.; Yamamoto, H. Chem. Lett., 1985, 599.

297. Tung, R. D.; Rich, D. H. Tetrahedron Lett., 1987, **28**, 1139.

298. Uchiyama, H.; Kobayashi, Y,; Sato, F. Chem. Lett., 1985, 467.

299. Kobayashi, Y.; Kitano, Y.; Takeda, Y.; Sato, F. Tetrahedron, 1986, **42**, 2937.

300. Takano, S.; Yanase, M.; Sugihara, T.; Ogasawara, K. J. Chem. Soc., Chem. Commun., 1988, 1538.

301. Caron, M.; Sharpless, K. B. J. Org. Chem., 1985, **50**, 1557.

302. Canas, M.; Poch, M.; Verdaguer, X.; Moyano, A.; Pericas, M. A.; Riera, A. Tetrahedron Lett., 1991, **32**, 6931.

303. Dai, L.; Lou, B.; Zhang, Y.; Guo, G. Tetrahedron Lett., 1986, **27**, 4343.

304. Burgos, C. E.; Ayer, D. E.; Johnson, R. A. J. Org. Chem., 1987, **52**, 4973.

305. Gao. L.; Murai, A. Chem. Lett., 1989, 357.

306. Caron, M.; Carlier, P. R.; Sharpless, K. B. J. Org. Chem., 1988, **53**, 5185.

307. Alvarez, E.; Nunez, M. T.; Martin, V. S. J. Org. Chem., 1990, **55**, 3429.

308. Shimizu, M.; Yoshida, A.; Fujisawa, T. Synlett, 1992, 204.

309. Bovicelli, P.; Lupattelli, P.; Bersani, M. T. Tetrahedron Lett., 1992, **33**, 6181.

310. Choudary, B. M.; Rani, S. S.; Kantam, M. L. Synth. Commun., 1990, **20**, 2313.

311. Bonini, C.; Giuliano, C.; Righi, G.; Rossi, L. Tetrahedron Lett., 1992, **33**, 7429.

312. Morgan, Jr., D. J.; Sharpless, K. B.; Traynor, S. G. J. Am. Chem. Soc., 1981, **103**, 462.

313. Denis, J. N.; Greene, A. E.; Serra, A. A.; Luche, M.-J. J. Org. Chem., 1986, **51**, 46.

314. Onaka, M.; Sugita, K.; Izumi, Y. Chem. Lett., 1986, 1327.

315. Onaka, M.; Sugita, K.; Takeuchi, H.; Izumi, Y. J. Chem. Soc., Chem. Commun., 1988, 1173.

316. Onaka, M.; Sugita, K.; Izumi, Y. J. Org. Chem., 1989, **54**, 1116.

317. Bonini, C.; Righi, G.; Sotgiu, G. J. Org. Chem., 1991, **56**, 6206.

318. Bonini, C.; Righi, G. Tetrahedron, 1992, **48**, 1531.

319. Roush, W. R.; Brown, R. J. J. Org. Chem., 1982, **47**, 1371.

320. Roush, W. R.; Brown, R. J.; DiMare, M. J. Org. Chem., 1983, **48**, 5083.

321. Roush, W. R.; Adam, M. A. J. Org. Chem., 1985, **50**, 3752.

322. Paterson, I.; Cumming, J. Tetrahedron Lett., 1992, **33**, 2847.

323. Kocovsky, P. Tetrahedron Lett., 1986, **27**, 5521.

324. Roush, W. R.; Hagadorn, S. M. Carbohydr. Res., 1985, **136**, 187.

325. Myers, A. G.; Widdowson, K. L. Tetrahedron Lett., 1988, **29**, 6389.

326. Myers, A. G.; Proteau, P. J.; Handel, T. M. J. Am. Chem. Soc., 1988, **110**, 7212.

327. McCombie, S. W.; Metz, W. A. Tetrahedron Lett., 1987, **28**, 383.

328. Uenishi, J.; Motoyama, M.; Nishiyama, Y.; Wakabayashi, S. J. Chem. Soc., Chem. Commun., 1991, 1421.

329. McCombie, S. W.; Nagabhushan, T. L. Tetrahedron Lett., 1987, **28**, 5395.

330. Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Viti, S. M. J. Org. Chem., 1982, **47**, 1378.

331. Viti, S. M. Tetrahedron Lett., 1982, **23**, 4541.

332. Honda, M.; Katsuki, T.; Yamaguchi, M. Tetrahedron Lett., 1984, **25**, 3857.

333. Gao, Y.; Sharpless, K. B. J. Org. Chem., 1988, **53**, 4081.

334. Johnson, M. R.; Nakata, T.; Kishi, Y. Tetrahedron Lett., 1979, 4343.

335. Chong, J. M.; Cyr, D. R.; Mar, E. K. Tetrahedron Lett., 1987, **28**, 5009.

336. Lipshutz, B. H.; Kotsuki, H.; Lew, W. Tetrahedron Lett., 1986, **27**, 4825.

337. Tius, M. A.; Fauq, A. H. J. Org. Chem., 1983, **48**, 4131.

338. Maruoka, K.; Hasegawa, M.; Yamamoto, H.; Suzuki, K.; Shimazaki, M.; Tsuchihashi, G. J. Am. Chem. Soc., 1986, **108**, 3827.

339. Suzuki, K.; Miyazawa, M.; Shimazaki, M.; Tsuchihashi, G. Tetrahedron Lett., 1986, **27**, 6237.

340. Maruoka, K.; Ooi, T.; Nagahara, S.; Yamamoto, H. Tetrahedron, 1991, **47**, 6983.

341. Maruoka, K.; Sato, J.; Yamamoto, H. Tetrahedron, 1992, **48**, 3749.

342. Maruoka, K.; Sato, K.; Yamamoto, H. J. Am. Chem. Soc., 1991, **113**, 5449.

343. Maruoka, K.; Ooi, T.; Yamamoto, H. J. Am. Chem. Soc., 1989, **111**, 6431.

344. Baldwin, J. E. J. Chem. Soc., Chem. Commun., 1976, 734.

345. Stork, G.; Cama, L. D.; Coulson, D. R. J. Am. Chem. Soc., 1974, **96**, 5268.

346. Nunez, M. T.; Rodriguez, M. L.; Martin, V. S. Tetrahedron Lett., 1988, **29**, 1979.

347. Evans, D. A.; Bender, S. L.; Morris, J. J. Am. Chem. Soc., 1988, **110**, 2506.

348. Reed, III, L. A.; Ito, Y.; Masamune, S.; Sharpless, K. B. J. Am. Chem. Soc., 1982, **104**, 6468.

349. Nicolaou, K. C.; Prasad, C. V. C.; Somers, P. K.; Hwang, C.-K. J. Am. Chem. Soc., 1989, **111**, 5330.

350. Nicolaou, K. C.; Prasad, C. V. C.; Somers, P. K.; Hwang, C.-K. J. Am. Chem. Soc., 1989, **111**, 5335.

351. McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. Tetrahedron Lett., 1985, **26**, 6301.

352. Pelter, A.; Ward, R. S.; Little, G. M. J. Chem. Soc., Perkin Trans. 1, 1990, 2775.

353. McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. Tetrahedron Lett., 1989, **30**, 7029.

354. Suzuki, M.; Morita, Y.; Yanagisawa, A.; Noyori, R. J. Am. Chem. Soc., 1986, **108**, 5021.

355. Suzuki, M.; Morita, Y.; Yanagisawa, A.; Baker, B. J.; Scheuer, P. J.; Noyori, R. J. Org. Chem., 1988, **53**, 286.

356. McIntosh, J. M.; Matassa, L. C. J. Org. Chem., 1988, **53**, 4452.

357. Tanis, S. P.; Chuang, Y.-H.; Head, D. B. J. Org. Chem., 1988, **53**, 4929.

358. Medina, J. C.; Kyler, K. S. J. Am. Chem. Soc., 1988, **110**, 4818.

359. White, J. D.; Jensen, M. S. J. Am. Chem. Soc., 1993, **115**, 2970.

360. Gao, Y.; Sharpless, K. B. J. Org. Chem., 1988, **53**, 4114.

361. Tanner, D.; Somfai, P. Tetrahedron Lett., 1987, **28**, 1211.

362. Tanner, D.; Somfai, P. Tetrahedron, 1988, **44**, 619.

363. Pickenhagen, W.; Bronner-Schindler, H. Helv. Chim. Acta, 1984, **67**, 947.

364. Ewins, R. C.; Henbest, H. B.; McKervey, M. A. J. Chem. Soc., Chem. Commun., 1967, 1085.

365. Montanari, F.; Moretti, I.; Torre, G. J. Chem. Soc., Chem. Commun., 1969, 135.

366. Pirkle, W. H.; Rinaldi, P. L. J. Org. Chem., 1977, **42**, 2080.

367. Rebek, Jr., J.; McCready, R. J. Am. Chem. Soc., 1980, **102**, 5602.

368. Curci, R.; Fiorentino, M.; Serio, M. R. J. Chem. Soc., Chem. Commun., 1984, 155.

369. Davis, F. A.; Chattopadhyay, S. Tetrahedron Lett., 1986, **27**, 5079.

370. Davis, F. A.; Sheppard, A. C. Tetrahedron, 1989, **45**, 5703.

371. Davis, F. A.; Harakal, M. E.; Awad, S. B. J. Am. Chem. Soc., 1983, **105**, 3123.

372. Julia, S.; Guixer, J.; Masana, J.; Rocas, J. J. Chem. Soc., Perkin Trans. 1, 1982, 1317.

373. Julia, S.; Masana, J.; Vega, J. C. Angew. Chem., Int. Ed. Engl., 1980, **19**, 929.

374. Banfi, S.; Colonna, S.; Molinari, H.; Julia, S.; Guixer, J. Tetrahedron, 1984, **40**, 5207.

375. Baures, P. W.; Eggleston, D. S.; Flisak, J. R.; Gombatz, K.; Lantos, I.; Mendelson, W.; Remich, J. J. Tetrahedron Lett., 1990, **31**, 6501.

376. Wynberg, H.; Greijdanus, B. J. Chem. Soc., Chem. Commun., 1978, 427.

377. Sheng, M. N.; Zajacek, J. G. J. Org. Chem., 1970, **35**, 1839.

378. Sharpless K. B.; Michaelson, R. C. J. Am. Chem. Soc., 1973, **95**, 6136.

379. Mihelich, E. D. Tetrahedron Lett., 1979, 4729.

380. Yamada, S.; Mashiko, M.; Terashima, S. J. Am. Chem. Soc., 1977, **99**, 1988.

381. Michaelson, R. C; Palermo, R. E.; Sharpless, K. B. J. Am. Chem. Soc., 1977, **99**, 1990.

382. Takai, K.; Oshima, K.; Nozaki, H. Tetrahedron Lett., 1980, **21**, 1657.

383. Takai, K.; Oshima, K.; Nozaki, H. Bull. Chem. Soc. Jpn., 1983, **56**, 3791.

384. Kagan, H. B.; Mimoun, H.; Mark, C.; Shurig, V. Angew. Chem., Int. Ed. Engl., 1979, **18**, 485.

385. Tani, K.; Hanafusa, M.; Otsuka, S. Tetrahedron Lett., 1979, 3017.

386. Groves, J. T.; Myers, R. S. J. Am. Chem. Soc., 1983, **105**, 5791.

387. Groves, J. T.; Viski, P. J. Org. Chem., 1990, **55**, 3628.

388. Mansuy, D.; Battioni, P.; Renaud, J.-P.; Guerin, P. J. Chem. Soc., Chem. Commun., 1985, 155.

389. Naruta, Y.; Tani, F.; Ishihara, N.; Maruyama, K. J. Am. Chem. Soc., 1991, **113**, 6865.

390. Konishi, K.; Oda, K.; Nishida, K.; Aida, T.; Inoue, S. J. Am. Chem. Soc., 1992, **114**, 1313.

391. Collman, J. P.; Lee, V. J.; Zhang, X.; Ibers, J. A.; Brauman, J. I. J. Am. Chem. Soc., 1993, **115**, 3834.

392. Kaku, Y.; Otsuka, M.; Ohno, M. Chem. Lett., 1989, 611.

393. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. J. Am. Chem. Soc., 1990, **112**, 2801.

394. Jacobsen, E. N.; Zhang, W.; Guller, M. L. J. Am. Chem. Soc., 1991, **113**, 6703.

395. Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. J. Am. Chem. Soc., 1991, **113**, 7063.

396. Lee, N. H.; Jacobsen, E. N. Tetrahedron Lett., 1991, **32**, 6533.

397. Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. Tetrahedron Lett., 1990, **31**, 7345,

398. Irie, R.; Noda, K.; Ito, Y.; Katsuki, T. Tetrahedron Lett., 1991, **32**, 1055.

399. Irie, R.; Ito, Y.; Katsuki, T. Synlett, 1991, **2**, 265,

400. Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. Tetrahedron Asymmetry, 1991, **2**, 481.

401. Hatayama, A.; Hosoya, N.; Irie, R.; Ito, Y.; Katsuki, T. Synlett, 1992, 407.

402. Hosoya, N.; Irie, R.; Katsuiki, T. Synlett, 1993, 261.

403. Sasaki, H.; Irie, R.; Katsuki, T. Synlett, 1993, 300.

404. Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. J. Org. Chem., 1992, **57**, 2768.

405. Keinan, E.; Sinha, S. C.; Sinha-Bagchi, A.; Wang, Z.-M.; Zhang, X.-L.; Sharpless, K. B. Tetrahedron Lett., 1992, **33**, 6411.

406. Kolb, H. C.; Sharpless, K. B. Tetrahedron 1992, **48**, 10515.

407. Hill, J. G.; Rossiter, B. E.; Sharpless, K. B. J. Org. Chem., 1983, **48**, 3607.

408. Bessodes, M.; Abushanab, E.; Antonakis, K. Tetrahedron Lett. 1984, **25**, 5899.

409. Meister, C.; Scharf, H.-D. Justus Liebigs Ann. Chem., 1983, 913.

410. Ko, S. Y. Ph. D Dissertation, Massachusetts Institute of Technology,

1986.

411. Erickson, T. J. J. Org. Chem., 1986, **51**, 934.

412. Marshall, J. A.; Audia, V. H. J. Org. Chem., 1987, **52**, 1106.

413. Kusakabe, M.; Kitano, Y.; Kobayashi, Y.; Sato, F. J. Org. Chem., 1989, **54**, 2085.

414. Camberlin, A. R.; Dezube, M.; Reich, S. H.; Sall, D. J. J. Am. Chem. Soc., 1989, **111**, 6247.

415. Walba, D. M.; Razavi, H. A.; Clark. N. A.; Parmar, D. S. J. Am. Chem. Soc., 1988, **110**, 8686.

416. Sharpless, K. B.; Martin, V. S. The Scripps Research Institute, La Jolla, CA, unpublished results.

417. Katsuki, T. Tetrahedron Lett., 1984, 25. 2821.

418. Yoshida, J.; Maekawa, T.; Morita, Y.; Isoe, S. J. Org. Chem., 1992, **57**, 1321.

419. Kobayashi, Y.; Ito, T.; Yamakawa, I.; Urabe, H.; Sato, F. Synlett, 1991, 811.

420. Gilloir, F.; Malacria, M. Tetrahedron Lett., 1992, **33**, 3859.

421. Muchowski, J. M.; Naef, R.; Maddox, M. L. Tetrahedron Lett., 1985, **26**, 5375.

422. Schwab, J. M.; Ray, T.; Ho, C.-K. J. Am. Chem. Soc., 1989, **111**, 1057.

423. Dung, J.-S.; Armstrong, R. W.; Anderson, O. P.; Williams, R. M. J. Org. Chem., 1983, **48**, 3592.

424. Scherkenbeck, J.; Barth, M.; Thiel, U.; Metten, K.-H.; Heinemann, F.; Welzel, P. Tetrahedron, 1988, **44**, 6325.

425. Meister, C.; Scharf, H. D. Justus Liebigs Ann. Chem., 1983, 913.

426. Lipshutz, B. H.; Sharma, S.; Dimock, S. H.; Behling, J. R. Synthesis, 1992, 191.

427. Hosokawa, T.; Makabe, Y.; Shinohara, T.; Murahashi, S. Chem. Lett., 1985, 1529.

428. Wershofen, S.; Claben, A.; Scharf, H.-D. Justus Liebigs Ann. Chem., 1989, 9.

429. Shimazaki, M.; Hara, H.; Suzuki, K.; Tsuchihashi, G. Tetrahedron Lett., 1987, **28**, 5891.

430. Hubscher, J.; Barner, R. Helv. Chim. Acta, 1990, **73**, 1068.

431. Hill, R. K.; Prakash, S. R. J. Am. Chem. Soc., 1984, **106**, 795.

432. White, J. D.; Theramongkol, P.; Kuroda, C.; Engebrecht, J. R. J. Org. Chem., 1988, **53**, 5909.

433. Baker, R.; Cummings, W. J.; Hayes, J. F.; and Kumar, A. J. Chem. Soc., Chem. Commun., 1986, 1237.

434. Kobayashi, Y.; Kitano, Y.; Sato, F. J. Chem. Soc., Chem. Commun., 1984, 1329.

435. Kuroda, C.; Theramongkol, P.; Engebrecht, J. R.; White, J. D. J. Org. Chem., 1986, **51**, 956.

436. Gani, D.; O'Hagan, D.; Reynolds, K.; Robinson, J. A. J. Chem. Soc., Chem. Commun., 1985, 1002.

437. Reynolds, K. A.; O'Hagan, D.; Gani, D.; Robinson, J. A. J. Chem. Soc., Perkin Trans. 1, 1988, 3195.

438. Martin, V. S.; Nunez, M. T.; Tonn, C. E. Tetrahedron Lett., 1988, **29**, 2701.

439. Pickard, S. T.; Smith, H. E.; Polavarapu, P. L.; Black, T. M.; Rauk, A.; Yang, D. J. Am. Chem. Soc., 1992, **114**, 6850.

440. Takano, S.; Sugihara, T.; Samizu, K.; Akiyama, M.; Ogasawara, K. Chem. Lett., 1989, 1781.

441. Suzuki, K.; Miyazawa, M.; Shimazaki, M.; Tsuchihashi, G. Tetrahedron, 1988, **44**, 4061.

442. Takano, S.; Kasahara, C.; Ogasawara, K. Chem. Lett., 1983, 175.

443. Yabe, Y.; Guillaume, D.; Rich, D. H. J. Am. Chem. Soc., 1988, **110**, 4043.

444. Shibuya, H.; Kawashima, K.: Ikeda, M.; Kitagawa, I. Tetrahedron Lett., 1989, **30**, 7205.

445. Clark, R. D.; Kurz, J. Heterocycles, 1985, **23**, 2005.

446. Nikam, S. S.; Martin, A. R.; Nelson, D. L. J. Med. Chem., 1988, **31**, 1965.

447. Hughes, P.; Clardy, J. J. Org. Chem., 1989, **54**, 3260.

448. Izawa, T.; Wang, Z.-q.; Nishimura, Y.; Kondo, S.; Umezawa, H. Chem. Lett., 1987, 1655.

449. Clayden, J.; Collington, E. W.; Warren, S. Tetrahedron Lett., 1992, **33**, 7043.

450. Dunigan, J.; Weigel, L. O. J. Org. Chem., 1991, **56**, 6225.

451. Tius, M. A.; Fauq, A. H. J. Am. Chem. Soc., 1986, **108**, 1035.

452. Grandjean, D.; Pale, P.; Chuche, J. Tetrahedron Lett., 1991, **32**, 3043.

453. Bonini, C.; Fabio, R. D. Tetrahedron Lett., 1988, **29**, 815.

454. Rodriguez, E. B.; Scally, G. D.; Stick, R. V. Aust. J. Chem., 1990, **43**, 1391.

455. Kuehne, M. E.; Matson, P. A.; Bornmann, W. G. J. Org. Chem., 1991, **56**, 513.

456. Magnus, P.; Mendoza, J. S. Tetrahedron Lett., 1992, **33**, 899.

457. Magnus, P.; Mendoza, J. S.; Stamford, A.; Ladlow, M.; Willis, P. J. Am. Chem. Soc., 1992, **114**, 10232.

458. Hirai, Y.; Chintani, M.; Yamazaki, T.; Momose, T. Chem. Lett., 1989,

1449.

459. Diez-Martin, D.; Kotecha, N. R.; Ley, S. V.; Mantegani, S.; Menendez, J. C.; Organ, H. M.; White, A. D.; Banks, B. J. Tetrahedron, 1992, **48**, 7899.

460. Nicolaou, K. C.; Ahn, K. H. Tetrahedron Lett., 1989, **30**, 1217.

461. Kotecha, N. R.; Ley, S. V.; Mantegani, S. Synlett, 1992, 395.

462. Kozikowski, A. P.; Stein, P. D. J. Org. Chem., 1984, **49**, 2301.

463. Schmidt, U.; Mundinger, K.; Mangold, R.; Lieberknecht, A. J. Chem. Soc., Chem. Commun., 1990, 1216.

464. Vaccaro, H. A.; Levy, D. E.; Sawabe, A.; Jaetsch, T.; Masamune, S. Tetrahedron Lett., 1992, **33**, 1937.

465. Ramaswamy, S.; Prasad, K.; Repic, O. J. Org. Chem., 1992, **57**, 6344.

466. White, J. D.; Bolton, G. L. J. Am. Chem. Soc., 1990, **112**, 1626.

467. Jung, M. E.; Gardiner, J. M. J. Org. Chem., 1991, **56**, 2614.

468. Hager, M. W.; Liotta, D. C. J. Am. Chem. Soc., 1991, **113**, 5117.

469. Baker, R.; Head, J. C.; Swain, C. J. J. Chem. Soc., Perkin Trans. 1, 1988, 85.

470. Szurdoki, F.; Novak, L.; Baitz-Gacs, E.; Szantay, C. Acta Chim. Hungarica-Models Chem., 1992, **129**, 303.

471. Rao, A. V. R.; Sharma, G. V. M.; Bhanu, M. M. Tetrahedron Lett., 1992, **33**, 3907.

472. Takano, S.; Sugihara, T.; Ogasawara, K. Tetrahedron Lett., 1991, **32**, 2797.

473. Still, W. C.; Ohmizu, H. J. Org. Chem., 1981, **46**, 5242.

474. Suga, T.; Ohta, S.; Ohmoto, T. J. Chem. Soc., Perkin Trans. 1, 1987, 2845.

475. Smith, III, A. B.; Sunazuka, T.; Leenay, T. L.; Kingery-Wood, J. J. Am. Chem. Soc., 1990, **112**, 8197.

476. Smith, III, A. B.; Kingery-Wood, J.; Leenay, T. L.; Nolen, E. G.; Sunazuka, T. J. Am. Chem. Soc., 1992, **114**, 1438.

477. Yamada, S.; Shiraishi, M.; Ohmori, M.; Takayama, H. Tetrahedron Lett., 1984, **25**, 3347.

478. Mori. K.; Ebata, T.; Takechi, S. Tetrahedron, 1984, **40**, 1761.

479. Brunner, H.; Sicheneder, A. Angew. Chem., Int. Ed. Engl., 1988, **27**, 718.

480. Mulzer, J.; Lammer, O. Chem. Ber., 1986, **119**, 2178.

481. Rayner, C. M.; Westwell, A. D. Tetrahedron Lett., 1992, **33**, 2409.

482. Rayner, C. M.; Sin, M. S.; Westwell, A. D. Tetrahedron Lett., 1992, **33**, 7237.

483. Gorthey, L. A.; Vairamani, M.; Djerassi, C. J. Org. Chem., 1984, **49**, 1511.

484. Nakagawa, N.; Mori, K. Agric. Biol. Chem., 1984, **48**, 2505.

485. Caldwell, C. G.; Bondy, S. S. Synthesis, 1990, 34.

486. Honda, M.; Komori, T. Tetrahedron Lett., 1986, **27**, 3369.

487. Baker, R.; Swain, C. J.; Head, J. C. J. Chem. Soc., Chem. Commun., 1985, 309.

488. Martin, V. S.; Nunez, M. T.; Ramirez, M. A.; Soler, M. A. Tetrahedron Lett., 1990, **31**, 763.

489. Kiefel, M. J.; Maddock, J.; Pattenden, G. Tetrahedron Lett., 1992, **33**, 3227.

490. Nicolaou, K. C.; Prasad, C. V. C.; Hwang, C.-K.; Duggan, M. E.; Veale, C. A. J. Am. Chem. Soc., 1989, **111**, 5321.

491. Stork, G.; Kobayashi, Y.; Suzuki, T.; Zhao, K. J. Am. Chem. Soc., 1990, **112**, 1661.

492. Sakaki, J.; Sugita, Y.; Sato, M.; Kaneko, C. J. Chem. Soc., Chem. Commun., 1991, 434.

493. Sugita, Y.; Sakaki, J.; Sato, M.; Kaneko, C. J. Chem. Soc., Perkin Trans. 1, 1992, 2855.

494. Tanner, D.; Somfai, P. Tetrahedron Lett., 1988, **29**, 2373.

495. Masamune, S.; Ma, P.; Okumoto, H.; Ellingboe, J. W.; Ito, Y. J. Org. Chem., 1984, **49**, 2834.

496. Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. J. Am. Chem. Soc., 1986, **108**, 3422.

497. Ireland, R. E.; Thaisrivongs, S.; Dussault, P. H. J. Am. Chem. Soc., 1988, **110**, 5768.

498. Barrett, A. G. M.; Edmunds, J. J.; Horita, K.; Parkinson, C. J. J. Chem. Soc., Chem. Commun., 1992, 1236.

499. Marshall, J. A.; Yashunsky, D. V. J. Org. Chem., 1991, **56**, 5493.

500. Lampilas, M.; Lett, R. Tetrahedron Lett., 1992, **33**, 773.

501. Iida, H.; Yamazaki, N.; Kibayashi, C. J. Org. Chem., 1987, **52**, 3337.

502. Baldwin, J. E.; Flinn, A. Tetrahedron Lett., 1987, **28**, 3605.

503. Suzuki, T.; Sato, O.; Hirama, M.; Yamamoto, Y.; Murata, M.; Yasumoto, T.; Harada, N. Tetrahedron Lett., 1991, **32**, 4505.

504. Colvin, E. W.; Robertson, A. D.; Wakharkar, S. J. Chem. Soc., Chem. Commun., 1983, 312.

505. Sturmer, R. Justus Liebigs Ann. Chem., 1991, 311.

506. Shimizu, I.; Hayashi, K.; Ide, N.; Oshima, M. Tetrahedron, 1991, **47**, 2991.

507. Shimizu, I.; Hayashi, K.; Oshima, M. Tetrahedron Lett., 1990, **31**, 4757.

508. Boeckman, Jr., R. K.; Pruitt, J. R. J. Am. Chem. Soc., 1989, **111**, 8286.

509. Sandararaman, P.; Barth, G.; Djerassi, C. J. Am. Chem. Soc., 1981, **103**,

5004.

510. Boschetti, A.; Panza, L.; Ronchetti, F.; Russo, G.; Toma, L. J. Chem. Soc., Perkin Trans. 1, 1988, 3353.

511. Raifeld, Y. E.; Vid, G. Y.; Mikerin, I. E.; Arshava, B. M.; Nikitenko, A. A. Carbohydr. Res., 1992, **224**, 103.

512. Marshall, J. A.; Crute III, T. D.; Hsi, J. D. J. Org. Chem., 1992, **57**, 115.

513. Schmidt, U.; Respondek, M.; Lieberknecht, A.; Werner, J.; Fischer, P. Synthesis, 1989, 256.

514. Ohta, S.; Nakai, A.; Aoki, T.; Suga, T. J. Sci. Hiroshima Univ., Ser. S: Phys. Chem., 1989, 49.

515. Bonadies, F.; Rossi, G.; Bonini, C. Tetrahedron Lett., 1984, **25**, 5431.

516. Yadav, J. S.; Reddy, P. S.; Jolly, R. S. Indian J. Chem., 1986, **25B**, 294.

517. Wood, J. L.; Jones, D. R.; Hirschmann, R.; Smith, III, A. B. Tetrahedron Lett., 1990, **31**, 6329.

518. Aebi, J. D.; Deyo, D. T.; Sun, C. Q.; Guillaume, D.; Dunlap, B.; Rich, D. H. J. Med. Chem., 1990, **33**, 999.

519. Hirai, Y.; Terada, T.; Amemiya, Y.; Momose, T. Tetrahedron Lett., 1992, **33**, 7893.

520. Masamune, S. Pure & Appl. Chem., 1988, **60**, 1587.

521. Blanchette, M. A.; Malamas, M. S.; Nantz, M. H.; Roberts, J. C.; Somfai, P.; Whritenour, D. C.; Masamune, S.; Kageyama, M.; Tamura, T. J. Org. Chem., 1989, **54**, 2817.

522. Hanessian, S.; Ugolini, A.; Hodges, P. J.; Beaulieu, P.; Dube, D.; Andre, C. Pure & Appl. Chem., 1987, **59**, 299.

523. Hanessian, S.; Ugolini, A.; Dube, D.; Hodges, P. J.; Andre, C. J. Am. Chem. Soc., 1986, **108**, 2776.

524. Dommerholt, F. J.; Thijs, L.; Zwanenburg, B. Tetrahedron Lett., 1991, **32**, 1499.

525. Dommerholt, F. J.; Thijs, L.; Zwanenburg, B. Tetrahedron Lett., 1991, **32**, 1495.

526. Marshall, J. A.; Sedrani, R. J. Org. Chem., 1991, **56**, 5496.

527. Boeckmann, Jr., R. K.; Barta, T. E.; Nelson, S. G. Tetrahedron Lett., 1991, **32**, 4091.

528. Brimacombe, J. S.; Kabir, K. M. Carbohydr. Res., 1986, **152**, 329.

529. Herunsalee, A.; Isobe, M.; Pikul, S.; Goto, T. Synlett, 1991, 199.

530. Takahashi, T.; Miyazawa, M.; Ueno, H.; Tsuji, J. Tetrahedron Lett., 1986, **27**, 3881.

531. Iimori, T., Still, W. C.; Rheingold, A. L.; Staley, D. L. J. Am. Chem. Soc., 1989, **111**, 3439.

532. Nicolaou, K. C.; Veale, C. A.; Webber, S. E.; Katerinopoulos, H. J. Am.

Chem. Soc., 1985, **107**, 7515.

533. Spada, M. R.; Ubukata, M.; Isono, K. Heterocycles, 1992, **34**, 1147.

534. Hamon, D. P. G.; Massy-Westropp, R. A.; Newton, J. L. Tetrahedron: Asymmetry, 1990, **1**, 771.

535. Tanner, D.; He, H. M.; Bergdahl, M. Tetrahedron Lett., 1988, **29**, 6493.

536. Tanner, D.; He, H. M. Tetrahedron, 1989, **45**, 4309.

537. Myers, A. G.; Harrington, P. M.; Kuo, E. Y. J. Am. Chem. Soc., 1991, **113**, 694.

538. Takeda, Y.; Matsumoto, T.; Sato, F. J. Org. Chem., 1986, **51**, 4728.

539. Marshall, J. A.; Blough, B. E. J. Org. Chem., 1990, **55**, 1540.

540. Diez-Martin, D.; Kotecha, N. R.; Ley, S. V.; Menendez, J. C. Synlett, 1992, 399.

541. Yadav, J. S.; Joshi, B. V.; Sahasrabudhe, A. B. Synth. Commun., 1985, **15**, 797.

542. Boeckman, Jr., R. K.; Tagat, J. R.; Johnston, B. H. Heterocycles, 1987, **25**, 33.

543. Maruoka, K.; Saito, S.; Ooi, T.; Yamamoto, H. Synlett, 1991, 579.

544. Yadav, J. S.; Deshpande, P. K.; Sharma, G. V. M. Tetrahedron, 1992, **48**, 4465.

545. Gurjar, M. K.; Reddy, A. S. Tetrahedron Lett., 1990, **31**, 1783.

546. Neumann, C.; Boland, W. Helv. Chim. Acta, 1990, **73**, 754.

547. Lambs, L.; Singh, N. P.; Biellmann, J.-F. J. Org. Chem., 1992, **57**, 6301.

548. Lambs, L.; Singh, N. P.; Biellmann, J.-F. Tetrahedron Lett., 1991, **32**, 2637.

549. Tonn, C. E.; Palazon, J. M.; Ruiz-Perez, C.; Rodriguez, M. L.; Martin, V. S. Tetrahedron Lett., 1988, **29**, 3149.

550. Bessodes, M.; Komiotis, D.; Antonakis, K. J. Chem. Soc., Perkin Trans. 1, 1989, 41.

551. Valverde, S.; Herradon, B.; Rabanal, R. M.; Martin-Lomas, M. Can. J. Chem., 1987, **65**, 339.

552. Komiotis, D.; Bessodes, M.; Antonakis, K. Carbohydr. Res., 1989, **190**, 153.

553. Millar, J. G.; Giblin, M.; Barton, D.; Underhill, E. W. J. Chem. Ecol., 1991, **17**, 911.

554. Nicolaou, K. C.; Webber, S. E. Synthesis, 1986, 453.

555. Nicolaou, K. C.; Webber, S. E. J. Chem. Soc., Chem. Commun., 1985, 297.

556. Barchi, Jr. J. J.; Moore, R. E.; Patterson, G. M. L. J. Am. Chem. Soc. 1984, **106**, 8193.

557. Valverde, S.; Herradon, B.; Rabanal, R. M.; Martin-Lomas, M. Can. J. Chem., 1987, **65**, 332.

558. Valverde, S.; Martin-Lomas, M.; Herradon, B. J. Carbohydr. Chem., 1987, **6**, 685.

559. Niwa, H.; Miyachi, Y.; Uosaki, Y.; Yamada, K. Tetrahedron Lett., 1986, **27**, 4601.

560. Niwa, H.; Miyachi, Y.; Okamoto, O.; Uosaki, Y.; Kuroda, A.; Ishikawa, H.; Yamada, K. Tetrahedron, 1992, **48**, 393.

561. Johnston, B. D.; Oehlschlager, A. C. Can. J. Chem., 1984, **62**, 2148.

562. Lee, A. W. M. J. Chem. Soc., Chem. Commun., 1984, 578.

563. Diez-Martin, D.; Grice, P.; Kolb, H. C.; Ley, S. V.; Madin, A. Synlett, 1990, 326.

564. Ley, S. V.; Armstrong, A.; Diez-Martin, D.; Ford, M. J.; Grice, P.; Knight, J. G.; Kolb, H. C.; Madin, A.; Marby, C. A.; Mukherjee, S.; Shaw, A. N.; Slawin, A. M. Z.; Vile, S.; White, A. D.; Williams, D. J.; Woods, M. J. Chem. Soc., Perkin Trans. 1, 1991, 667.

565. Hatakeyama, S.; Matsui, Y.; Suzuki, M.; Sakurai, K.; Takano, S. Tetrahedron Lett., 1985, **26**, 6485.

566. Sabol, J. S.; Cregge, R. J. Tetrahedron Lett., 1990, **31**, 27.

567. Hedtmann, U.; Hobert, K.; Klintz, R.; Welzel, P.; Frelek, J.; Strangmann-Diekmann, M. Angew. Chem., Int. Ed. Engl., 1989, **28**, 1515.

568. Bessodes, M.; Egron, M.-J.; Antonakis, K. J. Chem. Soc., Perkin Trans. 1, 1989, 2099.

569. Otera, J.; Niibo, Y.; Nozaki, H. Tetrahedron, 1991, **47**, 7625.

570. Crilley, M. M. L.; Edmunds, A. J. F.; Eistetter, K.; Golding, B. T. Tetrahedron Lett., 1989, **30**, 885.

571. Burke, S. D.; Cobb, J. E.; Takeuchi, K. J. Org. Chem., 1990, **55**, 2138.

572. Burke, S. D.; Cobb, J. E.; Takeuchi, K. J. Org. Chem., 1985, **50**, 3420.

573. Nishikimi, Y.; Iimori, T.; Sodeoka, M.; Shibasaki, M. J. Org. Chem., 1989, **54**, 3354.

574. Kitching, W.; Lewis, J. A.; Perkins, M. V.; Drew, R.; Moore, C. J.; Schurig, V.; Konig, W. A.; Francke, W. J. Org. Chem., 1989, **54**, 3893.

575. Page, P. C. B.; Rayner, C. M.; Sutherland, I. O. J. Chem. Soc., Chem. Commun., 1986, 1408.

576. Page, P. C. B.; Rayner, C. M.; Sutherland, I. O. J. Chem. Soc., Perkin Trans. 1, 1990, 1615

577. Baker, S. R.; Boot, J. R.; Morgan, S. E. Tetrahedron Lett., 1983, **24**, 4469.

578. Kabat, M. M.; Lange, M.; Wovklich, P. M.; Uskokovic, M. R. ibid., 1992, **33**, 7701.

579. Hatakeyama, S.; Osanai, K.; Numata, H.; Takao, S. Tetrahedron Lett.,

1989, **30**, 4845.

580. Evans, D. A.; Gauchet-Prunet, J. A.; Carreira, E. M.; Charette, A. B. J. Org. Chem., 1991, **56**, 741.

581. Rao, A. V. R.; Dhar, T. G. M.; Bose, D. S.; Chakraborty, T. K.; Gurjar, M. K. Tetrahedron, 1989, **45**, 7361.

582. Rao, A. V. R.; Bose, D. S.; Gurjar, M. K.; Ravindranathan, T. Tetrahedron, 1989, **45**, 7031.

583. Rao, A. V. R.; Dhar, T. G. M.; Chakraborty, T. K.; Gurjar, M. K. Tetrahedron Lett., 1988, **29**, 2069.

584. Genet, J. P.; Durand, J. O.; Savignac, M.; Pons, D. Tetrahedron Lett., 1992, **33**, 2497.

585. Hori, K.; Hikage, N.; Inagaki, A.; Mori, S.; Nomura, K.; Yoshii, E. J. Org. Chem., 1992, **57**, 2888.

586. Masamune, S.; Kaiho, T.; Garvey, D. S. J. Am. Chem. Soc., 1982, **104**, 5521.

587. Hatakeyama, S.; Sugawara, K.; Kawamura, M.; Takano, S., Synlett, 1990, 691.

588. Nicolaou, K. C.; Nugiel, D. A.; Couladouros, E.; Hwang, C.-K. Tetrahedron, 1990, **46**, 4517

589. Wang, Y.; Babirad, S. A.; Kishi, Y. J. Org. Chem., 1992, **57**, 468.

590. Libing, Y.; Ziquin, W. J. Chem. Soc., Chem. Commun., 1993, 232.

591. Rao, A. V. R.; Rao, S. P.; Bhanu, M. N. J. Chem. Soc. Chem. Commun., 1992, 859.

592. Sun, C.-Q.; Rich, D. H. Tetrahedron Lett., 1988, **29**, 5205.

593. Jung, M. E.; Lew, W. J. Org. Chem., 1991, **56**, 1347.

594. Shimizu, I.; Yamazaki, H. Chem. Lett., 1990, 777.

595. Marshall, J. A.; Andersen, M. W. J. Org. Chem., 1992, **57**, 5851.

596. Mori, K.; Okada, K. Tetrahedron, 1985, **41**, 557.

597. Abram, T. S.; Biddlecom, W. G.; Jennings, M. A.; Norman, P.; Tudhope, S. R. *Eur. Pat. Appl.*, EP 410244; Chem. Abstr., 1991, **115**, 135803c.

598. Cregge, R. J.; Lentz, N. L.; Sabol, J. S. J. Org. Chem., 1991, **56**, 1758.

599. Hamon, D. P. G.; Shirley, N. J. J. Chem. Soc., Chem. Commun., 1988, 425.

600. Ferraboschi, P.; Brembilla, D.; Grisenti, P.; Santaniello, E. J. Org. Chem., 1991, **56**, 5478.

601. Gosmini, C.; Dubuffet, T.; Sauvetre, R.; Normant, J.-F. Tetrahedron: Asymmetry, 1991, **2**, 223.

602. Alexakis, A.; Mutti, S.; Mangeney, P. J. Org. Chem. 1992, **57**, 1224.

603. Corey, E. J.; Hashimoto, S.; Barton, A. E. J. Am. Chem. Soc. 1981, **103**,

721.

604. Ernst, B.; Wagner, B. Helv. Chim. Acta, 1989, **72**, 165.

605. Lentz, N. L.; Peet, N. P. Tetrahedron Lett., 1990, **31**, 811.

606. Wirth, D.; Boland, W.; Muller, D. G. Helv. Chim. Acta, 1992, **75**, 751

607. Takeda, K.; Kawanishi, E.; Nakamura, H.; Yoshii, E. Tetrahedron Lett., 1991, **32**, 4925.

608. Romo, D.; Johnson, D. D.; Plamondon, L.; Miwa, T.; Schreiber, S. L. J. Org. Chem., 1992, **57**, 5060.

609. Ishibashi, Y.; Nishiyama, S.; Shizuri, Y.; Yamamura, S. Tetrahedron Lett., 1992, **33**, 521.

610. Chung, C. B.; Chang, S.-K.; Shim, S. C. Bull. Korean Chem. Soc., 1991, **12**, 122; Chem. Abstr., 1991, **115**, 49223g.

611. Marczak, S.; Masnyk, M.; Wicha, J. Tetrahedron Lett., 1989, **30**, 2845.

612. Buszek, K. R.; Fang, F. G.; Forsyth, C. J.; Jung, S. H.; Kishi, Y.; Scola, P. M.; Yoon, K. S. Tetrahedron Lett., 1992, **33**, 1553.

613. Yee, N. K. N.; Coates, R. M. J. Org. Chem., 1992, **57**, 4598.

614. Ghisalberti, E. L.; Twiss, E.; Rea, P. E. J. Chem. Res.(S), 1991, 202.

615. Mori, K.; Harashima, S. Tetrahedron Lett., 1991, **32**, 5995.

616. Ando, T.; Jacobsen, N. E.; Toia, R. F.; Casida, J. E. J. Agric. Food Chem., 1991, **39**, 600.

617. Rickards, R. W.; Thomas, R. D. Tetrahedron Lett., 1992, **33**, 8137.

618. Gill, M.; Smrdel, A. F. Tetrahedron: Asymmetry, 1990, **1**, 453.

619. Hashimoto, M.; Yanagiya, M.; Shirahama, H. Chem. Lett., 1988, 645.

620. Ray, N. C.; Raveendranath, P. C.; Spencer, T. A. Tetrahedron, 1992, **48**, 9427.

621. Kolb, M.; Van Hijfte, L.; Ireland, R. E. Tetrahedron Lett., 1988, **29**, 6769.

622. Van Hijfte, L.; Kolb, M. Tetrahedron, 1992, **31**, 6393.

623. Davies, M. J.; Heslin, J. C.; Moody, C. J. J. Chem. Soc., Perkin Trans. 1, 1989, 2473.

624. Coghlan, D. R.; Hamon, D. P. G.; Massy-Westropp, R. A.; Slobedman, D. Tetrahedron: Asymmetry, 1990, **1**, 299.

625. Oritani, T.; Yamashita, K. Phytochemistry, 1983, **22**, 1909.

626. Acemoglu, M.; Uebelhart, P.; Rey, M.; Eugster, C. H. Helv. Chim. Acta, 1988, **71**, 931.

627. Spur, B.; Crea, A.; Peters, W. Arch. Pharm., 1985, **318**, 225.

628. Corey, E. J.; Marfat, A.; Munroe, J.; Kim, K. S.; Hopkins, P. B.; Brion, F. Tetrahedron Lett., 1981, **22**, 1077.

629. Anorbe, B.; Martin, V. S.; Palazon, J. M.; Trujillo, J. M. Tetrahedron Lett., 1986, **27**, 4991.

630. Miyashita, M.; Hoshino, M.; Yoshikoshi, A. Chem. Lett., 1990, 791.

631. Nunez, M. T.; Martin, V. S. J. Org. Chem., 1990, **55**, 1928.

632. Scherowsky, G.; Gruneberg, K.; Kuhnpast, K. Ferroelectrics, 1991, **122**, 159.

633. Thijs, L.; Egenberger, D. M.; Zwanenburg, B. Tetrahedron Lett., 1989, **30**, 2153.

634. Hong, C. Y.; Kishi, Y. J. Org. Chem., 1990, **55**, 4242.

635. Freezou, J. P.; Julia, M.; Li, Y.; Liu, L. W.; Pancrazi, A. Synlett, 1990, 766.

636. Taber, D. F.; Silverberg, L. J.; Robinson, E. D. J. Am. Chem. Soc., 1991, **113**, 6639.

637. Bansal, R.; Cooper, G. F.; Corey, E. J. J. Org. Chem., 1991, **56**, 1329.

638. Mills, L. S.; North, P. C. Tetrahedron Lett., 1983, **24**, 409.

639. Toth, M.; Buser, H. R.; Pena, A.; Arn, H.; Mori, K.; Takeuchi, T.; Nikolaeva, L. N.; Kovalev, B. G. Tetrahedron Lett., 1989, **30**, 3405.

640. Mori, K.; Takeuchi, T. Justus Liebigs Ann. Chem., 1989, 453.

641. Toto, M.; Arun, H.; Mori, K.; Ninomiya, Y.; Komata, T.; Senda, S.; Takeuchi, T.; Yuya, M. *Jpn. Kokai Tokkyo Koho* JP 02 262 575 [90 262 575]; Chem. Abstr., 1991, **114**, 185136n.

642. Carvalho, C.; Cullen, W. R.; Fryzuk, M. D.; Jacobs, H.; James, B. R.; Kutney, J. P.; Piotrowska, K.; Singh, V. K. Helv. Chim. Acta, 1989, **72**, 205.

643. Izawa, T.; Wang, Z.-Q.; Nishimura, Y.; Kondo, S.; Umezawa, H. Chem. Lett., 1987, 1655.

644. Ko, O. H. Yakhak Hoechi, 1986, **30**, 329; Chem. Abstr., 1986, **107**, 175711n.

645. Reddy, K. S.; Ko, O. H.; Ho, D.; Persons, P. E.; Cassady, J. M. Tetrahedron Lett., 1987, **28**, 3075.

646. Williams, D. R.; Brown, D. L.; Benbow, J. W. J. Am. Chem. Soc., 1989, **111**, 1923.

647. Giese, B.; Rupaner, R. Justus Liebigs Ann. Chem., 1987, 231.

648. Noda, Y.; Kikuchi, M. Synth. Commun., 1985, **15**, 1245.

649. Guo-qiang, L.; Hai-jian, X.; Bi-chi, W.; Guong-zhong, G.; Wei-Shan, Z. Tetrahedron Lett., 1985, **26**, 1233.

650. Mori, K.; Umemura, T. Tetrahedron Lett., 1981, **22**, 4433.

651. Mori, K.; Umemura, T. Tetrahedron Lett., 1982, **23**, 3391.

652. Umemura, T.; Mori, K. Agric. Biol. Chem., 1987, **51**, 1973.

653. Takano, S.; Sugihara, T.; Ogasawara, K. Synlett, 1991, 279.

654. Nicolaou, K. C.; Veale, C. A.; Hwang, C.-K.; Hutchinson, J.; Prasad, C. V. C.; Ogilvie, W. W. Angew. Chem. Int. Ed. Engl., 1991, **30**, 299.

655. Nicolaou, K. C.; Duggan, M. E.; Hwang, C.-K. J. Am. Chem. Soc., 1989, **111**, 6666.

656. Fang, F. G.; Kishi, Y.; Matelich, M. C.; Scola, P. M. Tetrahedron Lett., 1992, **33**, 1557.

657. Sodeoka, M.; Iimori, T.; Shibasaki, M. Tetrahedron Lett., 1985, **26**, 6497.

658. Sodeoka, M.; Iimori, T.; Shibasaki, M. Chem. Pharm. Bull., 1991, **39**, 323.

659. Lee, E.; Shin, I.-J.; Kim, T.-S. J. Am. Chem. Soc., 1990, **112**, 260.

660. Dulplantier, A. J.; Masamune, S. J. Am. Chem. Soc., 1990, **112**, 7079.

661. Prestwich, G. D.; McG. Graham, S.; Kuo, J.-W.; Vogt, R. G. J. Am. Chem. Soc., 1989, **111**, 636.

662. Magnus, P.; Davies, M. J. Chem. Soc., Chem. Commun., 1991, 1522.

663. Sugiyama, S.; Honda, M.; Komori, T. Justus Liebigs Ann. Chem., 1990, 1069.

664. Scherowsky, G.; Gay, J. Liquid Crystals, 1989, **5**, 1253.

665. Scherowsky, G.; Gay, J.; Sharma, N. K. Mol. Cryst. Liq. Cryst., 1990, **178**, 179.

666. Hatakeyama, S.; Numata, H.; Osanai, K.; Takano, S. J. Chem. Soc., Chem. Commun., 1989, 1893.

667. Ebata, T.; Mori, K. Agri. Biol. Chem., 1989, **53**, 801.

668. Takabe, K.; Okisaka, K.; Uchiyama, Y.; Katagiri, T.; Yoda, H. Chem. Lett., 1985, 561.

669. Kitahara, T.; Kiyota, H.; Kurata, H.; Mori, K. Tetrahedron, 1991, **47**, 1649.

670. Furukawa, J.; Iwasaki, S.; Okuda, S. Tetrahedron Lett., 1983, **24**, 5257.

671. Holoboski, M. A.; Koft, E. J. Org. Chem., 1992, **57**, 965.

672. Mori, K.; Brevet, J.-L. Synthesis, 1991, 1125.

673. Tius, M. A.; Cullingham, J. M. Tetrahedron Lett., 1989, **30**, 3749.

674. Arm, C.; Pfander, H. Helv. Chim. Acta, 1984, **67**, 1540.

675. Latli, B.; Prestwich, G. D. J. Labelled Comp. Radiopharm., 1991, **29**, 1167.

676. Prestwich, G. D.; Eng, W.-s.; Robles, S.; Vogt, R. G.; Wisniewski, J. R.; Wawrzenczyk, C. J. Biol. Chem., 1988, **263**, 1398.

677. Ho, W.; Tarkan, O.; Kiorpes, T. C.; Tutwiler, G. F.; Mohrbacher, R. J. J. Med. Chem., 1987, **30**, 1094.

678. Kitano, Y.; Kobayashi, Y.; Sato, F. J. Chem. Soc., Chem. Commun., 1985, 498.

679. Moon, S.-S.; Chen, J. L.; Moore, R. E.; Patterson, G. M. L. J. Org. Chem., 1992, **57**, 1097.

680. Horita, K.; Nagato, S.; Oikawa, Y.; Yonemitsu, O. Chem. Pharm. Bull., 1989, **37**, 1705.

681. Millar, J. G.; Giblin, M.; Barton. D.; Morrison, A.; Underhill, E. W. J. Chem. Ecol., 1990, **16**, 2317.

682. Morimoto, Y.; Oda, K.; Shirahama, H.; Matsumoto, T.; Omura, S. Chem. Lett., 1988, 909.

683. Cosse, A. A.; Cyjon, R.; Moore, I.; Wysoki, M.; Becker, D. J. Chem. Ecol., 1992, **18**, 165.

684. Becker, D.; Cyjon, R.; Cosse, A.; Moore, I.; Kimmel, T.; Wysoki, M. Tetrahedron Lett., 1990, **31**, 4923.

685. Nicolaou, K. C.; Duggan, M. E.; Hwang, C.-K. J. Am. Chem. Soc., 1989, **111**, 6676.

686. Marshall, J. A.; Flynn, K. E. J. Am. Chem. Soc., 1984, **106**, 723.

687. Gorgen, G.; Boland, W.; Preiss, U.; Simon, H. Helv. Chim. Acta, 1989, **72**, 917.

688. Honda, M.; Ueda, Y.; Sugiyama, S.; Komori, T. Chem. Pharm. Bull., 1991, **39**, 1385.

689. Farkas, I.; Pfander, H. Helv. Chim. Acta, 1990, **73**, 1980.

690. Urones, J. G.; Marcos, I. S.; Cuadrado, J. S.; Basabe, P.; Lithgow, A. M. Phytochemistry, 1990, **29**, 1247.

691. Urones, J. G.; Marcos, I. S.; Basabe, P.; Sexmero, M.-J.; Diez, D.; Garrido, N. M.; Prieto, J. E. S. Tetrahedron, 1990, **46**, 2495.

692. Ojika, M.; Kigoshi, H.; Yoshikawa, K.; Nakayama, Y.; Yamada, K. Bull. Chem. Soc. Jpn., 1992, **65**, 2300.

693. Inoue, S.; Ikeda, H.; Sato, S.; Horie, K.; Ota, T.; Miyamoto, O.; Sato, K. J. Org. Chem., 1987, **52**, 5495.

694. Eisai Co., Ltd. Jpn. Kokai Tokkyo Koho JP 59 29 678 [84 29 678]; C. A., 1984, *101*, 111227.

695. Eisai Co., Ltd. Jpn. Kokai Tokkyo Koho JP 59 31 726 [84 31 726]; C. A., 1984, *101*, 91290.

696. Takano, S.; Sugihara, T.; Ogasawara, K. Synlett, 1990, 451.

697. Gleason, J. G.; Hall, R. F.; Perchonock, C. D.; Erhard, K. F.; Frazee, J. S.; Ku, T. W.; Kondrad, K.; McCarthy, M. E.; Mong, S.; Crooke, S. T.; Chi-Rosso, G.; Wasserman, M. A.; Torphy, T. J.; Muccitelli, R. M.; Hay, D. W.; Tucker, S. S.; Vickery-Clark, L. J. Med. Chem., 1987, **30**, 959.

698. Lai, C. K.; Gut, M. J. Org. Chem., 1987, **52**, 685.

699. Kabat, M. M. J. Fluorine Chem., 1991, **53**, 249.

700. Xiao, X.-y.; Prestwich, G. D. J. Labelled Comp. Radiopharm., 1991, **29**, 883.

701. Nishitoba, T.; Sato, H.; Oda, K.; Sakamura, S. Agric. Biol. Chem., 1988, **52**, 211.

702. Xiao, X. Y.; Sen, S. E.; Prestwich, G. D. Tetrahedron Lett., 1990, **31**,

2097.

703. Yamada, Y.; Seo, C. H.; Okada, H. Agric. Biol. Chem., 1981, **45**, 1741.

704. Marshall, J. A.; Peterson, J. C.; Lebioda, L. J. Am. Chem. Soc., 1984, **106**, 6006.

705. Marshall, J. A.; Flynn, K. E. J. Am. Chem. Soc., 1983, **105**, 3360.

706. Hosokawa, T.; Kono, T.; Shinohara, T.; Murahashi, S. J. Organometal. Chem., 1989, **370**, C13.

707. White, J. D.; Avery, M. A.; Choudhry, S. C.; Dhingra, O. P.; Kang, M.-c; Whittle, A. J. J. Am. Chem. Soc., 1983, **105**, 6517.

708. White, J. D.; Kang, M.-c; Sheldon, B. G. Tetrahedron Lett., 1983, **24**, 4539.

709. Jung, M. E.; Jung, Y. H. Tetrahedron Lett., 1989, **30**, 6637.

710. Trost, B. M.; Nubling, C. Carbohydr. Res., 1990, **202**, 1.

711. Walkup, R. D.; Cunningham, R. T. Tetrahedron Lett., 1987, **28**, 4019.

712. Hanessian, S.; Cooke, N. G.; DeHoff, B.; Sakito, Y. J. Am. Chem. Soc., 1990, **112**, 5276.

713. Wilson, S. R.; Haque, M. S. Tetrahedron Lett., 1984, **25**, 3147.

714. Mori, K.; Seu, Y-B. Tetrahedron, 1985, **41**, 3429.

715. Paquette, L. A.; Sweeney, T. J. J. Org. Chem., 1990, **55**, 1703.

716. Paquette, L. A.; Sweeney, T. J. Tetrahedron, 1990, **46**, 4487.

717. Ewing, W. R.; Harris, B. D.; Bhat, K. L.; Joullie, M. M. Tetrahedron, 1986, **42**, 2421.

718. Murakami, M.; Matsuura, M.; Aoki, T.; Nagata, W. Synlett, 1990, 681.

719. England, P.; Chun, K. H.; Moran, E. J.; Armstrong, R. W. Tetrahedron Lett., 1990, **31**, 2669.

720. England, P.; Chun, K. H,; Moran, E. J.; Armstrong, R. W. Tetrahedron Lett., 1990, **31**, 2669.

721. Ziegler, F. E.; Kneisley, A.; Wester, R. T. Tetrahedron Lett., 1986, **27**, 1221.

722. Ziegler, F. E.; Kneisky, A. Tetrahedron Lett., 1985, **26**, 263.

723. Owens, K. A.; Berson, J. A. J. Am. Chem. Soc., 1990, **112**, 5973.

724. Ikegami, S.; Okamura, H.; Kuroda, S.; Katsuki, T.; Yamaguchi, M. Bull. Chem. Soc. Jpn., 1992, **65**, 1841.

725. Mihelich, E. D. Procter & Gamble Co., Miami Valley Laboratories, unpublished results.

726. Overman, L. E.; Lin, N. H. J. Org. Chem., 1985, **50**, 3669.

727. Discordia, R,P.; Dittmer, D. C. J. Org. Chem. 1990, **55**, 1414.

728. Burke, S. D.; Pacofsky, G. J.; Piscopio, A. D. J. Org. Chem., 1992, **57**, 2228.

729. Kim, Y. G.; Cha, J. K. Tetrahedron Lett., 1988, **29**, 2011.

730. Zhou, B.; Xu, Y. J. Org. Chem., 1988, **53**, 4419.

731. Aggarwal, S. K.; Bradshaw, J. S.; Eguchi, M.; Parry, S.; Rossiter, B. E.; Markides, K. E.; Lee, M. L. Tetrahedron, 1987, **43**, 451.

732. Mori, K.; Otsuka, T.; Oda, M. Tetrahedron, 1984, **40**, 2929.

733. Bessodes, M.; Saiah, M.; Antonakis, K. J. Org. Chem., 1992, **57**, 4441.

734. Saiah, M.; Bessodes, M.; Antonakis, K. Tetrahedron: Asymmetry, 1991, **2**, 111.

735. Paquette, L. A., Maynard, G. D. Angew. Chem., Int. Ed. Engl., 1991, **30**, 1368.

736. Paquette, L. A., Maynard, G. D. J. Am. Chem. Soc., 1992, **114**, 5018.

737. Verner, E. J.; Cohen, T. J. Am. Chem. Soc., 1992, **114**, 375.

738. Agnel, G.; Negishi, E. J. Am. Chem. Soc., 1991, **113**, 7424.

739. Ronald, R. C.; Ruder, S. M.; Lillie, T. S. Tetrahedron Lett., 1987, **28**, 131.

740. Ziegler, F. E.; Wester, R. T. Tetrahedron Lett., 1986, **27**, 1225.

741. Ziegler, F. E.; Shirchack, E. P.; Wester, R. T. Tetrahedron Lett., 1986, **27**, 1229.

742. Ziegler, F. E.; Kneisley, A.; Thottathil, J. K.; Wester, R. T. J. Am. Chem. Soc., 1988, **110**, 5434.

743. Dai, L.-x; Lou, B.-l; Zhang, Y.— z. J. Am. Chem. Soc. 1988, **110**, 5195.

744. Evans, D. A; Kaldor, S. W.: Jones, T. K.; Clardy, J.; Stout, T. J. J. Am. Chem. Soc., 1990, **112**, 7001.

745. Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Straub, J. A.; Palkowitz, A. D. J. Org. Chem., 1990, **55**, 4117.

746. Chemin, D.; Alami, M.; Linstrumelle, G. Tetrahedron Lett., 1992, **33**, 2681.

747. Brown, S. M.; Davies, S. G.; de Sousa, J. A. A. Tetrahedron: Asymmetry, 1991, **2**, 511.

748. Mori, K.; Otsuka, T. Tetrahedron, 1985, **41**, 553.

749. Mori, K.; Otsuka, T. Tetrahedron, 1985, **41**, 3253.

750. Alexander, D. L.; Lin, C. H. Prostaglandins, 1986, **32**, 647.

751. Yadav, J. S.; Gadgil, V. R. J. Chem. Soc., Chem. Commun., 1989, 1824.

752. Trost, B. M.; Dumas, J. J. Am. Chem. Soc., 1992, **114**, 1924.

753. Marshall, J. A.; Markwalder, J. A. Tetrahedron Lett., 1988, **29**, 4811.

754. Peschke, B.; Lubmann, J.; Drybusch, M.; Hoppe, D. Chem. Ber., 1992, **125**, 1421.

755. Kufner, U.; Schmidt, R. R., Angew. Chem., Int. Ed. Engl., 1986, **25**, 89.

756. Hoppe, D.; Kramer, T. Angew. Chem., Int. Ed. Engl., 1986, **25**, 160.

757. Nonoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. J. Am. Chem.

Soc., 1990, **112**, 316.

758. Page, P. C. B.; Carefull, J. F.; Powell, L. H.; Sutherland, I. O., J. Chem. Soc., Chem. Commun., 1985, 822.

759. Bailey, M.; Staton, I.; Ashton, P. R.; Marko, I. E.; Ollis, W. D. Tetrahedron: Asymmetry, 1991, **2**, 495.

760. Bonini, C. Tetrahedron Lett., 1990, **31**, 5369.

761. Claremon, D. A.; Lumma, P. K.; Phillips, B. T. J. Am. Chem. Soc., 1986, **108**, 8265.

762. Davis, F. A.; Reddy, R. T. J. Org. Chem., 1992, **57**, 2599.

763. Jung, M. E.; Jung, Y. H.; Miyazawa, Y. Tetrahedron Lett., 1990, **31**, 6983.

764. Mitch, C. H.; Zimmerman, D. M.; Snoddy, J. D.; Reel, J. K.; Cantrell, B. E. J. Org. Chem., 1991, **56**, 1660.

765. Aristoff, P. A.; Johnson, P. D.; Harrison, A. W. J. Am. Chem. Soc., 1985, **107**, 7967.

766. Nakagawa, N.; Mori, K. Agric. Biol. Chem., 1984, **48**, 2799.

767. Hanzawa, Y.; Kawagoe, K.; Ito, M.; Kobayashi, Y. Chem. Pharm. Bull., 1987, **35**, 1633.

768. Morales, E. Q.; Vazquez, J. T.; Martin, J. D. Tetrahedron: Asymmetry, 1990, **1**, 319.

769. Alvarez, E.; Manta, E.; Martin, J. D. Tetrahedron Lett., 1988, **29**, 2093.

770. Frater, G.; Müller, U. Helv. Chim. Acta, 1989, **72**, 653.

771. Mori, K.; Puapoomchareon, P. Justus Liebigs Ann. Chem., 1991, 1053.

772. Jacquier, R.; Lazaro, R.; Raniriseheno, H.; Viallefont, P. Tetrahedron Lett., 1984, **25**, 5525.

773. Ikegami, S.; Hayama, T.; Katsuki, T.; Yamaguchi, M. Tetrahedron Lett., 1986, **27**, 3403.

774. Kawai, M.; Gardner, J. H.; Rich, D. H. Tetrahedron Lett., 1986, **27**, 1877.

775. Jacquier, R.; Lazaro, R.; Raniriseheno, H.; Viallefont, P. Tetrahedron Lett., 1986, **27**, 4735.

776. Maemoto, S.; Mori, K. Chem. Lett., 1987, 109.

777. Gonnella, N. C.; Nakanishi, K.; Martin, V. S.; Sharpless, K. B. J. Am. Chem. Soc., 1982, **104**, 3775.

778. Stary, I.; Kocovsky, P. J. Am. Chem. Soc., 1989, **111**, 4981.

779. Stary, I.; Zajicek, J.; Kocovsky, P. Tetrahedron, 1992, **48**, 7229.

780. Calverley, M. J. Synlett, 1990, 157.

781. Ito, T.; Okamoto, Y.; Matsumoto, T. Bull. Chem. Soc. Jpn., 1985, **58**, 3631.

782. Rao, A. V. R.; Khrimian, A. P.; Krishna, P. R.; Yadagiri, P.; Yadav, J. S. Synth. Commun., 1988, **18**, 2325.

783. Yadav, J. S.; Radhakrishna, P. Tetrahedron, 1990, **46**, 5825.

784. Crombie, L.; Jarrett, S. R. M. Tetrahedron Lett., 1989, **30**, 4303.

785. Crombie, L.; Horsham, M. A.; Jarrett, S. R. M. J. Chem. Soc., Perkin Trans. 1, 1991, 1511.

786. Hatakeyama, S,; Sugawara, K.; Kawamura, M.; Takano, S. Tetrahedron Lett., 1991, **32**, 4509.

787. Yanagisawa, A.; Nomura, N.; Noritake, Y.; Yamamoto, H. Synthesis, 1991, 1130.

788. Mehmandoust, M.; Petit, Y.; Larcheveque, M. Tetrahedron Lett., 1992, **33**, 4313.

789. Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E. J. Am. Chem. Soc., 1989, **111**, 6682.

790. Marples, B. A.; Rogers-Evans, M. Tetrahedron Lett., 1989, **30**, 261.

791. Rao, A. V. R.; Yadav, J. S.; Reddy, K. B.; Mehendale, A. R. J. Chem. Soc., Chem. Commun., 1984, 453.

792. Rao, A. V. R.: Yadav, J. S.; Reddy, K. B.; Mehendale, A. R. Tetrahedron, 1984, **40**, 4643.

793. Rao, A. V. R.; Chanda, B.; Borate, H. B.; Gupta, M. Indian J. Chem., 1986, **25B**, 9.

794. Holland, H. L.; Viski, P. J. Org. Chem., 1991, **56**, 5226.

795. Mori, K.; Otsuka, T. Tetrahedron, 1983, **39**, 3267.

796. Nicolaou, K. C.; Zipkin, R. E.; Dolle, R. E.; Harris, B. D. J. Am. Chem. Soc., 1984, **106**, 3548.

797. Marson, C. M.; Benzies, D. W. M.; Hobson, A. D. Tetrahedron, 1991, **47**, 5491.

798. Keegan, D. S.; Midland, M. M.; Werley, R. T.; McLoughlin, J. I. J. Org. Chem., 1991, **56**, 1185.

799. Ogata, M.; Matsumoto, H.; Takahashi, K.; Shimizu, S.; Kida, S.; Murabayashi, A.; Shiro, M.; Tawara, K. J. Med. Chem., 1987, **30**, 1054.

800. Discordia, R. P.; Murphy, C. K.; Dittmer, D. C. Tetrahedron Lett., 1990, **31**, 5603.

801. Lewis, M. D.; Menes, R. Tetrahedron Lett., 1987, **28**, 5129.

802. Dominguez, D.; Cava, M. P. J. Org. Chem., 1983, **48**, 2820.

803. Russell, A. T.; Procter, G. Tetrahedron Lett., 1987, **28**, 2041.

804. Okamoto, S.; Kobayashi, Y.; Sato, F. Tetrahedron Lett., 1989, **30**, 4379.

805. Kobayashi, Y.; Shimazaki, T.; Taguchi, H.; Sato, F. J. Org. Chem., 1990, **55**, 5324.

806. Vanhessche, K.; der Eycken, E. V.; Vandewalle, M. Tetrahedron Lett., 1990, **31**, 2337.

807. Evans, D. A.; Polniaszek, R. P.; DeVries, K. M.; Guinn, D. E.; Mathre, D. J. J. Am. Chem. Soc., 1991, **113**, 7613.

808. Wang, Z. Tetrahedron Lett., 1989, **30**, 6611.

809. Thomas, E. J.; Watts, J. P. J. Chem. Soc., Chem. Commun., 1990, 467.

810. Roush, W. R.; Spada, A. P. Tetrahedron Lett., 1982, **23**, 3773.

811. Ibuka, T.; Tanaka, M.; Yamamoto, Y. J. Chem. Soc., Chem. Commun., 1989, 967.

812. Gao, L.-x.; Murai, A. Tetrahedron Lett., 1992, **33**, 4349.

813. Dyer, U. C.; Kishi, Y. J. Org. Chem., 1988, **53**, 3383.

814. Baker, R.; Castro, J. J. Chem. Soc., Perkin Trans. 1, 1990, 47.

815. Back, T. G.; Blazecka, P. G.; Krishna, M. V. Tetrahedron Lett., 1991, **32**, 4817.

816. Calverley, M. J. Tetrahedron, 1987, **43**, 4609.

817. Ekhato, I. V.; Silverton, J. V.; Robinson, C. H. J. Org. Chem., 1988, **53**, 2180.

818. Kametani, T.; Tsubuki, M.; Tatsuzaki, Y.; Honda, T. J. Chem. Soc., Perkin Trans. 1, 1990, 639.

819. Kawatani, T.; Tatsuzaki, Y.; Tsukubi, M.; Honda, T. Heterocycles, 1989, **29**, 1247.

820. Kusakabe, M.; Sato, F. J. Org. Chem., 1989, **54**, 3486.

821. Honda, T.; Kobayashi, Y.; Tsubuki, M. Tetrahedron Lett., 1990, **31**, 4891.

822. Kitano, Y.; Kusakabe, M.; Kobayashi, Y.; Sato, F. J. Org. Chem., 1988, **54**, 994.

823. Zhou, W.-S.; Wei, D. Tetrahedron: Asymmetry, 1991, **2**, 767.

824. Baldwin, J. E.; Adlington, R. M.; Bebbington, D.; Russell, A. J. Chem. Soc., Chem. Commun., 1992, 1249.

825. Smith, III, A. B.; Hale, K. J.; Laakso, L. M.; Chen, K.; Riera, A. Tetrahedron Lett., 1989, **30**, 6963.

826. Benechie, M.; Khuong-Huu, F. Synlett, 1992, 266.

827. Chong, J. M. Tetrahedron, 1989, **45**, 623.

828. Nakano, T.; Obata, M.; Yamaguchi, Y.; Marubayashi, N.; Ikeda, K.; Morimoto, Y. Chem. Pharm. Bull., 1992, **40**, 117.

829. Sigrist-Nelson, K.; Krasso, A.; Muller, R. K. M.; Fischli, A. E. Eur. J. Biochem., 1987, **166**, 453.

830. Conte, V.; Furia, F. D.; Licini, G.; Modena, G.; Sbampato, G.; Valle, G. Tetrahedron: Asymmetry, 1991, **2**, 257.

831. Conte, V.; Furia, F. D.; Licini, G.; Modena, G. Tetrahedron Lett., 1989, **30**, 4859.

832. Bortolini, O.; Furia, F. D.; Licini, G.; Modena, G.; Rossi, M. Tetrahedron

Lett., 1986, **27**, 6257.

833. Cashman, J. R.; Olsen, L. D.; Bornheim, L. M. J. Am. Chem. Soc., 1990, **112**, 3191.

834. Phillips, M. L.; Berry, D. M.; Panetta, J. A. J. Org. Chem., 1992, **57**, 4047.

Radical Cyclization Reactions

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1. Introduction

Radical cyclization reactions are among the most powerful and versatile methods for the construction of mono- and polycyclic systems. The advantages these reactions offer to the synthetic organic chemist include high functional group tolerance and mild reaction conditions combined with high levels of regio- and stereochemistry. Furthermore, the recent progress in radical chemistry has led to the development of a broad range of very useful practical methods to conduct radical cyclization reactions. In general, radical cyclization reactions comprise three basic steps: selective radical generation, radical cyclization, and conversion of the cyclized radical to the product (Eq. 1).

(1)
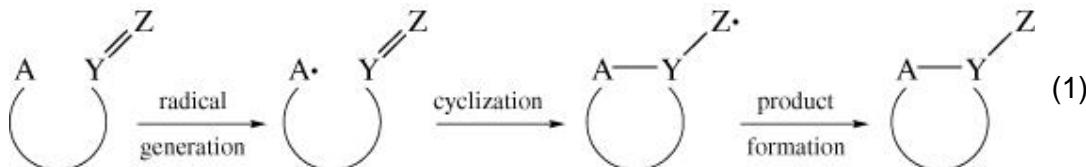
For the generation of the initial radical a broad variety of suitable precursors can be employed, such as halides, thio- and selenoethers, alcohols, aldehydes and hydrocarbons. The cyclization step usually involves the intramolecular addition of a radical to a multiple bond. Most often carbon–carbon multiple bonds are employed; however, there are also examples known for the addition to carbon–oxygen and carbon–nitrogen bonds. Depending on the method employed, the cyclized radical is converted to the desired product by trapping with a radical scavenger, by a fragmentation reaction, or by an electron transfer reaction.

The section Mechanism, Regio- and Stereochemistry provides an introduction to the key features of radical cyclization with a special emphasis on the factors

controlling the regio- and stereochemistry. The section Scope and Limitations covers the different methods used to conduct radical cyclization. The basic principles of radical chemistry and general practical considerations when conducting radical cyclizations are not discussed in detail. Several excellent review articles (1-5) and books (6-8) dealing with these topics are available. The study of one of these reviews or books is highly recommended, especially for readers who are not familiar with radical chemistry.

2. Mechanism, Regio- and Stereochemistry

2.1. Mechanism and Regiochemistry

To achieve synthetically useful radical cyclization, several basic requirements have to be fulfilled:

1. Methods must be available that allow the selective generation of the initial radical from suitable precursors and that effect the transformation of the cyclized radicals to the final products (see Scope and Limitations).

2. The rate constant of ring closure is of special importance because cyclization of the initial radical must be faster than its reaction with the trapping reagent.

3. Each of the reaction steps must be faster than the unwanted side reactions of radicals such as reaction with the solvent or radical recombination.

From these requirements a lower rate constant limit for the cyclization step can be estimated with $k_c \gg 10^2 - 10^3$ s^{-1}, although much larger rate constants ($k_c > 10^5 s^{-1}$) are usually better suited for synthetic applications. Because of its central importance, the rate of cyclization is included in the following discussion.

The regiochemistry of radical cyclization is important because it determines the ring size of the product. In principle, two competing pathways are possible— attack of the radical at the terminal end of the multiple bond (endo cyclization) or attack at the "inner" atom (exo cyclization). Fortunately, radical cyclizations are usually highly regioselective, and exo cyclization (formation of the smaller ring) is often strongly favored over endo cyclization (formation of the larger ring).

2.1.1. Formation of Small Rings

Radical cyclizations to form 3- and 4-membered ring systems are of limited value in synthesis, and only a few examples are known. Because of the large ring strain, the rate of 3-exo cyclization of the butenyl radical **1** is rather low, and the cyclopentylcarbinyl radical **2** so formed rapidly reopens. (9) The equilibrium usually lies far to the side of the acyclic radical. The formation of cyclobutane radicals **3** by 4-exo cyclization of pentenyl radical **4** is even slower and is also reversible (Eq. 2). (10)

(2)

$k_c \, 2 \times 10^3 \text{ s}^{-1}$ $k_c \, 1 \text{ s}^{-1}$

$k_{c'} \, 1 \times 10^8 \text{ s}^{-1}$ $k_{c'} \, 5 \times 10^8 \text{ s}^{-1}$
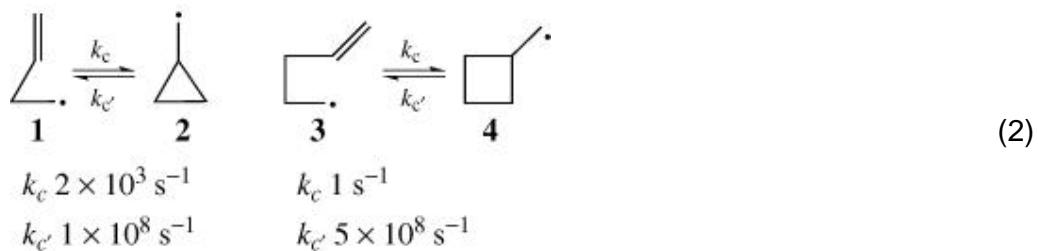
To achieve synthetically useful small ring formation, the cyclized radicals must be trapped selectively prior to reopening or substituents must be introduced that accelerate the cyclization. The first concept is illustrated in the reaction of thioallyl esters **5**, where the intermediate cyclobutylcarbinyl radicals **6** are trapped by rapid β fragmentation (Eq. 3). (11) The second strategy is illustrated by

(3)

R^1	R^2	
$PhCH_2$	H	(47%)
$PhCH_2$	Me	(43%)
$n\text{-}C_{10}H_{21}$	H	(60%)
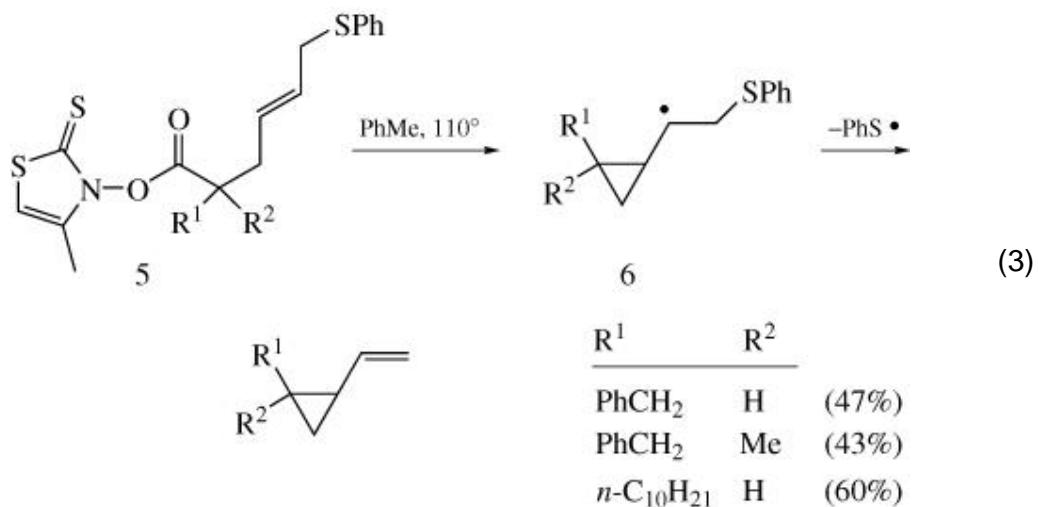
the cyclization of acrylate ester **7** that is activated by the ethoxycarbonyl group at the double bond and the *gem*-diethoxy substituents at the 2 position (Eq. 4). (12)

(4)
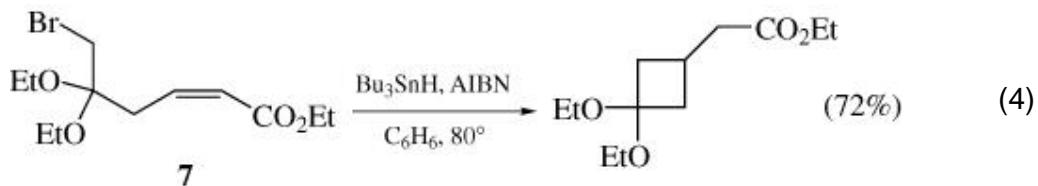
2.1.2. Formation of 5- and 6-Membered Rings

Cyclopentyl rings are almost always formed by 5-exo cyclization of 5-hexenyl radicals, whereas cyclohexyl rings are formed either by 6-endo cyclizations of 5-hexenyl radicals or by 6-exo cyclization of 6-heptenyl radicals. However, the discussion concentrates on cyclizations of 5-hexenyl radicals because they represent the most useful class of radical cyclizations in organic synthesis.

The cyclization reactions of 5-hexenyl and 6-heptenyl radicals are exothermic and irreversible reactions with a preference for formation of the smaller ring size by cyclization in the exo mode. (13, 14) For the parent 5-hexenyl radical **8**, this preference results in a ratio of 98:2 in favor of the 5-membered over the 6-membered ring (Eq. 5).

$$k_{5\text{-exo}} \quad 2 \times 10^5 \ s^{-1}$$
$$k_{6\text{-endo}} \quad 4 \times 10^3 \ s^{-1}$$

$$98 : 2$$

(5)
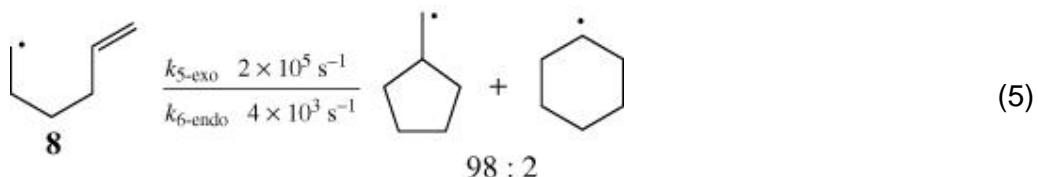
Although the exo mode is again favored, cyclization of 6-heptenyl radical **9** is about 40 times slower than cyclization of the hexenyl radical. Therefore, reactions competing with the cyclization (e.g., reduction of the initial radical) are of much greater importance. Another potential problem of the heptenyl system is caused by a 1,5-hydrogen shift, yielding the resonance-stabilized allyl radical **10** (Eq. 6). This intramolecular H shift is thermodynamically favored in many systems,

$$k_{6\text{-exo}} \quad 5 \times 10^3 \ s^{-1}$$
$$k_{7\text{-endo}} \quad 7 \times 10^2 \ s^{-1}$$

$$88 : 12$$

(6)

$$k_{allyl} \ k_{6\text{-exo}}$$
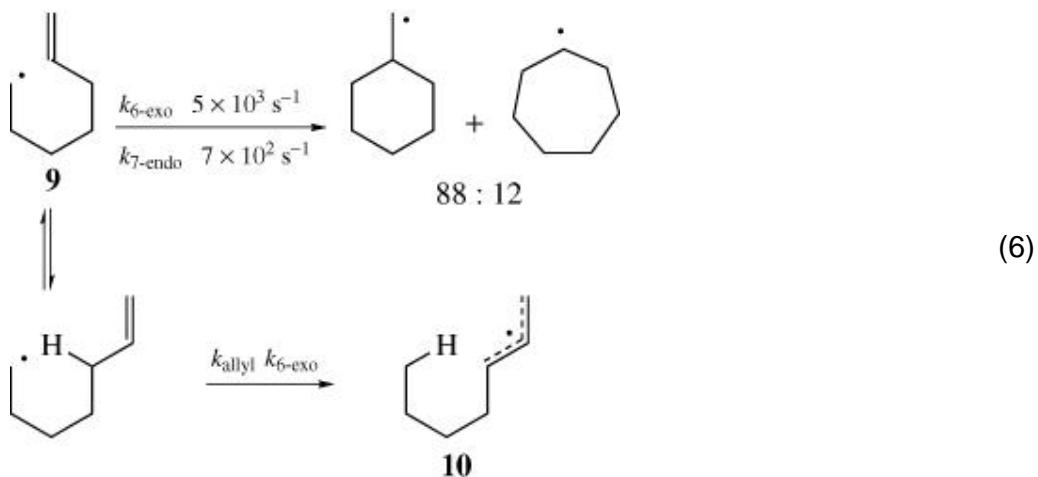
but is kinetically disfavored in smaller rings for stereoelectronic reasons and in larger rings for entropic reasons. Nevertheless, the 6-exo cyclization of

heptenyl radicals is still a very useful reaction, especially if the exo cyclization is accelerated by the introduction of appropriate substituents.

The preferred formation of the thermodynamically disfavored exo product from the 5-hexenyl radical is best rationalized by a stereoelectronically controlled cyclization with the chair-like transition state **11**. (13, 15) This arrangement reflects the early transition state of the reaction with a favorable overlap between the SOMO of the radical and the LUMO of the alkene. The forming C - C bond is very long (ca. 2.3–2.4 Å), and the angle of attack of the radical on the alkene (106°) is close to the angle for the unstrained bimolecular reaction (109°). The corresponding 6-endo transition state **12** is energetically less favored because of

11
5-exo

12
6-endo
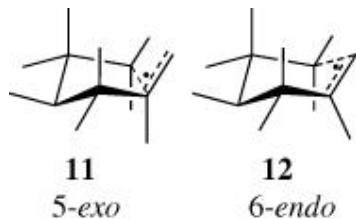
the poorer overlap of the orbitals and the higher degree of ring strain. A comparable model has also been derived for the 6-heptenyl radical. (13)

Although hexenyl and heptenyl radicals have an intrinsic preference for exo ring closure, the regioselectivity can be altered or even reversed by the character of the radical (alkyl, vinyl, aryl), the substituents on the radical, or the nature of the radical acceptor (e.g., double or triple bond).

Introduction of alkyl substituents at the 2, 3, 4, or 6 positions of the hexenyl chain usually enhances the rate and improves the regioselectivity in favor of 5-ring formation. (16) Alkyl substituents in the 1 position usually have little effect, whereas substituents in the 5 position sufficiently retard exo cyclization to let 6-ring cyclization become an effective competing reaction. (10)

	k_{rel} (exo)		exo : endo
	1.0	0.02	98 : 2
1	1.4	0.02	99 : 1
2	1.6	< 0.5	> 99 : 1
3	22	< 0.5	> 99 : 1
4	14	< 0.5	> 99 : 1
5	0.022	0.04	36 : 64
6	2.4	< 0.01	> 99 : 1

Electron-withdrawing substituents at the terminal end of the double bond usually accelerate radical cyclizations owing to favorable FMO interactions. They can be employed to overcome the influence of deactivating substituents and often prove essential for obtaining reasonable yields in the 6-exo closure of heptenyl radicals. In the example shown in Eq. 7, an electron-withdrawing alkoxycarbonyl group is used to accelerate the 6-exo cyclization of the nucleophilic alkyl radical. (17)

(7)
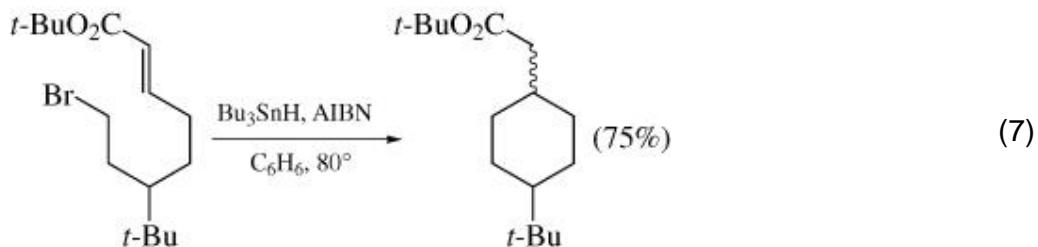
Radicals bearing endocyclic α -carbonyl substituents often yield preferentially products from 6-endo closure by either kinetic or thermodynamic control. Thus, the incorporation of a ketone (but not an ester or amide) group inside the ring causes a strong preference for 6-ring formation. (18, 19) Even in 6-substituted hexenyl radicals 6-endo cyclization still prevails (Eq. 8). Presumably, 5-exo cyclization of

(8)

R = H   (56%)   >97 : <3
R = Me (73%)   75 : 25
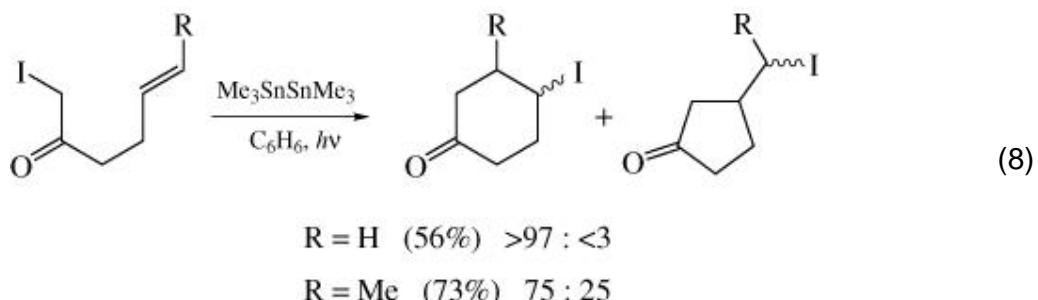
the ketone-substituted radical is retarded because the geometry that allows a stabilizing interaction between the radical and the carbonyl group is distorted in the 5-exo transition state. (18)

It has further been shown that the ring closure of radicals that are stabilized by two nitrile or alkoxycarbonyl groups is reversible. (20, 21) By application of suitable reaction conditions it is possible to obtain selectively the thermodynamically favored 6-endo product **13** (Eq. 9). (22)

(76%)

13

(9)
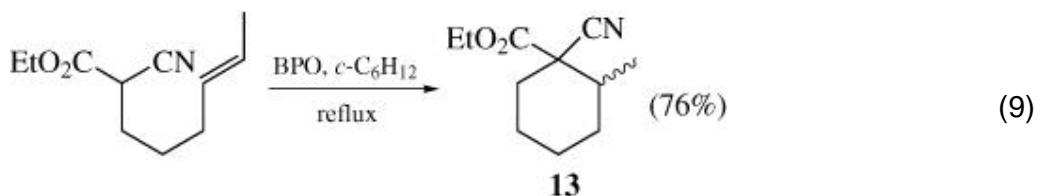
Radical cyclizations onto carbon–carbon triple bonds (5-hexynyl radicals) are somewhat slower than 5-hexenyl cyclizations ($k_c \approx 10^4$ s^{-1}). (13) Nevertheless, they are of great synthetic utility because of the good selectivity in favor of 5-ring formation. In addition, the newly formed exocyclic double bond can further be functionalized. Substitution of the alkyne moiety with a trialkylsilyl group seems to accelerate the cyclization, and through the influence of the activating silyl group, even 6-exo cyclizations are possible (Eq. 10). (23)

$$ \text{(10)} $$
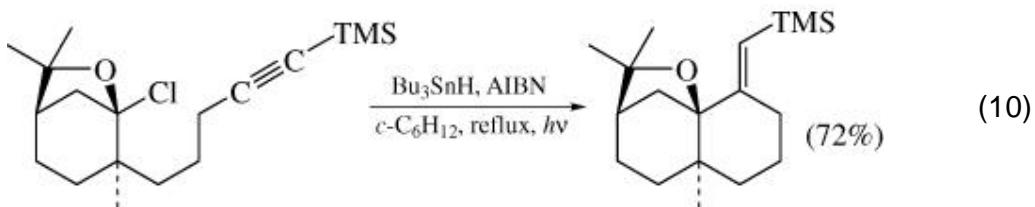
Vinyl radicals are very reactive and undergo regiospecific exo ring closure under kinetically controlled conditions. (24) However, if the intermediate radicals have a sufficient lifetime, for example, when a low concentration of radical scavenger is present, varying amounts of 6-membered ring products are formed (Eq. 11). (25)

$$ \text{(11)} $$

[Bu$_3$SnH]	
0.02 M	75 : 25
1.7 M	>97 : <3
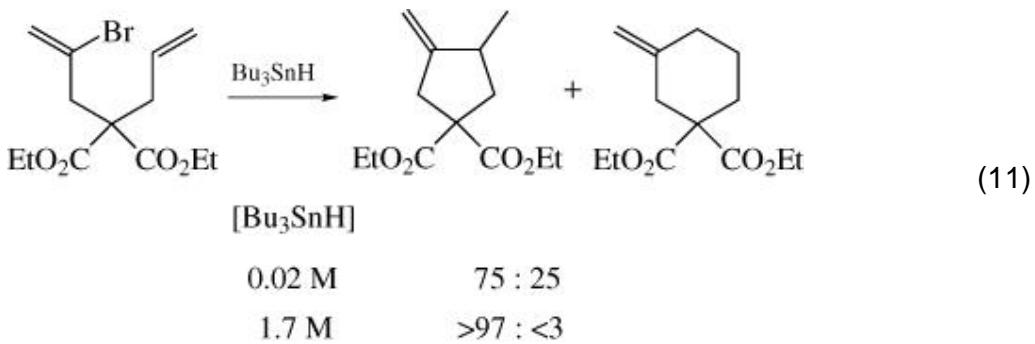
Formation of the more stable cyclohexane derivative is usually not due to a competing endo cyclization. Radical **15** is formed by a rapid rearrangement of the intermediate methylenecyclopentyl radical **14** via a reversible 3-exo cyclization (Eq 12). (26)

(12)
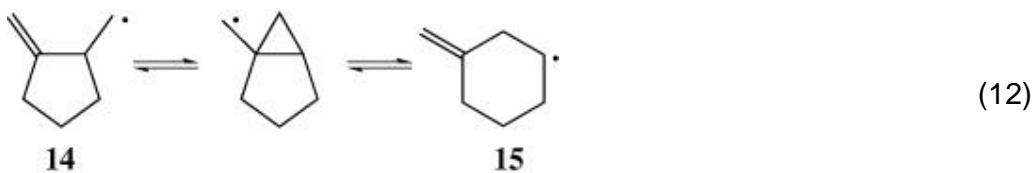
As shown in the example in Eq. 13, the increased cyclization rate of vinyl radicals can be used to conduct 6-exo cyclizations. (27) The stereochemistry of the initial precursor **16** is not retained in the product **17** owing to the facile inversion of vinyl radicals.

(13)
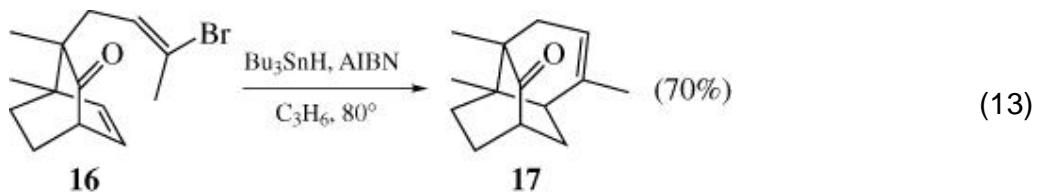
Vinyl radicals are generated either by halogen abstraction from vinyl halides or by reversible addition of stannyl radicals to triple bonds. An illustrative example of the latter reaction is shown in Eq. 14. (28)

(14)
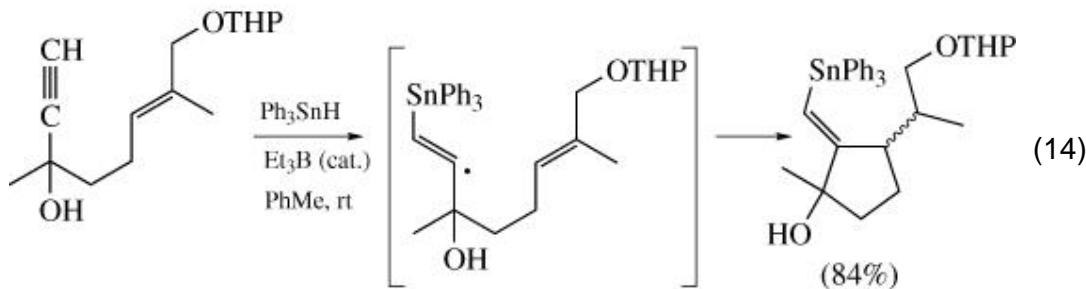
Aryl radicals **18** are widely employed for the formation of benzo-fused ring systems because of their high cyclization rates and excellent exo selectivities. (13) This preference for 5-exo cyclization is maintained even with the 5,5-disubstituted radical **18c** (Eq. 15). (29)

$$\text{(15)}$$

	R^1	X	k_c (s^{-1}, 25°)
a	H	CH$_2$	3.1×10^8
b	H	O	5.3×10^9
c	Me	O	1.7×10^9
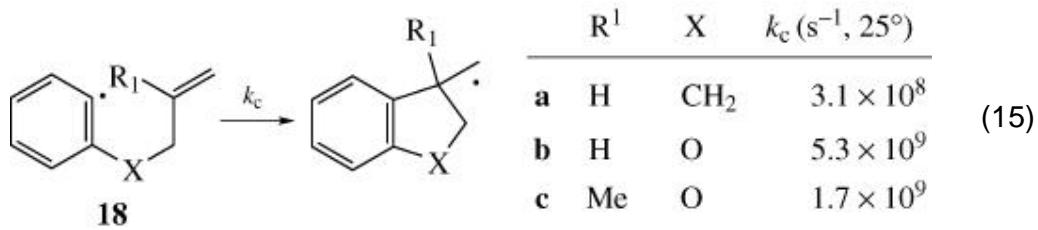
As illustrated in Eq. 16, the endo product **19** can be obtained preferentially by inclusion of a radical stabilizing group at the internal alkene atom. (30)

$$\text{(16)}$$
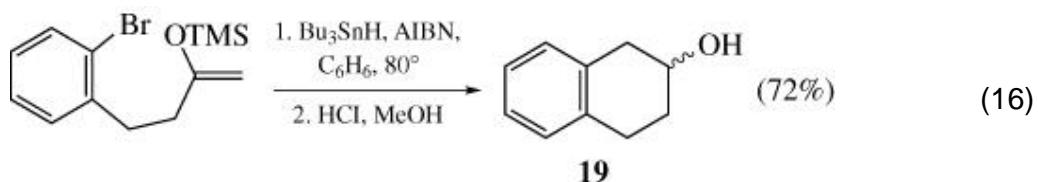
As in vinyl radical cyclizations, ring expansion of the intermediate 5-exo radical is possible, and mixtures of 5- and 6-membered ring products are sometimes observed. This isomerization is promoted by activating substituents like a carbonyl group (Eq. 17). (31, 32)

$$\text{(17)}$$
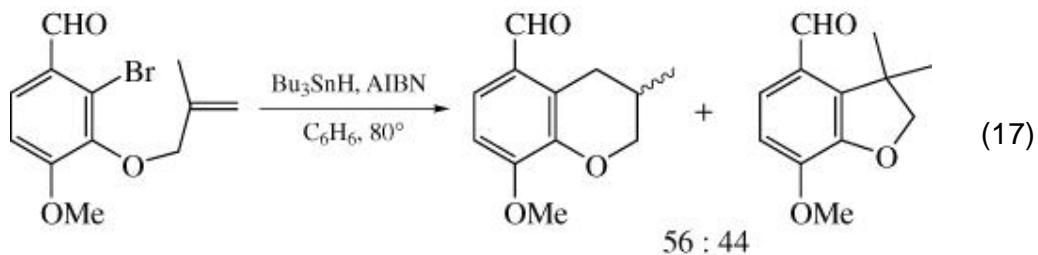
The cyclization rate constants (k_c » 10^5–10^6 s^{-1}) and regioselectivities of acyl radicals are very similar to those of alkyl radicals. Examples of the formation of 5- (33) and 6-membered ring ketones (34) (Eq. 18) by exo cyclizations of hexenyl or

$$(18)$$
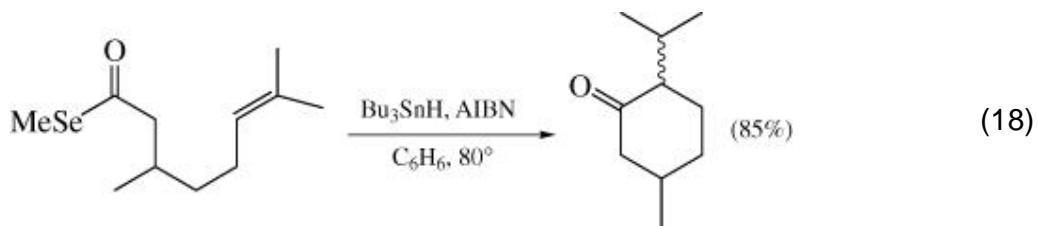
heptenyl radicals are known, and synthesis of the bridged ring system **20** is even possible (Eq. 19). (35)

$$(19)$$
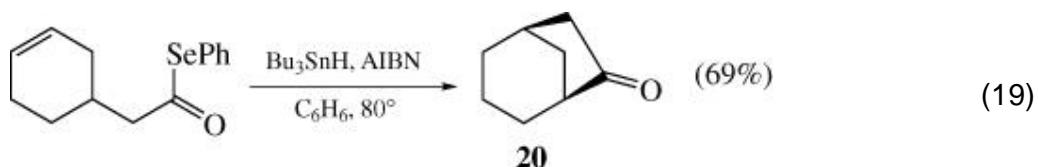
A serious side reaction in these types of reactions is decarbonylation of the intermediate acyl radicals prior to cyclization. The rate of decarbonylation depends mainly on the stabilization of the formed alkyl radical. Therefore, systems that form stabilized radicals or have low cyclization rates yield larger amounts of decarbonylated products. (33)

High regioselectivities and yields are also obtained in the cyclization of alkoxycarbonyl radicals to cyclopentanones, although only a few examples are known (Eq. 20). (36)

$$(20)$$
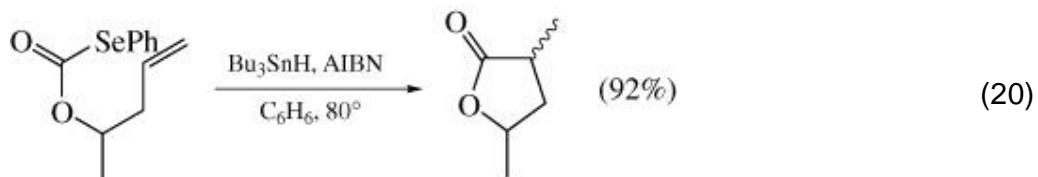
In general, radical cyclization reactions are not restricted to additions to carbon–carbon multiple bonds, and other multiple bonds can also be employed. Cyclizations onto carbon–nitrogen multiple bonds of oximes (37) and nitriles (38) resemble the corresponding additions to carbon–carbon multiple bonds. These cyclizations are irreversible and occur exclusively in the exo mode (attack at the carbon atom). Nitriles are valuable precursors

because the resulting imines can be hydrolyzed to the corresponding ketones (Eq. 21).

$$\text{(21)}$$

(72%)
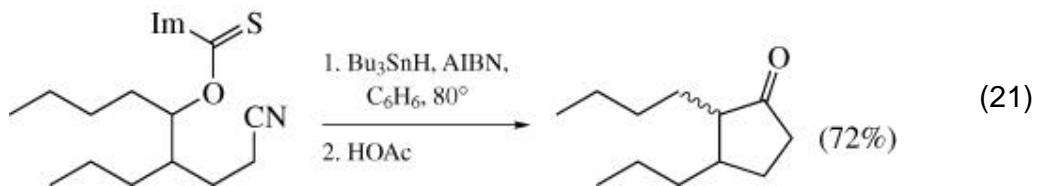
Radical additions onto carbon–oxygen double bonds are restricted to aldehydes and some ketones, because ester and amide carbonyl groups are usually not reactive enough. The ring closure is fast, yielding exclusively the exo products. However, the cyclization is reversible, and the equilibrium often lies on the side of the open-chain radical. (39) Because of the increased strain of the cyclopentane ring, fragmentation of the alkoxy radical is much faster when compared to the cyclohexane system. Therefore, the application of this kind of reaction is restricted mainly to the formation of 6-membered rings. (40)

$k_c \; 9 \times 10^5 \; s^{-1}$
$k_c' \; 5 \times 10^8 \; s^{-1}$

$k_c \; 1 \times 10^6 \; s^{-1}$
$k_c' \; 1 \times 10^7 \; s^{-1}$
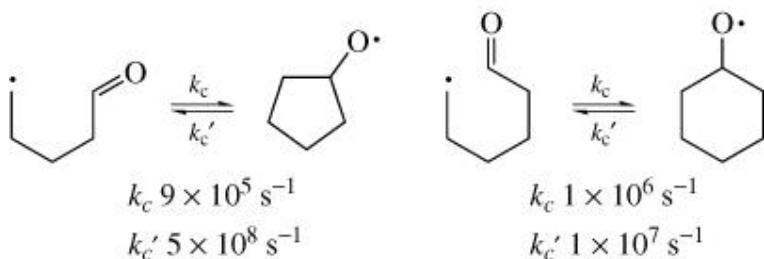
One way to overcome these unfavorable equilibria is selective trapping of the cyclic alkoxy radical with a stannane. It has been shown that hydrogen abstraction from the stannane by an alkoxy radical is about 100 times faster than abstraction by the initial carbon–centered radical. It is therefore possible to obtain useful yields of the cyclic product provided that the equilibrium constant is not too small. An example of radical cyclization onto an aldehyde is shown in Eq. 22. This reaction shows furthermore that in a competing system 6-exo cyclization to form cyclohexanol **21** dominates over the possible 5-exo cyclization onto a carbon–carbon double bond. (41)

(22)
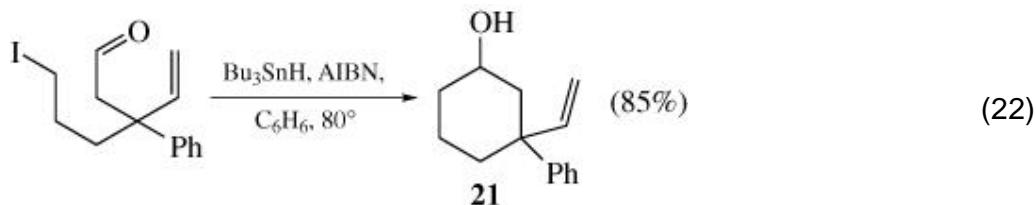
However, the formation of cyclopentanols is more difficult because ring opening of the five-membered ring is extremely rapid. To obtain useful yields, the equilibrium has to be shifted to the side of the cyclized radical by incorporation of suitable substituents. (42)

If the hexenyl chain contains a nitrogen (43) or oxygen (44) atom in the 3 or 4 position, the rate and the regioselectivity of the radical cyclization reaction are enhanced, owing to a better orbital overlap in the 5-exo transition state. In contrast to the carbocyclic radical **22a**, (45) the 5-substituted hexenyl radicals **22b** and **22c** show a strong preference for 5-ring products (Eq. 23).

	X	23 : 24
a	CH_2	36 : 64
b	O	100 : 0
c	NSO_2Ph	100 : 0

(23)
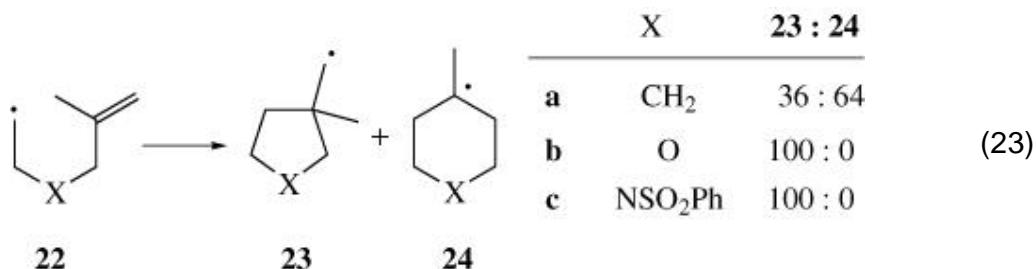
Radical-stabilizing oxygen or nitrogen atoms in the α position to the radical (2 position) retard the cyclization, and byproduct formation often dominates. (46, 47) The poor behavior of these radicals is attributed to increased geometric constraint imposed by delocalization of the radical. (46) Nevertheless, a few examples are known in the literature, even for cyclization of 6-heptenyl radicals (Eq. 24). (48)

(24)
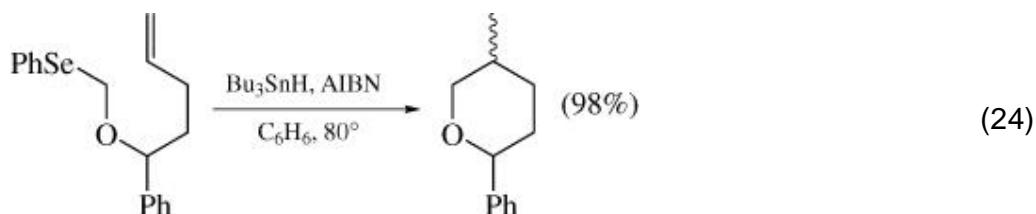
Cyclization reactions of systems with an ester or amide group in the radical chain provide a synthetically useful access to lactams and lactones. The regioselectivity is high and favors 5-exo cyclization; the rate of cyclization is usually in a synthetically useful range ($k_c \gg 10^5\ s^{-1}$). An example of the formation of a γ -lactone is shown in Eq. 25. (49)

$$\text{(25)}$$

(66%)
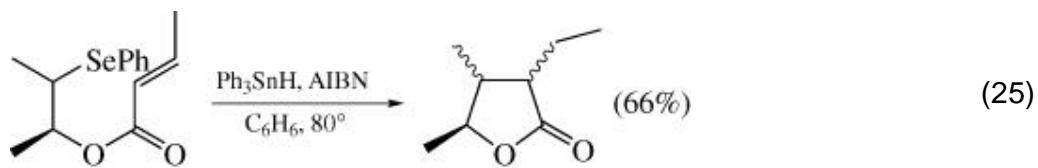
However, if the initial radical is in the α position to the carbonyl group, cyclization is strongly decelerated. Presumably the retardation is due to the preferred *trans* configuration of esters and amides and to the barriers to rotation about the ester/amide bond. (50) Therefore, the radical cyclization reaction of allyl esters and allyl amides gives either relatively poor yields or methods have to be employed that tolerate low cyclization rates. A representative example is shown in Eq. 26. (18, 51)

(83%)

$$\text{(26)}$$
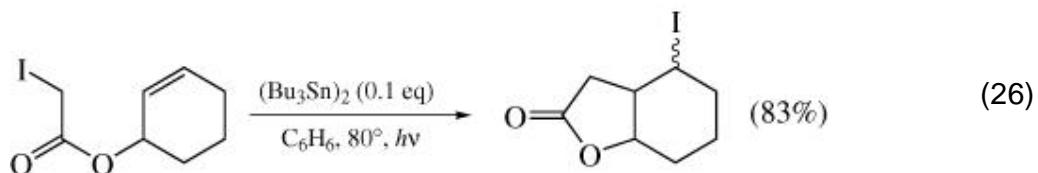
Several procedures have been developed to overcome these problems. The most popular is the so-called bromoacetal method, in which the ester carbonyl is introduced after the cyclization of an easily accessible bromoacetal precursor (Eq. 27). (52, 53)

$$(81\%)$$

$$(27)$$
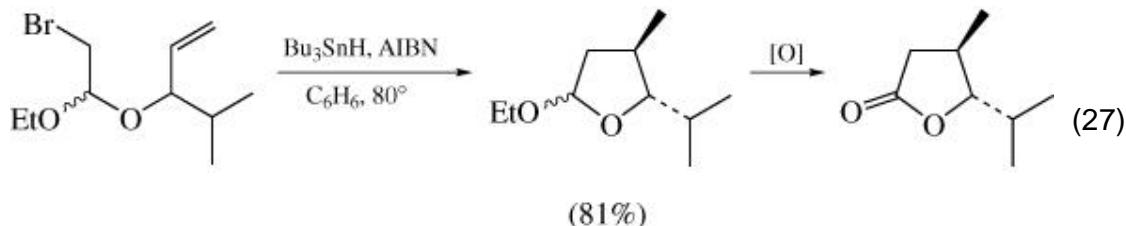
Furthermore, amide cyclization can be accelerated by substitution of the amide nitrogen with strong electron-withdrawing groups like tosyl or trifluoroacetyl (Eq. 28). (54)

$$(85\%)$$

$$(28)$$
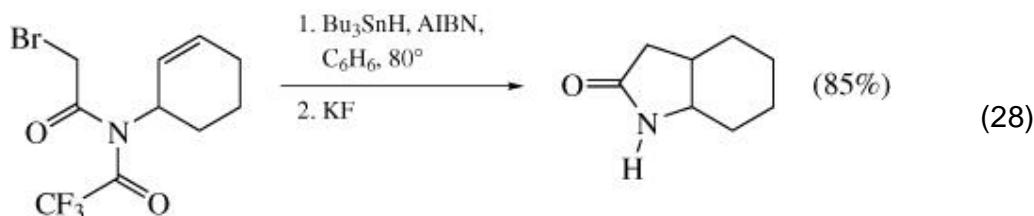
If silicon atoms are part of the radical chain, the regioselectivity of cyclization strongly depends on the substitution site. In simple 2- and 3-(dimethyl-sila)hexenyl radicals, the cyclization rate is reduced ($k_c \gg 10^4 \text{ s}^{-1}$) and cyclizations occur mainly in an endo fashion. The corresponding 4-substituted radical, however, cyclizes mainly in the exo mode. (55)

Of greater synthetic interest are the 5-hexenyl cyclizations of bromomethylsilyl ethers of allylic alcohols. (56, 57) Although the silicon atom is in the position α to the radical center, products of exo cyclization are formed (Eq. 29). Introduction

$$(80\%)$$

$$(29)$$
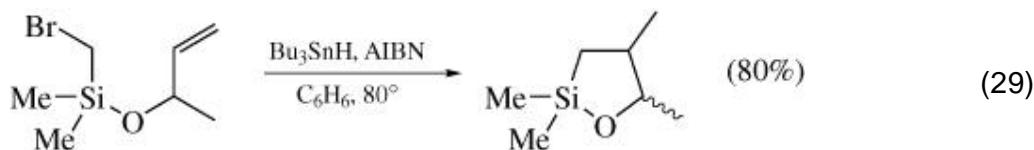
of a 5-substituent can reverse the regioselectivity, and six-membered rings are obtained in good yields (Eq. 30). (58)

(30)

(70%)
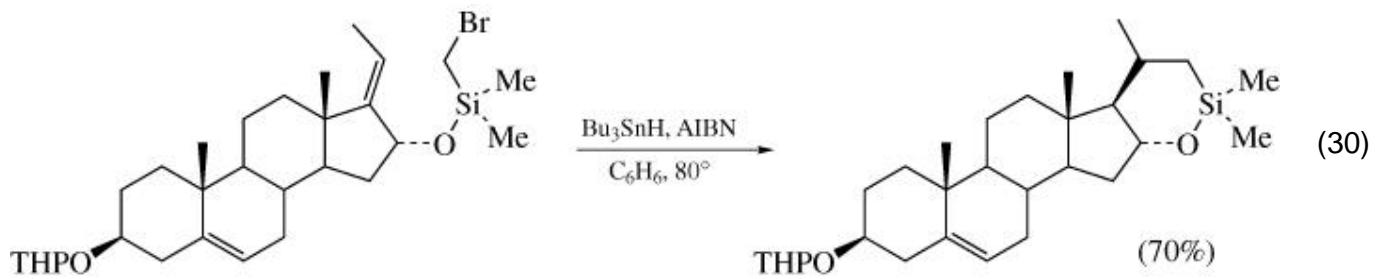
After cyclization, the carbon–silicon bond can either be cleaved reductively to give the hydrocarbon (57) or oxidized to yield the alcohol. (59) Thus, the heterocycles formed in this type of reaction usually serve the temporary purpose of stereoselectively introducing an alkyl or hydroxyalkyl group adjacent to an alcohol.

In related reactions, heterocyclic 5- and 6-membered rings are formed by cyclization of heteroatom-centered radicals. Radicals on oxygen and nitrogen have been employed in synthesis. In comparison to their carbon counterparts, oxygen radicals show enhanced reactivity and high cyclization rates ($k_c \gg 10^8$ s^{-1}). The cyclizations are irreversible and strictly exo selective even if steric hindrance is involved (Eq. 31). (60)

(31)

However, there are only a few examples of oxygen radical cyclizations in the literature (61, 62) owing to fast-competing reactions such as 1,5-hydrogen abstraction or β -fragmentation and to the limited methods for generation of these radicals.

With nitrogen-centered radicals one has to distinguish between aminyl and iminyl radicals. Alkyl-substituted aminyl radicals like **25** cyclize very slowly ($k_c \gg 10^3$ s^{-1}), and reopening of the cyclized radical **26** has a similar rate constant (Eq. 32). (63, 64)

(32)

25

k_c 3×10^3 s^{-1}
$k_{c'}$ 7×10^3 s^{-1}

26
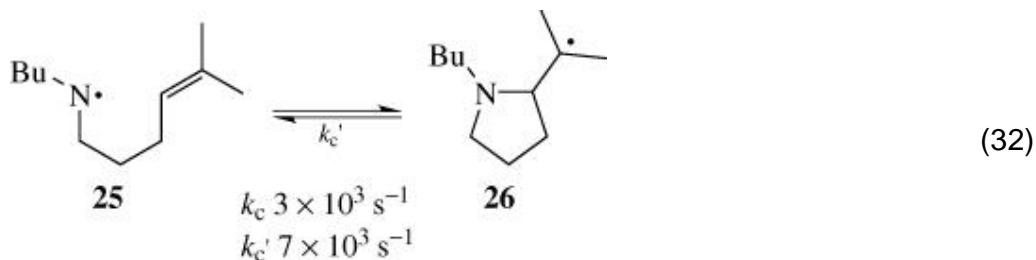
Increasing the electrophilicity at nitrogen accelerates ring closure and thereby shifts the equilibrium toward the cyclized radical. This can be done either by protonation or complexation to a metal center. (65) The 5-hexenyl cyclizations yield 5-ring products regioselectively from exo cyclization. A metal-complexed aminyl radical can be formed from amine **27** (Eq. 33). (66) One way of generating an

(81%)

(33)

27
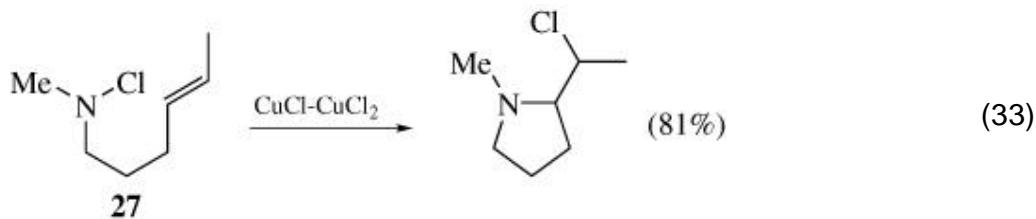
aminium radical cation such as **29** is photolysis of the corresponding *N*-hydroxy-pyridine-2-thione carbamate **28** under acidic conditions (Eq. 34). (67, 68)

t-BuSH, MeCN
CH$_2$(CO$_2$H)$_2$, *hv*

(34)

(92%)

28   **29**
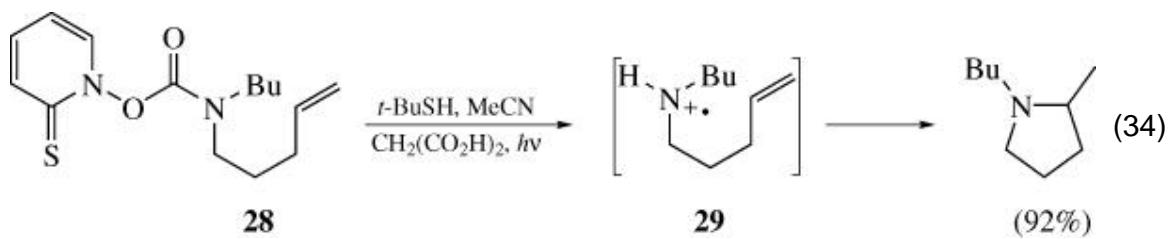
Iminyl radicals were introduced to synthesis very recently. They behave more like carbon-centered radicals and show a preference for cyclizations in the 5-exo mode. (69)

2.1.3. Formation of Medium-Sized Rings

Like many other methods, the formation of medium-sized rings by radical cyclizations is usually difficult. Only a few examples of the construction of 7-

and 8-membered rings are known. The rates of 7-ring ($k_c \approx 7 \times 10^2\ \text{s}^{-1}$)[13] and 8-ring cyclizations are at the lower limit of synthetic utility. Furthermore, 7-octenyl radicals show reversed regioselectivity, preferentially cyclizing in the 8-endo mode. Therefore, 7- and 8-membered rings are usually constructed by endo ring closure of 6-heptenyl and 7-octenyl radicals, respectively.

Radicals derived from α -keto esters by oxidative methods are especially useful for the formation of medium-sized rings (Eq. 35). (70) This is probably due

(35)

(69%) 2.5 : 1
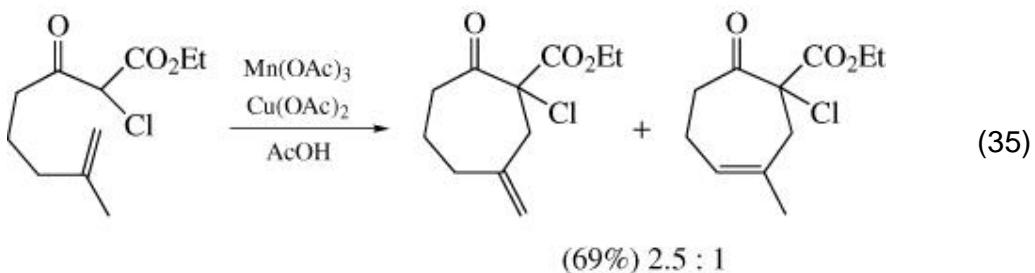
to the increased rate of endo cyclization of α -carbonyl substituted radicals and the absence of fast radical traps for these electron-poor radicals under oxidizing conditions.

The rate of 7-ring closure can be enhanced further if reactive acyl or aryl radicals are employed for the cyclization. Examples of this kind of reaction are shown in Eqs. 36 (71) and 37. (35) Whereas the first cyclization proceeds in a 7-endo mode, the second is an example of a rare 7-exo ring closure.

(36)

(65%)

$$\text{(71\%)} \quad \text{(37)}$$
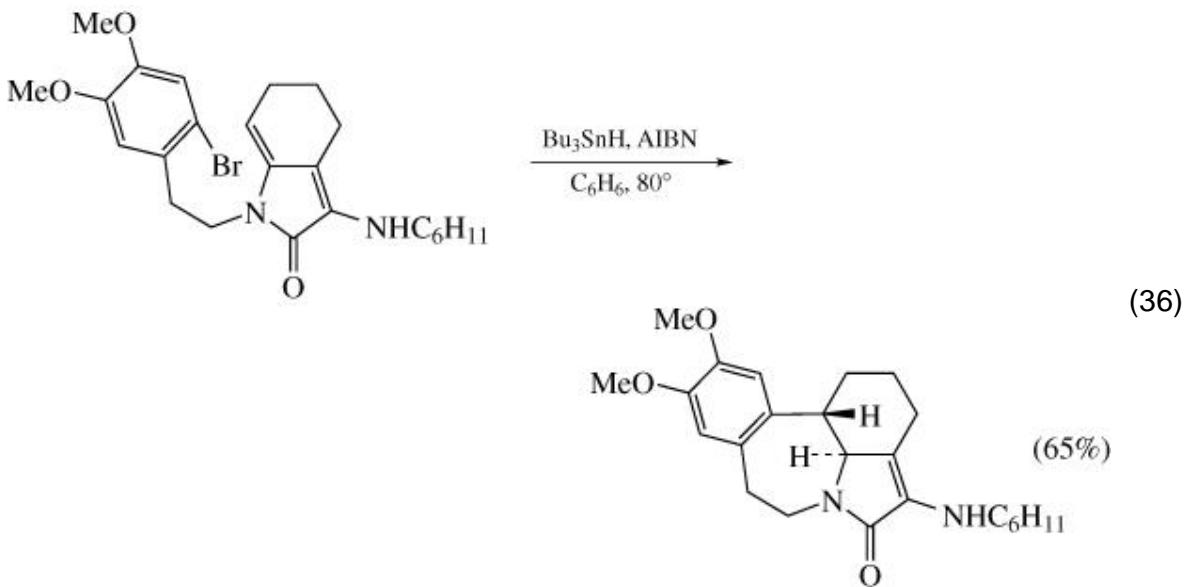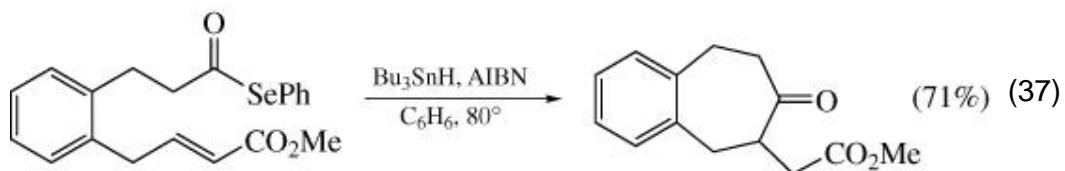
In cyclizations of heptenyl radicals with α -silyl ether groups in the chain, the product **30** formed from 7-endo ring closure is preferred over 6-exo (Eq. 38).

$$\text{(92\%)} \quad \text{(38)}$$

30
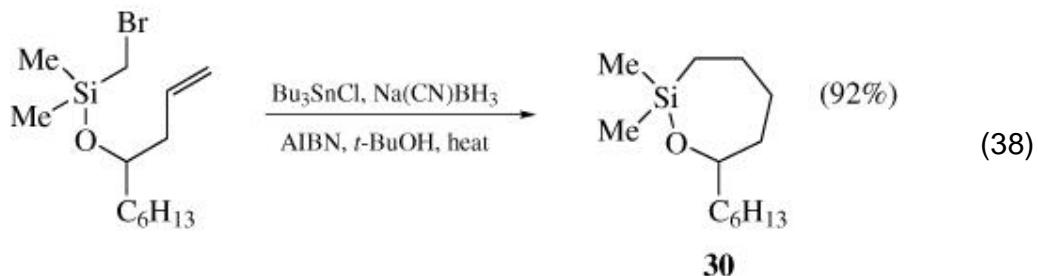
However, the regiochemistry can be reversed if a substituent is introduced at the terminal end of the alkene. (72)

In a different approach, medium-sized rings are often easily accessed by radical ring-expansion methods. This type of sequential radical reaction involves a cyclization that is followed by fragmentation of an unstable radical intermediate. Usually a carbon–oxygen double bond is employed as radical acceptor, and the regiochemistry of the fragmentation step is directed by a radical-stabilizing substituent like an alkoxycarbonyl group. (73) The general principle is illustrated by expansion of the 6-membered β -keto ester **31** to the 7-membered homolog **32**, shown in Eq. 39. (74, 75)

(39)
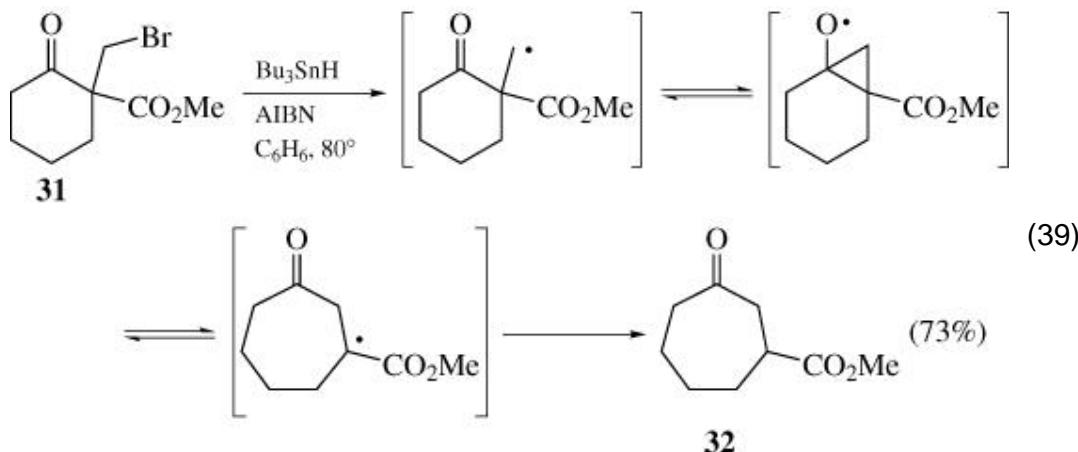
This method is also suitable for ring expansions by three or four carbon atoms, but not by two atoms because of the low rate of 4-exo closure. A radical-stabilizing substituent is essential to obtain useful yields. (73)

The problem of reversibility of the rearrangement can be overcome by introduction of the trialkylstannyl substituent in the position β to the rearranged radical. The fast β elimination of the stannyl group in radical **33** shifts the equilibrium to the side of ring-expanded product **34**. An example is shown in Eq. 40. (76)

(40)
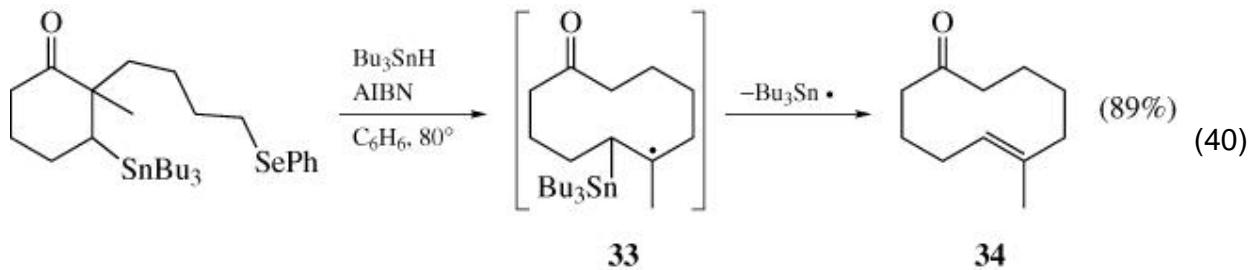
2.1.4. Macrocyclizations

Radical cyclization reactions can be employed for the construction of 10- to 20-membered macrocycles. (77, 78) These cyclizations resemble intermolecular radical additions and consequently occur preferentially in the endo mode. They are controlled by steric and polar effects, and to obtain reasonable yields it is usually essential to accelerate the cyclization by substitution of the alkene with an electron-withdrawing substituent (Eq. 41).

(41)
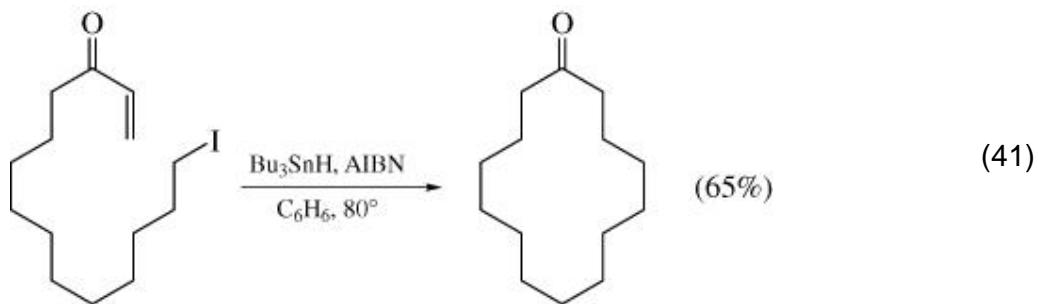
2.2. Stereochemistry

Radical cyclization reactions often proceed with high levels of stereoselectivity. Intensive theoretical and empirical studies have resulted in guidelines for rationalization and prediction of the configuration at new stereogenic centers. (13, 15) Because radical reactions have early transition states, the interpretation of selectivity usually focuses on the conformational bias of the radical and not on steric interactions in the final product.

2.2.1. Formation of Monocycles

The stereochemistry of 5-hexenyl radical cyclizations can often be rationalized with the guidelines originally proposed by Beckwith. (16) According to this model, the main diastereomer is formed via transition state **35**, which resembles a cyclohexane in the chair form with the

35
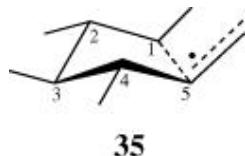
chair substituents adopting pseudoequatorial orientations. Thus, cyclizations of 3-substituted radicals yield mainly 3,5-*cis* disubstituted 5-rings, whereas 2- and 4-substituted radicals preferentially give the corresponding *trans* products.

The stereoselectivity of 1-substituted hexenyl radicals depends strongly on the size and electronic properties of the substituent. 5-Hexenyl radicals with simple alkyl groups react in accordance with the Beck with guidelines, yielding preferentially the 1,2-*cis* product 36 (Eq. 42). (79)

$$(42)$$

36

cis : trans = 5 : 1
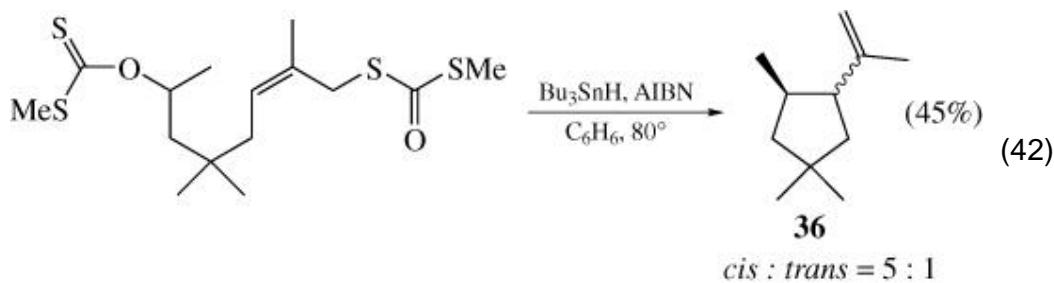
Preferred formation of *trans* disubstituted products is sometimes observed with precursors bearing polar substituents. This is illustrated by the example in Eq. 43, where the silyloxy substituent in the 1-position leads to complete inversion of the stereoselectivity in favor of the *trans* product. (80)

$$(43)$$

cis : trans = 1 : 7
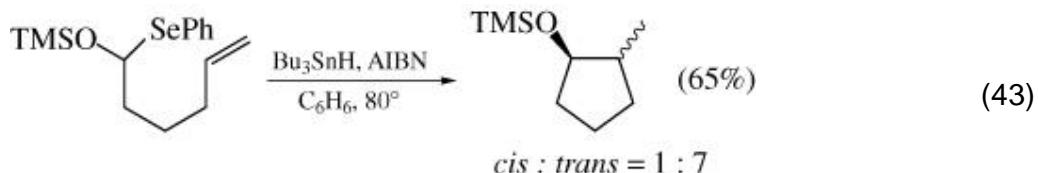
With the more polar sulfone substituent, exclusive formation of *trans* product **37** is observed (Eq. 44). (81) The high selectivity is attributed to steric and electronic

$$(44)$$

37

trans : cis = > 95 : 5
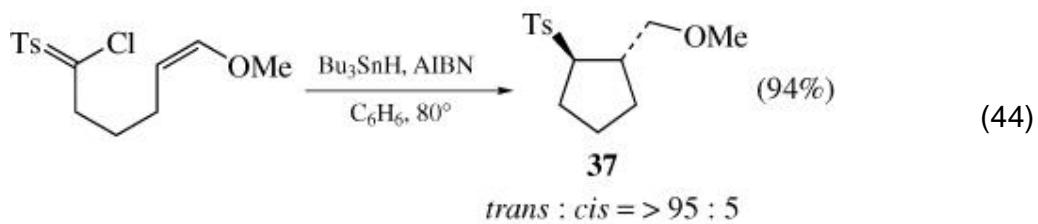
repulsions between the oxygen atoms of the sulfone and the methoxy group of the enol ether. 5-Hexenyl cyclizations of simple radicals with ester or keto substituents in the 1 position show virtually no stereoselectivity. (18)

Good stereoselectivities are frequently observed in the cyclizations of complex precursors. This is illustrated by the reaction of a complex tetrasubstituted precursor **38** that can be derived from a carbohydrate substrate (Eq. 45). Of the four

$$\text{(45)}$$

(63%) 78 : 22
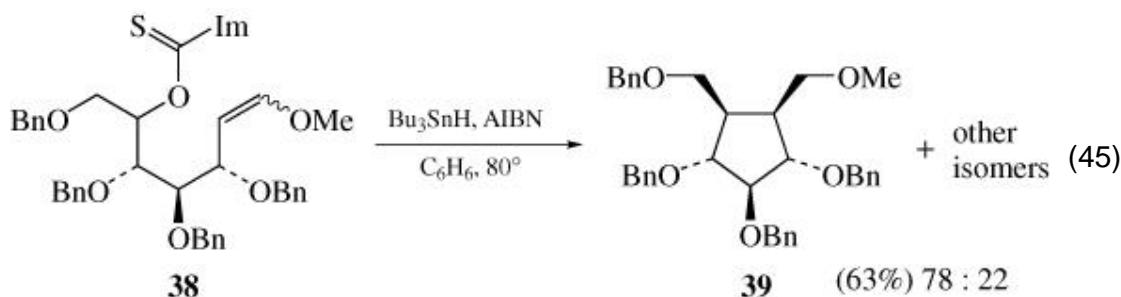
possible diastereomers, **39** is formed as the main product in accordance with the Beckwith rules. (82) However, in complex systems, additional factors like allylic strain and boat-like transition states have to be considered for the derivation of transition state models. (83)

Chiral auxiliaries can be also employed to direct addition of the radical to the alkene. The cyclization of a hexenyl radical bearing a chiral 8-phenylmenthyl ester at the 1 position gives the four isomeric cyclopentane isomers in a modest *cis:trans* ratio, but a considerably higher *S:R* selectivity of 4:1 (Eq. 46). (84)

$$\text{(46)}$$

cis : trans = 1.6 : 1   *cis : trans* = 1: 1.5

40 : 41 = 4 : 1 (90%)
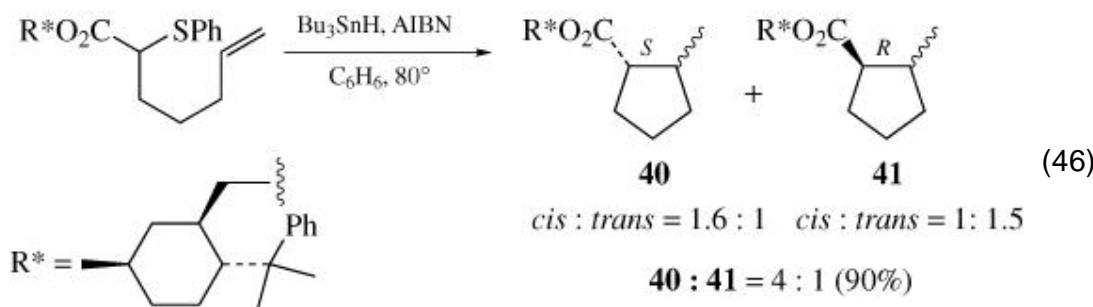
Cyclization of a hexenyl radical substituted with a chiral camphor sultam derivative yields the two diastereomeric methylenecyclopentanes **42** and **43** in a ratio of 9:1 (Eq. 47). (85)

42 : 43 = 9 : 1 (78%)

(47)
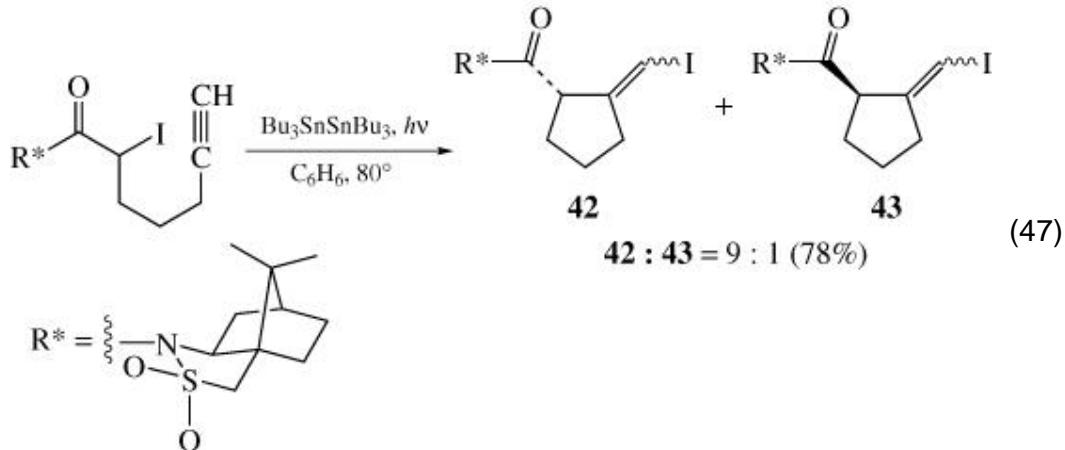
Rationalization of the stereoselectivities in the formation of heterocyclic rings is more difficult than in carbocyclic systems. Detailed theoretical and mechanistic studies of the influence of heteroatoms on the cyclization are not available. However, some trends emerge from examples in the literature.

If one carbon atom in the radical is substituted by oxygen, the Beckwith rules still apply. This is illustrated in the cyclization of the 2-substituted iodoethyl allyl ether **44** that preferentially yields the *trans* product (Eq. 48). (86)

cis : trans = 21 : 79 (77%)

(48)
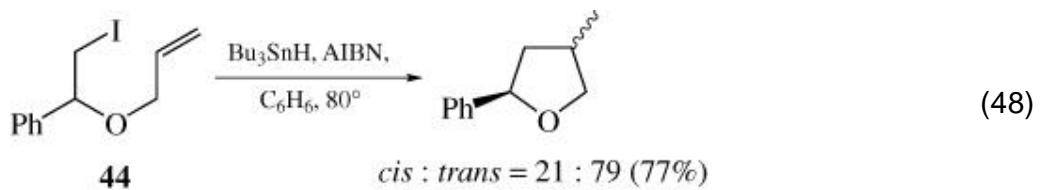
On the contrary, introduction of a nitrogen atom in the 3 position of a 2-substituted radical gives mainly the 2,4-*cis*-substituted pyrrolidine derivative (Eq. 49). (87)

R	*cis : trans*	
H	62 : 38	(90%)
Me	60 : 40	(85%)
Pr	60 : 40	(75%)
Ph	55 : 45	(85%)

(49)
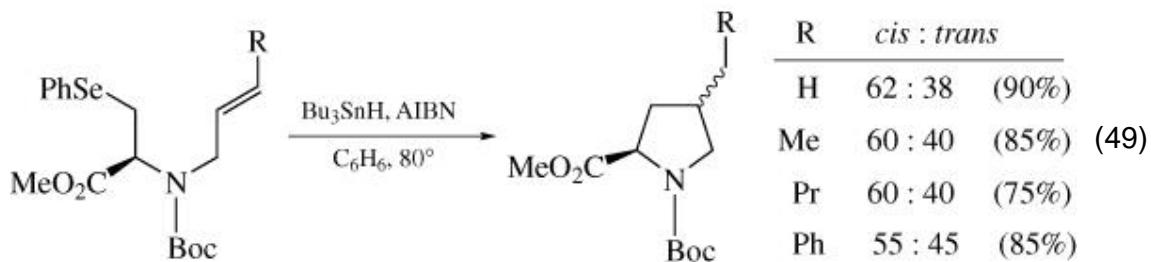
Hexenyl radicals with an ester or amide linkage in the chain show similar stereoselectivities. As in carbocyclic systems, 1-substituted radicals preferentially yield the 1,5-*trans*-disubstituted lactone **45** (88) (Eq. 50) or lactam **46** (89) (Eq. 51). The reasons for the selectivities are unclear, but as the amides and esters behave similarly,

$$\text{(50)}$$

45

trans : cis = > 99 : 1

$$\text{(51)}$$

46

trans : cis = 83 : 17
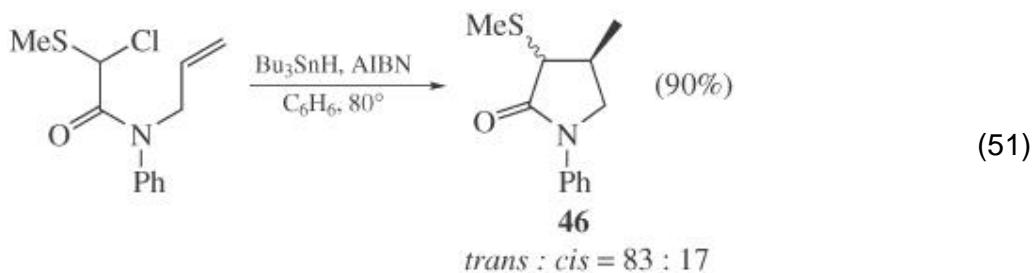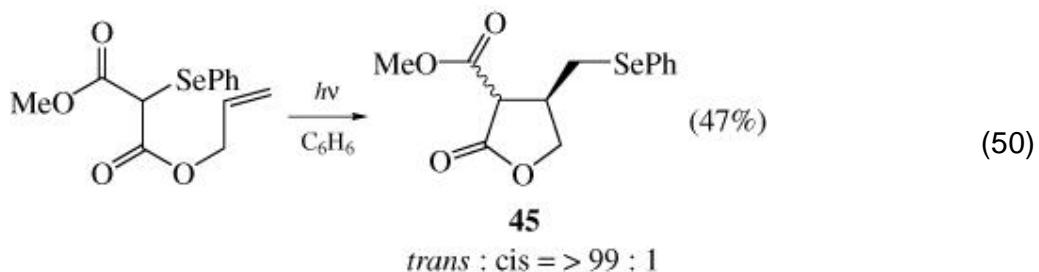
the stereoselectivity is probably determined by the carbonyl substituent in the ring.

Interestingly, the stereoselectivities in these systems seem to depend on the nitrogen substituent of the amide. This is demonstrated by cyclization of the hexenyl-type radicals with substituents in the 4 position. Whereas the benzyl substituted radical preferentially gives the 4,5-*trans*-substituted product, introduction of the tosyl group on nitrogen results in complete reversal of the selectivity (Eq. 52). (90, 91)

R	*cis : trans*	
CH$_2$Ph	10 : 90	(98%)
Ts	90 : 10	(89%)

$$\text{(52)}$$
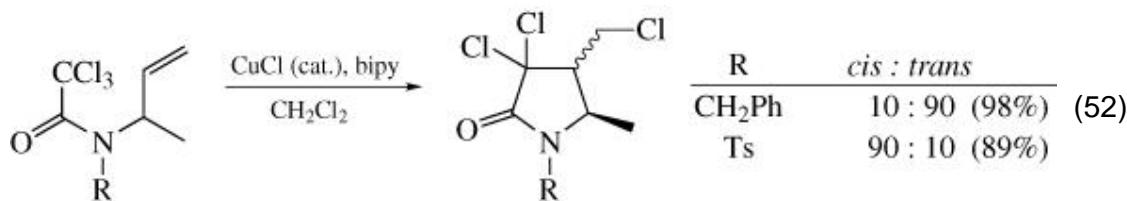
For the stereoselectivity of 6-exo cyclization of heptenyl radicals, a model can be applied that resembles the Beckwith model. Again, the preferred transition state adopts a chair-like conformation with the substituents in pseudoequatorial orientation. Thus, 2- and 4-substituted radicals should give preferentially *cis* products, and 1-, 3-, and 5-substituted radicals *trans* products. However, cyclizations of 2-, 3-, and 4-methyl-substituted radicals all exhibit a very small preference for the *trans* product (Eqs. 53–55). (17)

$$cis : trans = 43 : 57 \ (92\%) \tag{53}$$

$$cis : trans = 35 : 65 \ (91\%) \tag{54}$$

$$cis : trans = 37 : 63 \ (80\%) \tag{55}$$
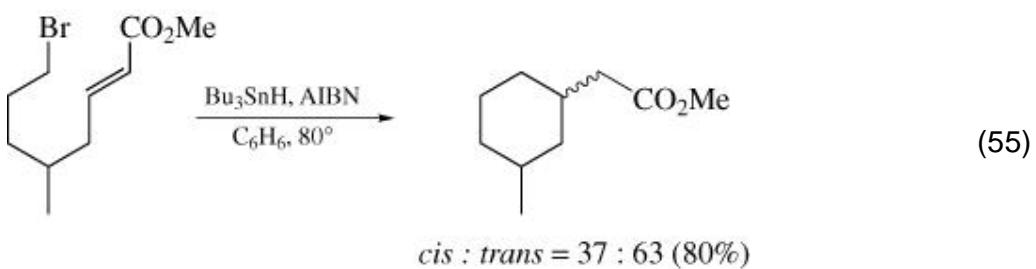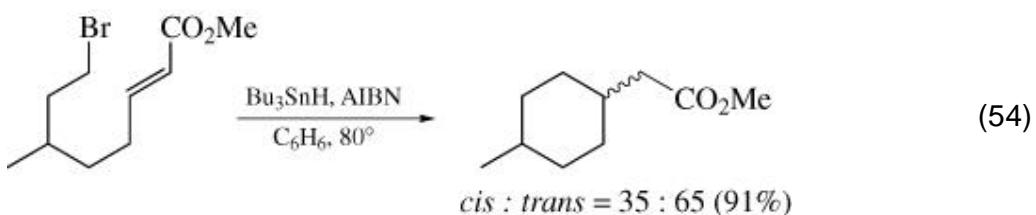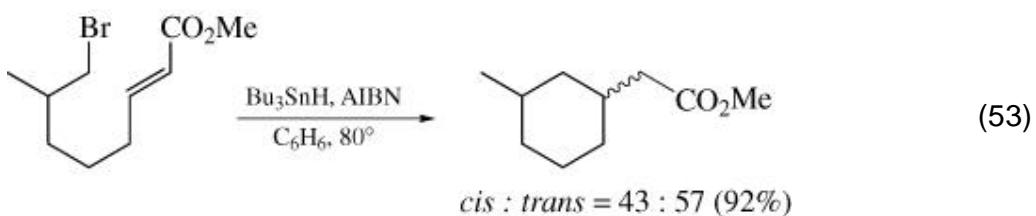
Therefore, the cyclohexane model seems to be of only limited value for heptenyl cyclization, and other possible transition states such as cycloheptane-like conformers, should also be considered. Nevertheless, in accordance with the model, an example is known of selective formation of *cis*-**48** from 4-substituted precursor **47** (Eq. 56) (92) and *trans*-**50** from 5-substituted precursor **49** (Eq. 57). (93)

$$(78\%) \quad (56)$$

$$(97\%) \qquad (57)$$
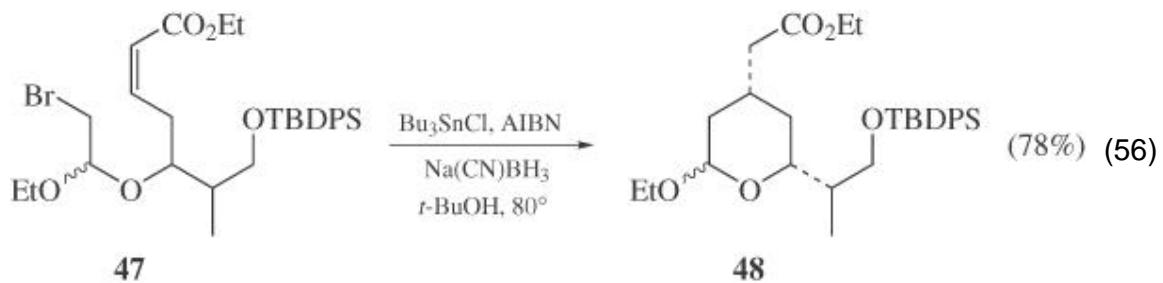
Furthermore, the *trans* product is also strongly favored in the cyclization of a heptenyl radical with a phenyl substituent in the 3 position. (48)

Heptenyl radicals with a substituent in the 1 position seem to cyclize preferentially to 1,6-*trans*-substituted 6-membered rings. Two representative examples for carbocyclic (37) and heterocyclic systems (94) are shown in Eqs. 58 and 59.

$$(71\%) \qquad (58)$$

cis : trans = 33 : 67

$$(74\%) \qquad (59)$$
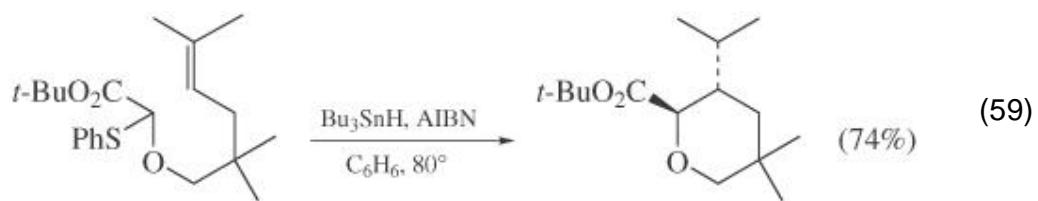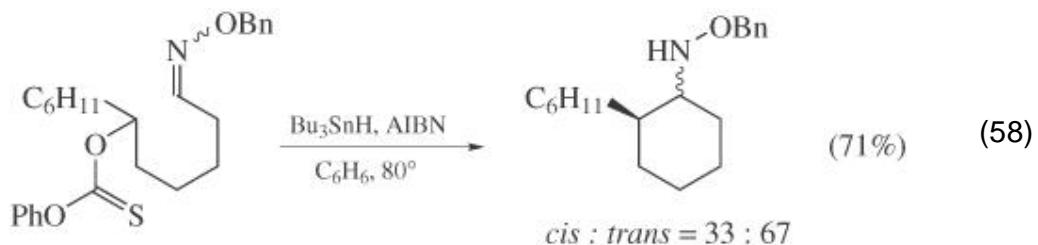
No data are available for the stereoselectivities in the formation of 7- and 8-membered rings. The stereoselectivities of radical macrocyclizations are comparable to the results in intermolecular radical reactions owing to the small influence of ring constraints. Stereoselectivity is observed in the cyclization onto acrylamide **51** bearing the 2,5-dimethylpyrrolidine chiral auxiliary. The endo: exo ratio of the four isomeric products is about 8:1; the two exo products **(53a/b)** are formed with no stereoselectivity, whereas the products from the endo cyclization **(52a/b)** are a 93: 7 mixture of diastereomers (Eq. 60). (95)

$$R : S = 14 : 1 \qquad R : S = 1 : 1$$

$$52 : 53 = 8 : 1 \ (40\text{-}45\%)$$

(60)
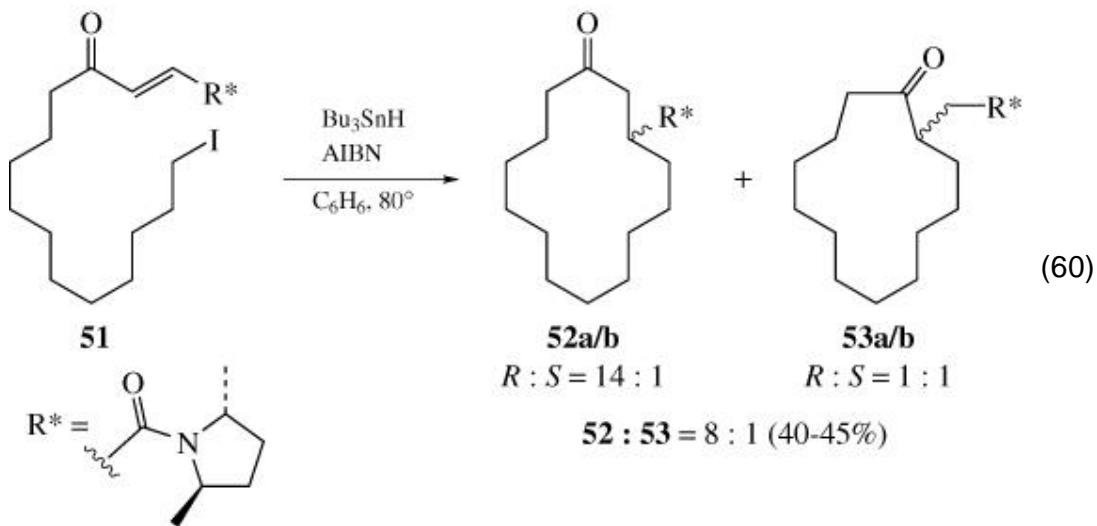
These results indicate that asymmetric induction is effective only if attack occurs at the α position of the chiral amide.

2.2.2. Formation of Bi- and Polycycles

The formation of bi- and polycyclic systems by radical cyclization constitutes a powerful synthetic method. (5) As in monocyclic systems, 5- and 6-ring cyclizations are the most frequently applied reactions. Annulations are usually achieved either by cyclization of a radical onto a cyclic alkene or by addition of a cyclic radical to a multiple bond in the side chain. Both reaction types afford preferentially the *cis* ring-fused products (5,5- 5,6- and 6,6-bicycles) owing to steric constraint imposed by the ring system. Two examples of these complementary methods are shown in Eqs. 61 (96) and 62. (97)

(61)

95 : 5

(62)
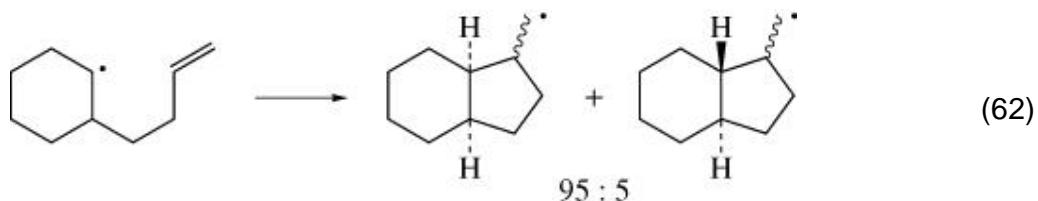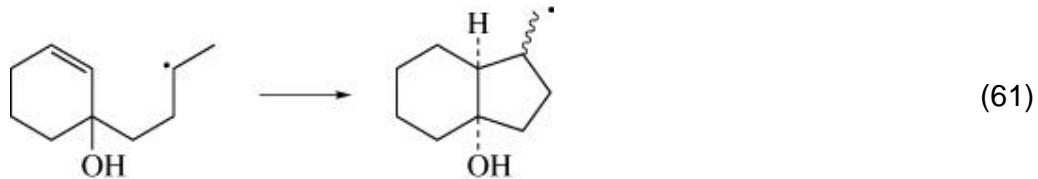
In addition to the geometry of ring fusion, cyclization also controls the stereochemistry at the 5- or 6-position of the newly formed ring. As in open-chain systems, the 1,5- or 1,6-*cis* configuration is usually preferred (Eq. 63). (49)

$n = 1, 70 : 30$ (61%)
$n = 2, 80 : 20$ (63%)

(63)
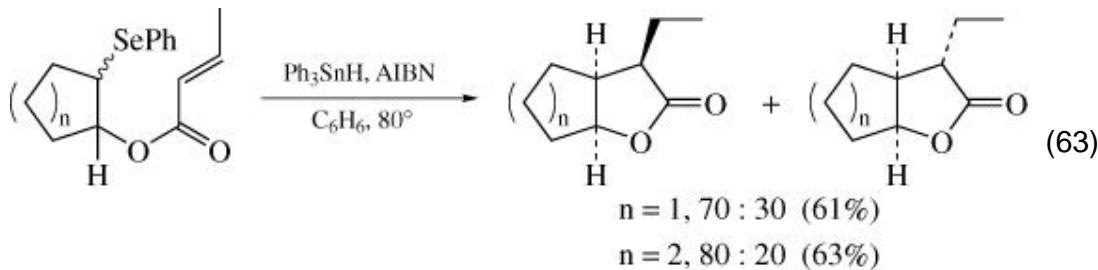
The stereoselectivities are rationalized by competing cyclohexane-like transition states preferentially adopting chair- or boat-like conformations (Beckwith model). However, in more complex systems, the 1,5- or 1,6-*trans* configuration is sometimes favored. In these cases, more detailed insight is necessary to rationalize the results. (83)

Cyclizations of highly functionalized precursors **54** derived from carbohydrates are intriguing (Eq. 64). In all cases, ring closure yields *cis*-annulated carbocycles

$$\text{(64)}$$

	R^1	R^2	
a	H	H	77 : 23
b	OBn	H	99 : 1
c	H	OBn	>1 : 99
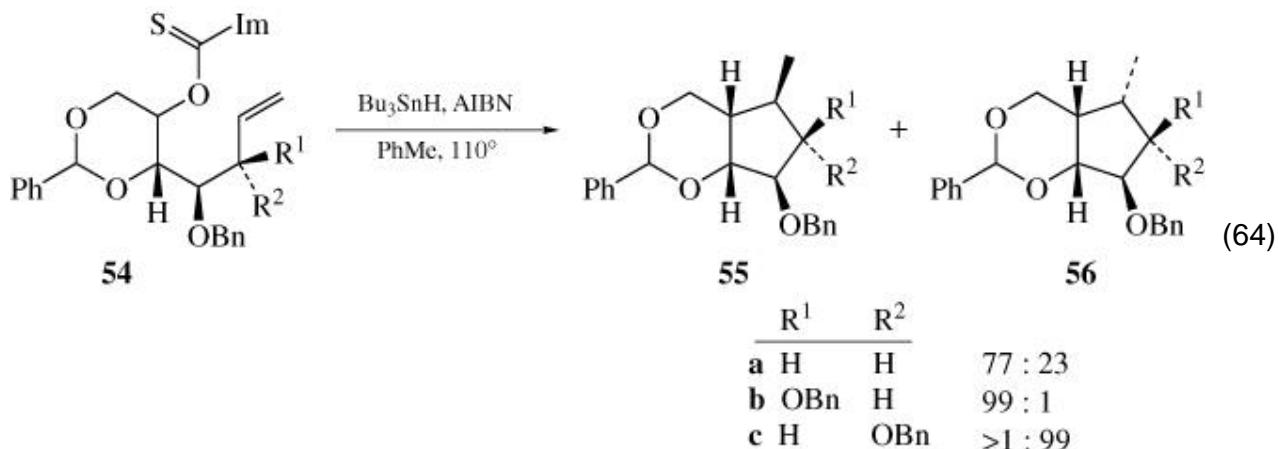
as mixtures of diastereomers. The stereochemistry of the bicycles is controlled primarily by the configuration at the C-4 carbon of the radical. The C-4 α -configurated radical gives 1,5-*trans*-(**55b**), and the 4 β -substituted radical gives 1,5-*cis*-(**56c**), both with high selectivity. The C-4 deoxy precursor (**54a**) shows diminished selectivity in favor of 1,5-*trans*-(**55a**). (82)

In constrained systems, the formation of *trans*-annulated polycycles is sometimes observed. A prominent example is the synthesis of *trans*-perhydroindanes via radical cyclization of bicyclic lactone **57** (Eq. 65). (98, 99) The tricyclic products

$$\text{(65)}$$

58 : 59 = 7 : 1 (93%)
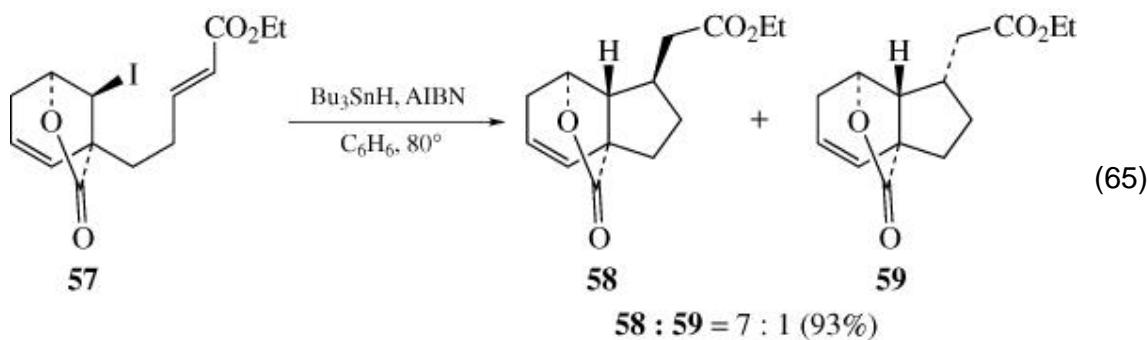
58 and **59** contain 5,5-*cis* and 5,6-*trans* ring fusions. The smaller, less flexible 5-ring lactone takes precedence in the formation of the *cis*-fused bicycle. In accordance with the Beckwith guidelines, the main isomer **58** possesses a 1,5-*cis* configuration.

Cyclization onto cyclic alkenes is the second common strategy used to build up stereoselectively *cis*-fused bi- and polycyclic systems. In these reactions, ring closure generates a cyclic prochiral radical in the α position to the ring junction. The consecutive reaction of this center is often stereoselective, and the attack of a radical trap occurs preferentially *anti* to the neighboring

substituent. The synthetic potency of this method is illustrated in the elegant synthesis of (+)-prostaglandin $F_{2\alpha}$. (100) In the key step, two new chiral centers are stereoselectively generated by 5-ring annulation and consecutive trapping of bicyclic radical **60** with alkene **61** (Eq. 66).

(66)

(58%)
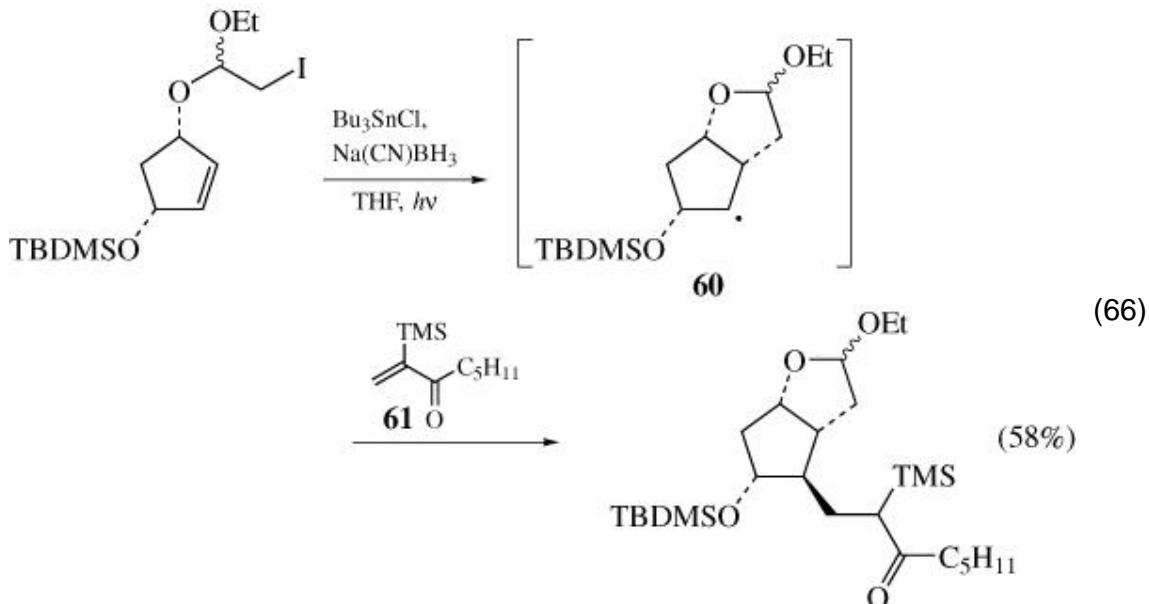
The high stereoselectivities of radical annulations are often used for the regio-and stereoselective introduction of alkyl substituents in cyclic systems. A prominent example of this type of reaction is the silylmethyl radical cyclization. This reaction is employed for stereoselective introduction of a methyl or hydroxymethyl group adjacent to a hydroxy group. The radical precursor is prepared by reaction of the allylic alcohol with (bromomethyl)chlorodimethylsilane. Radical cyclization gives the siloxane ring, which can be converted either into the *cis*-dihydroxy (57) or the α -methylated derivative. (101) In the total synthesis of talaromycin A **(62)**, this method was used to introduce stereoselectively the 1,3-diol unit (Eq. 67). (59)

(67)

62 (84%)
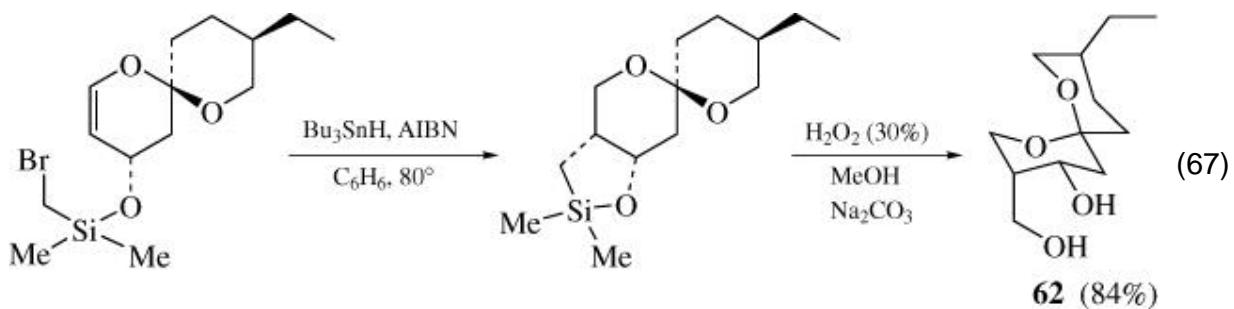
The 5-ring radical annulation of 7- and 8-membered rings preferentially yields *trans*-fused ring systems. (102, 103) The altered stereochemistry is rationalized by the different conformational bias compared to the 5- and 6-membered analogs. Introduction of ring substituents has only a slight influence on the *trans:cis* ratio (Eq. 68). (104, 105)

$$R^1, R^2 = H \qquad\qquad 87:13\ (51\%)$$
$$R^1 = OH, R^2 = H \qquad >99:<1\ (65\%)$$
$$R^1 = H, R^2 = OH \qquad 83:17\ (42\%)$$
$$R^1, R^2 = O \qquad\qquad 95:5\ (65\%)$$

(68)
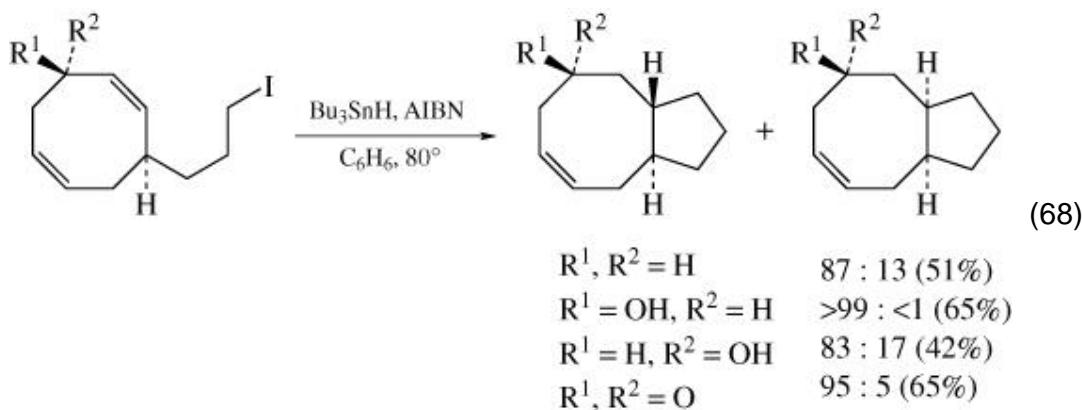
Other valuable methods for the construction of bi- and polycyclic systems are tandem reaction sequences (see Scope and Limitations). In these transformations, two or more consecutive radical cyclizations are connected in a reaction series. Contrary to simple cyclizations, the first-formed cyclized radical is not immediately trapped to the product, but instead serves as the initial radical of the second cyclization step. Although the overall transformations can be quite complex, the stereochemistry of the reaction can be rationalized if each step is treated separately.

This concept is exemplified by the synthesis of linear and angular triquinanes by a radical tandem cyclization. (106) In Eq. 69, two consecutive 5-exo cyclizations build up a tricyclic system **63** where all rings are exclusively *cis* fused. (107)

Bu₃SnH, AIBN

C₆H₆, 80°

$$Bu_3SnH, AIBN$$
$$C_6H_6, 80°$$

(69)

(72%)

63
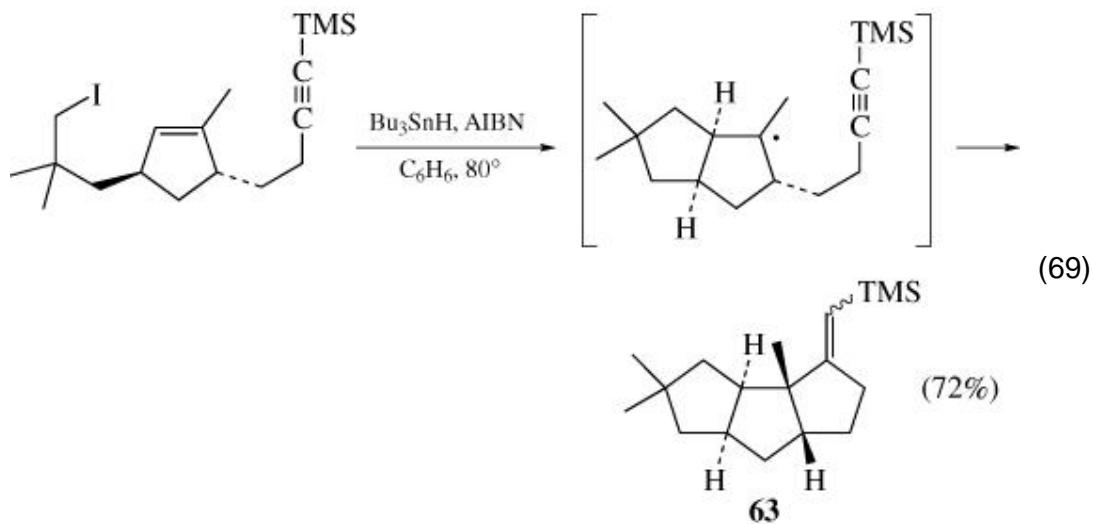
3. Scope and Limitations

The following section provides a discussion of the most popular methods for conducting radical cyclization reactions with special emphasis on the scope and limitations of every method.

3.1. Metal Hydride Methods

In this type of radical cyclization, metal hydrides are used as precursors and/or promoters of radical chain reactions.

3.1.1. Tin Hydride Method

The use of organotin hydrides is by far the most popular and general method for conducting radical cyclizations. (108) In a chain reaction, the initial radical **65** is generated from a suitable precursor **64** by atom or group abstraction by the trialkylstannyl radical **66**. After cyclization has taken place, trapping of cyclic radical **67** by tin hydride gives the reduced cyclic product together with the chain-propagating trialkylstannyl radical **66** (Eq. 70).

$$R^1X \; + \; R_3Sn\cdot \xrightarrow{-R_3SnX} R^1\cdot \xrightarrow{\text{cyclization}} R^2\cdot \xrightarrow{+R_3SnH} R^2H \; + \; R_3Sn\cdot \quad (70)$$
$$\quad 64 \qquad\quad 66 \qquad\qquad\qquad 65 \qquad\qquad\qquad 67 \qquad\qquad\qquad\qquad\quad 66$$
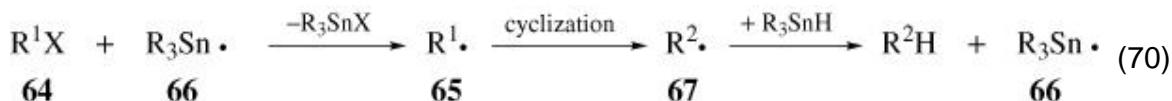
The chain reaction is usually initiated by thermally or photolytically induced homolytic cleavage of a chemical initiator, azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO). A correct match of initiator and reaction temperature is essential for a successful cyclization. (109) For initiation at low temperatures (as low as –78°) a mixture of triethylborane/oxygen can be used. (110)

A broad range of functional groups can serve as radical precursors. In order of decreasing reactivity, these include iodides, bromides, phenyl selenides, nitro groups, (111) chlorides, and phenyl sulfides, Iodides and bromides are the most common precursors and they can be used to generate all kinds of radicals including the reactive aryl and vinyl radicals as well as nucleophilic and electrophilic alkyl, stabilized benzyl, and allyl radicals. Numerous examples of these reactions can be found in the tables.

The use of phenyl selenides as precursors can be advantageous for different reasons. They can readily be synthesized by a number of methods and are usually more stable than halides (e.g., against solvolysis). Nevertheless, phenyl selenides are reactive enough for the generation of simple alkyl

radicals from alkyl phenyl selenides. An illustrative example is shown in Eq. 71. (112)

$$(80\%) \qquad (71)$$
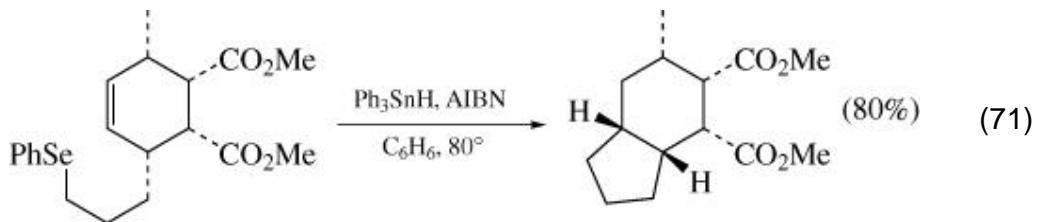
In addition, acyl phenyl selenides and phenyl selenocarbonates are the precursors of choice for generation of acyl (Eq. 72) (33) and alkoxycarbonyl radicals (Eq. 73). (36)

$$(86\%) \qquad (72)$$

$$(99\%) \qquad (73)$$
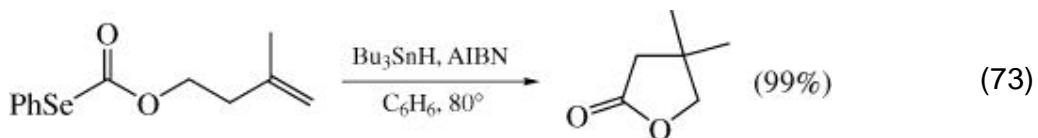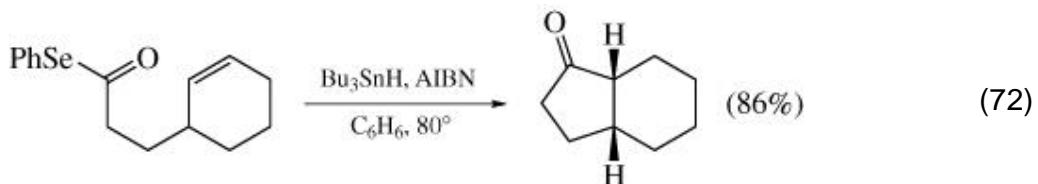
Use of the less reactive phenylthio group is usually restricted to the generation of stabilized radicals. For example, phenyl sulfides are preferred precursors for acylamino radicals because the corresponding halides are prone to solvolysis (Eq. 74). (113)

$$(89\%) \qquad (74)$$
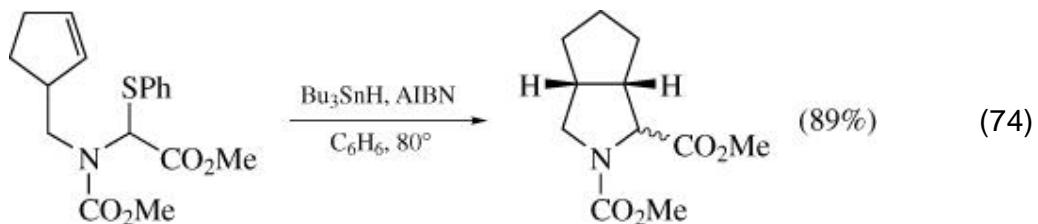
Alcohols **68** can serve as precursors for alkyl radicals via the corresponding thioxanthates **69**, thiocarbamates **70**, or thiocarbonates **71**. (114) The deoxygenated radical is formed via the addition/fragmentation mechanism illustrated in Eq. 75.

$$(75)$$
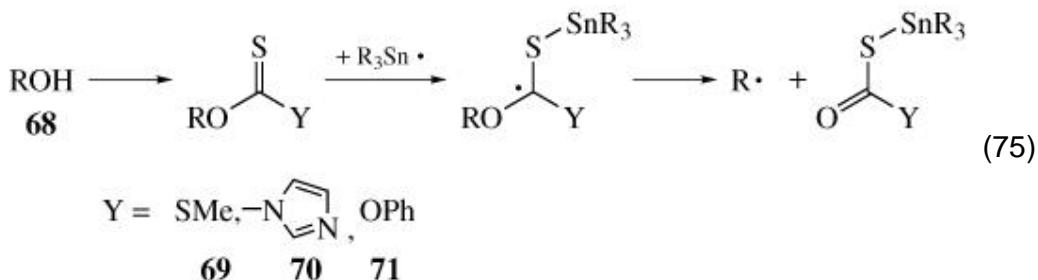
This method is best suited for the formation of secondary radicals because the tertiary precursors are difficult to synthesize and fragmentation of the primary radical is often too slow. The utility of the method is demonstrated by the cyclization of the highly functionalized carbohydrate derivative **72** shown in Eq. 76. (82)

$$(76)$$
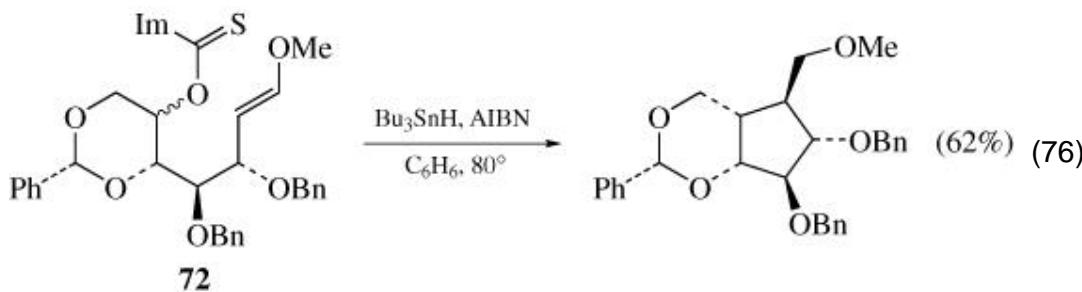
Aldehydes and ketones can be employed as precursors for α-oxysubstituted radicals. The carbonyl group can be reacted with tin hydride either directly (115) or via the corresponding mixed thio- (81) or selenoacetals. (116, 117) An example of the latter method is shown in Eq. 77.
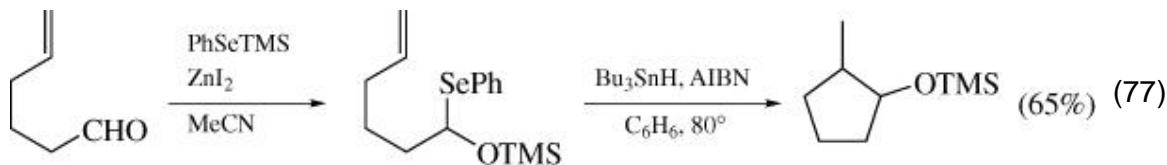
Alkynes can serve as precursors for vinyl radicals by reversible addition of a stannyl radical to the triple bond. The reversibility of the addition is important because the stannyl radical adds unselectively to all multiple bonds of a system and only the radicals with a favorable pathway will cyclize faster than they revert to the alkyne. (118) This method is of great synthetic utility because the precursors are readily prepared and the stannyl group is easily removed after the cyclization by protodestannylation. (119) A representative example is provided in Eq. 78. (120)
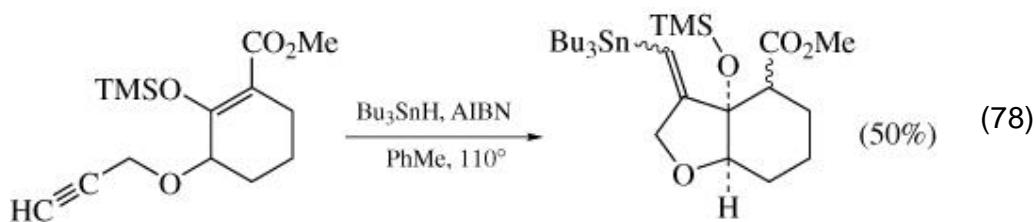
The most crucial point in tin hydride mediated cyclizations is competition between cyclization of the initial radical and its reduction by tin hydride. Since the cyclization is a unimolecular reaction and hydride abstraction is bimolecular, the undesired direct reduction can be suppressed by employing low concentrations of tin hydride. However, in these cases, precautions should be taken to ensure that the chain is efficiently propagated. Therefore, the most reactive precursor available should be employed. The two most popular methods for minimizing tin hydride concentration without the need for large solvent volumes are syringe pump addition of tin hydride and procedures that involve the use of catalytic amounts (0.1 equiv) of trialkyltin hydride or chloride in the presence of a coreductant like sodium borohydride (121) or sodium cyanoborohydride. (122) The borohydride recycles tin hydride by reduction of the tin halide formed during the reaction. This method is restricted to halide precursors because only tin halides will be reduced to the tin hydride. Equation 79 provides an example in which this method has been used to conduct a slow 7-endo cyclization reaction. (72)

(79)
(92%)
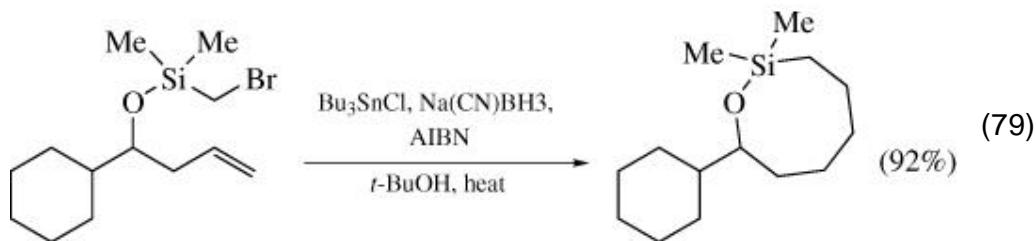
The catalytic procedure also simplifies isolation of the desired product because only catalytic amounts of tin compounds have to be removed after the reaction. The removal of tin residues often constitutes an important practical problem, and several special workup procedures have been developed. (18, 123)

An alternative approach to overcoming the problem of direct reduction of the initial radical is the use of metal hydrides that are slower hydrogen donors. One possible substitute for tributyltin hydride is the germanium analog. Hydrogen transfer from tributylgermanium hydride to alkyl radicals is 10–20 times slower than from tin hydride, and the germanyl radical is a powerful halogen atom abstractor. (124) In Eq. 80, tributylgermanium hydride is used to promote a slow 6-exo cyclization. (50)

(82%)
(80)
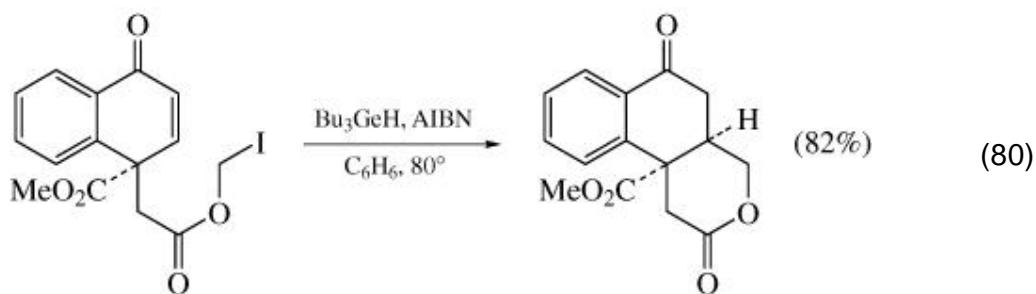
Another suitable tin hydride substitute is tris(trimethylsilyl)silane, a ~10 times slower hydrogen atom donor than tin hydride. (125) In addition, tris(trimethylsilyl)silane is nontoxic, and workup of the reaction mixture is usually simple. (126) Equation 81 shows an example in which tris(trimethylsilyl)silane is employed for a macrocyclization reaction. (127)

$$(81)$$

$$(55\%)$$
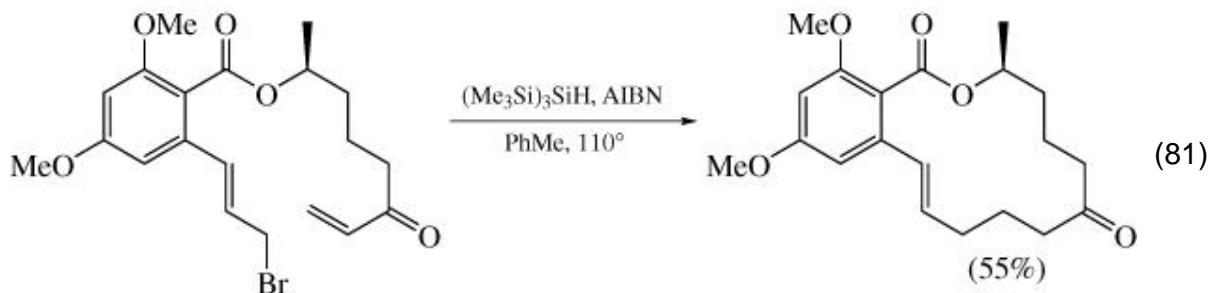
3.1.2. Mercury Hydride Method

The mercury hydride method is closely related to the tin method because metal hydrides are propagating the radical chain in both procedures. Precursors for the mercury hydride method are organomercury(II) halides or acetates. They are reduced by sodium borohydride, sodium cyanoborohydride, or tin hydride in an appropriate solvent (methanol, tetrahydrofuran, or dichloromethane). The so-formed transient alkylmercury(II) hydride **73** partly decomposes, thereby initiating the radical chain (Eq. 82). (128) The chain is

$$(82)$$
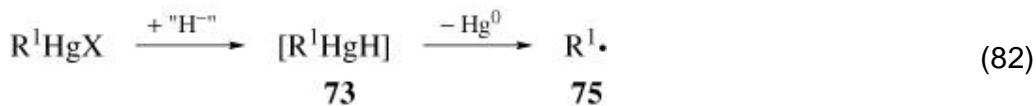
propagated by hydrogen abstraction by cyclized radical **74** from the alkylmercury hydride followed by spontaneous cleavage of the alkylmercury bond (Eq. 83).

$$(83)$$
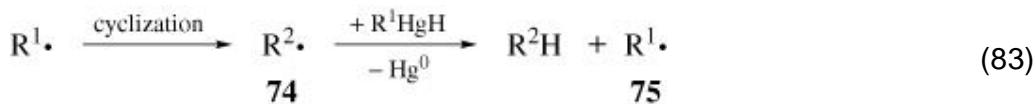
As in the tin method, direct reduction of the initial radical **75** always competes with cyclization. As mercury hydrides are very good hydrogen donors (~10 times faster than tin hydrides), only fast cyclizations can be conducted successfully. (129) However, the mercury hydride method has several advantages, including convenient reaction conditions (low temperature, no initiator needed), easy workup (metallic mercury is removed by filtration), and easy preparation of the alkylmercury halides. Methods for the preparation of the precursors include transmetalation of boranes, oxymercuration of cyclopropanes, mercuration of ketone hydrazones, and oxy- or

amidomercuration of alkenes. (6, 130) A representative example of the most important method (oxymercuration of alkenes) is shown in Eq. 84. (131)

(90%) (84)
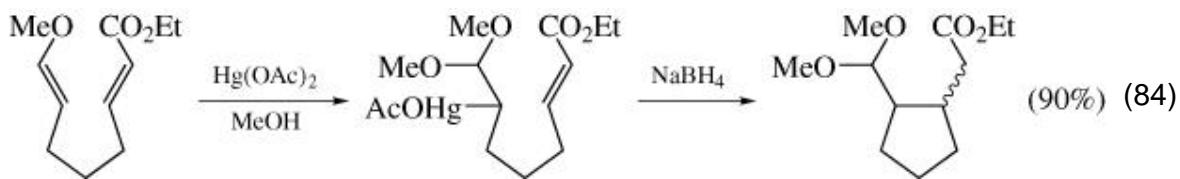
3.2. Fragmentation Methods

As an alternative to metal hydride based reactions, the chain-transfer agent Y·(76) is not generated by hydrogen abstraction from a stannane, but by a fragmentation reaction of cyclic radical **77** or **78**. As shown in Eqs. 85 and 86, the
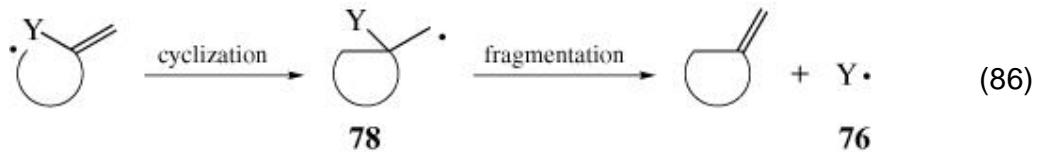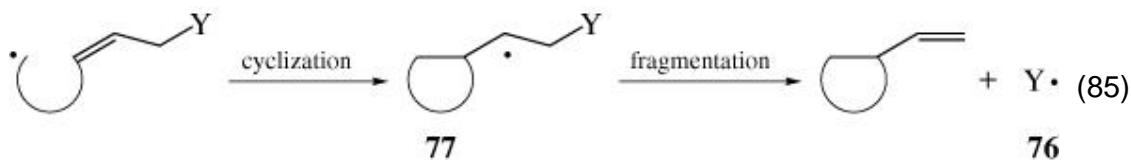
chain carrier can be included in either an allylic or vinylic radical acceptor. The use of allylic systems is more common because the alkene substituent sterically and sometimes also electronically biases the addition toward the desired regioselectivity. Vinylation usually needs an activating substituent that directs the addition to the carbon bearing the radical leaving group.

The most important advantage of the fragmentation method is the absence of any metal hydride and therefore there is no competing direct reduction of the initial radical. As usual, all reactions of the sequence have to be faster than unwanted side reactions of the intermediate radicals (recombination, reaction with the solvent). Hence relatively slow cyclizations can be conducted and less reactive precursors can be employed. Furthermore, the cyclizations do not yield reduced products (tin method) and the double bond is retained during the reaction.

Vinyl- and allylstannanes have proven to be especially useful radical accepting groups. (132) As in the tin hydride method, trialkylstannyl radicals carry the chain and therefore similar conditions (initiation, solvent, etc.) and precursors can be employed. Representative examples of both types of reactions are provided in Eqs. 87 and 88. (133, 134)

$$(65\%) \qquad (87)$$

$$(90\%) \qquad (88)$$
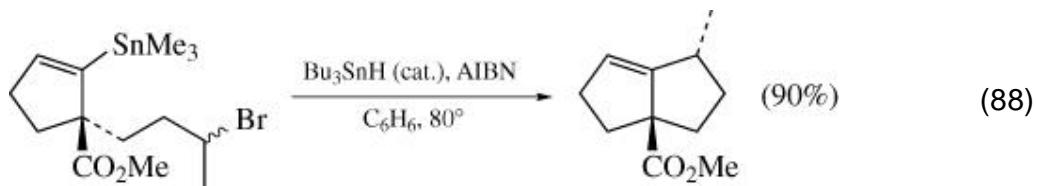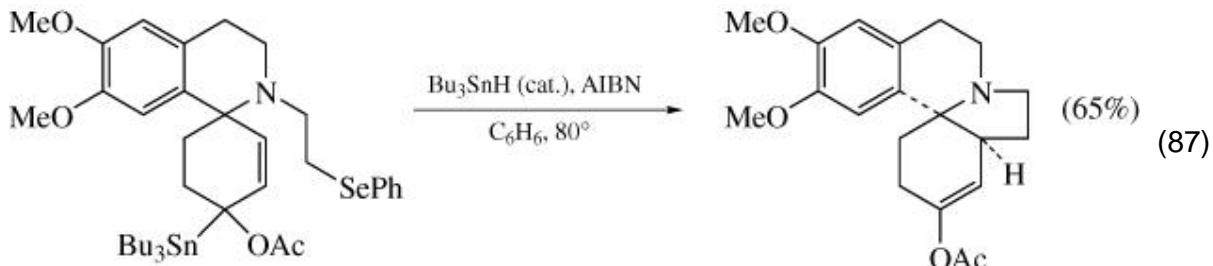
Generation of the initial radical in the fragmentation method is not restricted to atom or group abstraction methods; it can also be generated by reversible addition to a multiple bond. (135) The example in Eq. 89 shows a radical isomerization of an allyl sulfone **79** that involves a cyclization step. (136)

$$(75\%) \qquad (89)$$
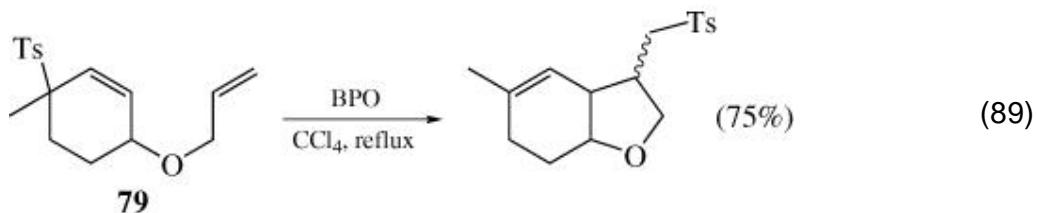
In a method that is closely related to the fragmentation method, the chain-carrying radical is generated via homolytic substitution rather than a fragmentation reaction. Radicals are formed from alkylcobalt derivatives, which can readily be prepared from the corresponding alkyl halides. (137) The cobalt–carbon bonds are very weak, and homolytic substitution at carbon can take place. (138) The released cobalt(II) radical functions as the chain carrier

and abstracts a halogen atom from the starting halide. To obtain reasonable rates for the abstraction reaction, only activated precursors like polyhalogenated alkanes or sulfonyl iodides can be employed. However, this method constitutes one of the few radical reactions by which three-membered rings can be formed. An example of this reaction is shown in Eq. 90. (139, 140)

$$\text{(90)}$$
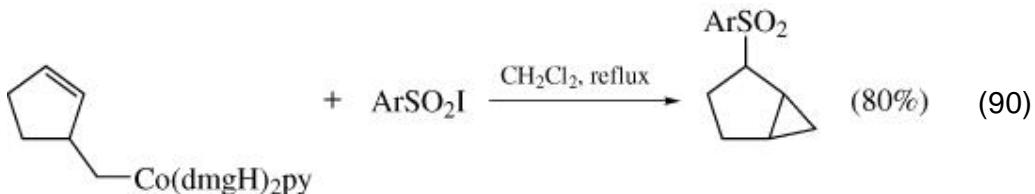
Radical cyclizations via homolytic substitution reactions are not restricted to reactions at carbon atoms. There are examples in the literature in which the substitution takes place at selenium (141) or silicon. (142)

3.3. Thiohydroxamate Method (Barton Method)

One of the most important radical chain methods where alkyltin radicals are not part of the reaction is the thiohydroxamate or Barton method. This is a useful method that can be employed for a broad variety of transformations that proceed via radicals (e.g., inter- and intramolecular bond formation or functional group interconversion). (143, 144) The radical precursors are thiohydroxamate esters **80** that can easily be prepared from carboxylic acids. (145-147) Although thiohydroxamate esters **80** can often be isolated, they are usually prepared and reacted in situ. The radical chain is initiated by thermolysis or by visible light photolysis of thiohydroxamate esters **80**. (148) The propagating steps involve addition of the cyclic radical to the thiohydroxamate unit followed by a rapid fragmentation of the ensuing intermediate **81** to generate the initial alkyl radical **82** (Eq. 91). (149)

$$\text{(91)}$$
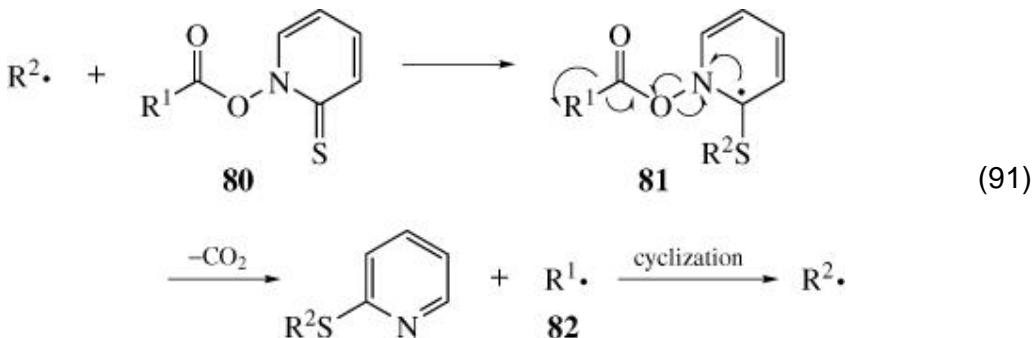
In contrast to the metal hydride based reactions, the chain-terminating step is not hydrogen abstraction but transfer of a thiopyridyl group that can be employed for further transformations. The lower rate limit for radical cyclizations that can be conducted successfully by this method is determined by the rate of addition of the uncyclized radical to the starting thiohydroxamate. For primary radicals, the rate of this reaction is very similar to the rate of hydrogen abstraction from tin hydride. As in the metal hydride methods, the formation of uncyclized products can be suppressed by lowering the concentration of the precursor. An example of a cyclization that is conducted by the thiohydroxamate method is shown in Eq. 92. (150)
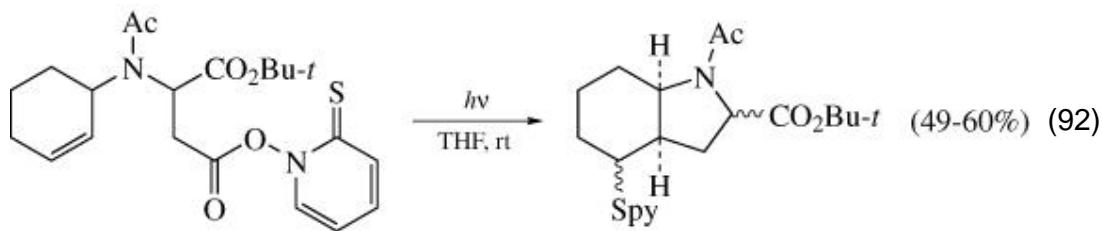
Use of the thiohydroxamate method is not restricted to the generation of carbon-centered radicals. If carbamate derivatives are used as precursors, aminyl radicals can be generated. (151) High yields of cyclic products are obtained in acidic reaction media. (68, 152) Presumably, the nitrogen is protonated under these conditions and the resulting aminyl radical cation cyclizes more rapidly. If a good hydrogen donor like a thiol is present, the cyclic radicals abstract hydrogen to form the reduced products, and the radical chain is propagated by the liberated thiol radical (Eq. 93). (153)
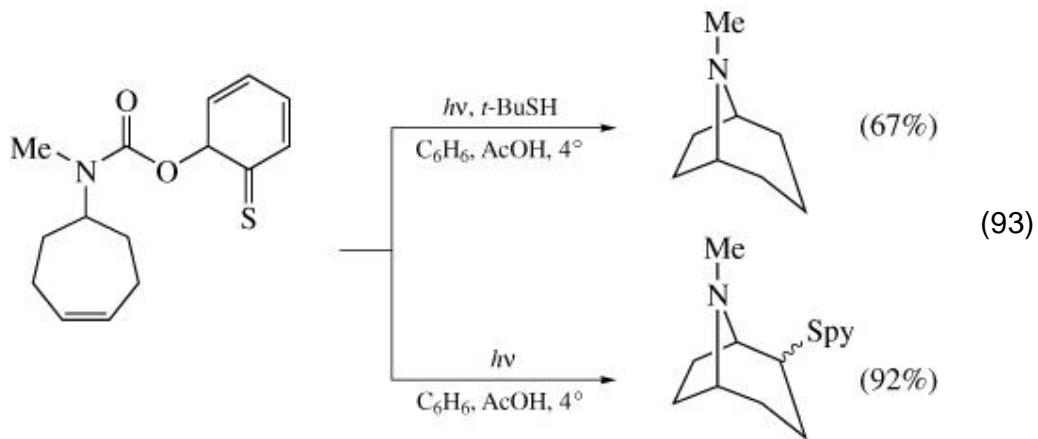
3.4. Atom Transfer Methods

The introduction of two new substituents to a multiple bond via a radical chain addition is one of the basic transformations in radical chemistry. A prominent example is the anti-Markownikov addition of hydrogen bromide to alkenes (Kharasch reaction). This type of reaction constitutes the shortest possible radical chain because the initial radical is formed by direct reaction of the substrate with the final radical of the chain. For cyclization reactions, this usually means that the net transformation is isomerization of the starting material. The atom transfer method is ideally suited for conducting slow radical cyclizations because there is no fast radical trap (like tin hydride) present in the reaction medium. The lower rate limits for the cyclization and the atom-transfer step are determined by the unwanted chain termination reactions (radical–radical recombination, reaction with solvent). The cyclization step is usually fast enough because the ring closure is an exothermic reaction (a π bond is converted to a σ bond). However, to obtain suitable rates for the atom-transfer step, the initial radical should be thermodynamically more stable than the cyclic radical.

Depending on the atom that is transferred during the cyclization, the reactions can be divided into hydrogen or halogen transfer methods.

3.4.1. Hydrogen Atom Transfer Method

Because of the low rates of hydrogen abstraction, application of the hydrogen transfer method is restricted to cyclizations of precursors with activated C-H bonds. (1) Useful precursors (e.g., malonates or acetoacetates) bear multiple radical stabilizing substituents like carbonyl or nitrile groups. Cyclization of these electrophilic radicals is often reversible, and because of the slow hydrogen abstraction of the cyclic radical, thermodynamically controlled products can be obtained. (1, 20, 21)

An illustrative example is shown in Eq. 94. (22) This reaction is initiated by benzoyl peroxide (BPO), a common initiator for hydrogen transfer reactions. Because

$$(94)$$
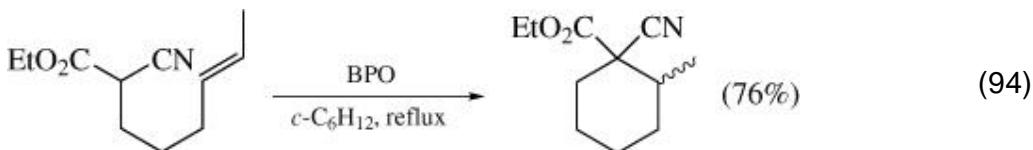
of the short reaction chain length resulting from the inefficiency of hydrogen transfer, a large amount of peroxide is necessary. From mechanistic studies it is known that the initial radical cyclizes almost exclusively to the 5-ring. (18)

However, because of the long lifetime of the intermediate radicals, thermodynamic equilibrium is established via reopening and 6-endo cyclization to the thermodynamically favored 6-membered ring.

However, because of the slow and unselective nature of bimolecular hydrogen transfer and the limited variety of suitable precursors, hydrogen atom transfer cyclizations are of only limited value for organic synthesis. Furthermore, equivalent radical cyclizations can often be conducted more conveniently by the tin hydride or halogen atom transfer methods.

3.4.2. Halogen Atom Transfer Method

The halogen atom transfer method is synthetically more useful than the hydrogen atom transfer method. The increased rate of the halogen transfer step results in a more efficient chain process. In addition, the halogen atom is retained in the final product. Suitable precursors for these cyclizations are iodides and polyhaloalkanes. With the latter, low-valent metals are often employed to promote the reaction. Copper(I) salts and ruthenium(II) complexes efficiently catalyze the cyclization of perchlorocarbonyl compounds such as trichloroacetates, trichloroacetamides, and α , α -dichloro esters. A recent review provides an extensive summary of the work in this area. (154) A representative example is shown in Eq. 95. (91)

(98%)　　　　(95)
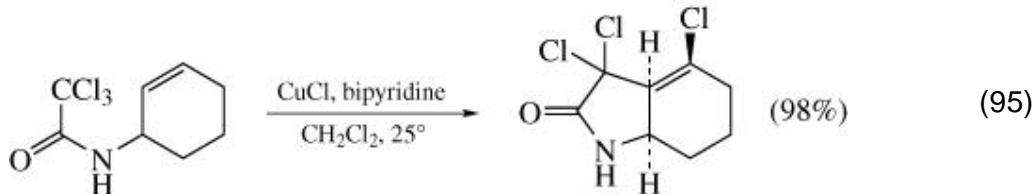
Because there is no good hydrogen donor present, metal-promoted reactions have proven to be especially useful for conducting slow cyclizations. An illustrative example is provided in Eq. 96 where an unfavored bridged system is formed. (155)

(88%)　　　　(96)
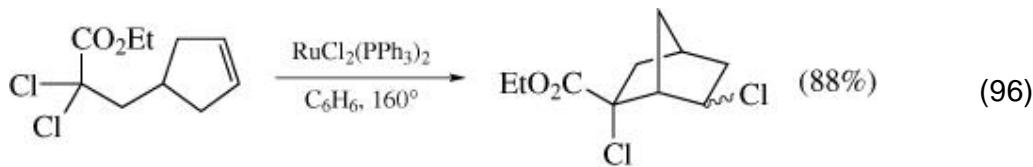
Metal catalysis is not necessary if α -iodo carbonyl compounds are employed as radical precursors. (156) These iodo compounds are excellent substrates for halogen transfer reactions because abstraction of an iodine atom by the intermediate cyclic radical is exceptionally fast ($k > 10^7$ s^{-1}). (157) These reactions can be run at high concentrations, and they are usually initiated by photolysis in the presence of catalytic amounts of a hexaalkylditin. The cyclic products are formed in high yields under kinetic control and can be isolated or further transformed in situ. Again, this method is suited for conducting slow cyclizations, such as formation of large rings, formation of bridged ring systems, or cyclization of α -iodo esters. Equation 97 provides an example of a relatively slow 6-endo cyclization. (18) The intermediate iodide **83** is not isolated but is directly reduced with tin hydride.
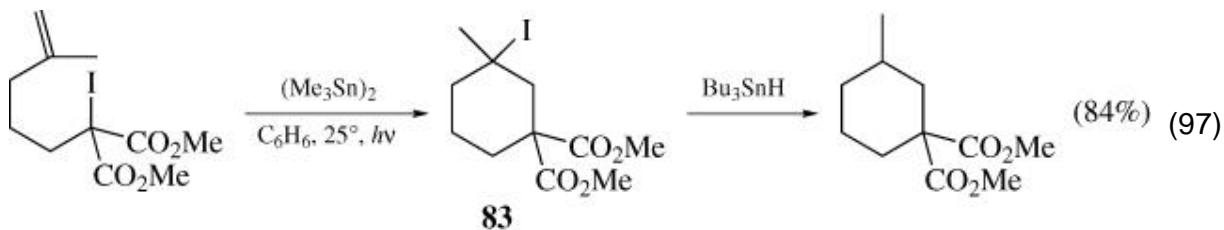
However, cyclization of unstabilized radicals by the iodine transfer method is more restricted. In these cases, the intermediate radical and the initial radical are often of similar stability and therefore iodine atom transfer is rather slow. Nevertheless, iodine transfer cyclizations are possible if the initial radical is tertiary and the intermediate is primary or secondary. The reaction chains are usually short and the yields mediocre. (158) The isomerization reactions of alkynyl iodides to cyclic vinyl iodides are high-yielding and fast cyclizations (Eq. 98). (159, 160) This
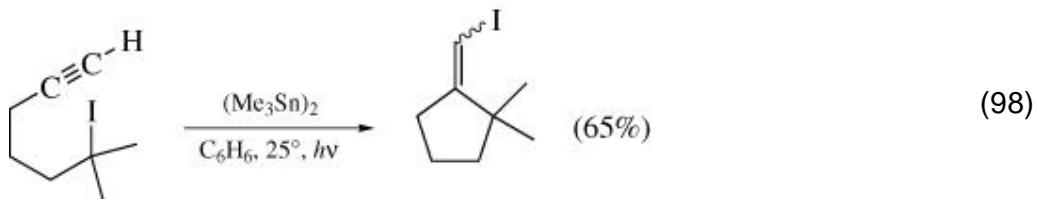
is due to the fast and exothermic abstraction of iodine atoms by the intermediate vinyl radical.

The atom transfer method is not restricted to the generation of carbon–centered radicals. Because oxygen–halogen and nitrogen–halogen bonds are relatively weak, they can be used for heteroatom radical cyclizations

via the atom transfer method. *N*-Halo amines and amides can serve as precursors for aminyl and amidyl radicals. (64) The halogen transfer cyclizations are usually promoted by protonation or addition of low valent metals (TiCl$_3$, CuCl/ CuCl$_2$). (161) A representative example of a copper-catalyzed cyclization is presented in Eq. 99. (162)
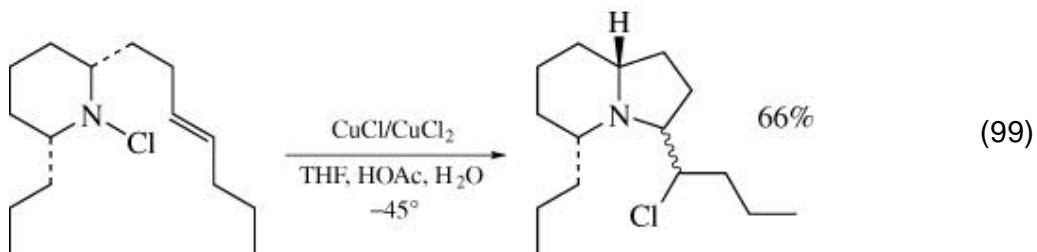
The products of these cyclization reactions are nitrogen mustards that are valuable precursors for further transformations via aziridinium ions. (163) Atom transfer cyclizations can also be conducted with *N*-nitrosoamines and *N*-nitrosoamides. These cyclizations are initiated by photolysis, and a nitroso group is transferred instead of halogen. (164) Atom transfer cyclizations involving oxygen-centered radicals employ hypohalites as precursors. These are generated in situ from the corresponding alcohols. (165, 166) For example, this method has been used in the synthesis of the spiroketal **84** (Eq. 100). (61)
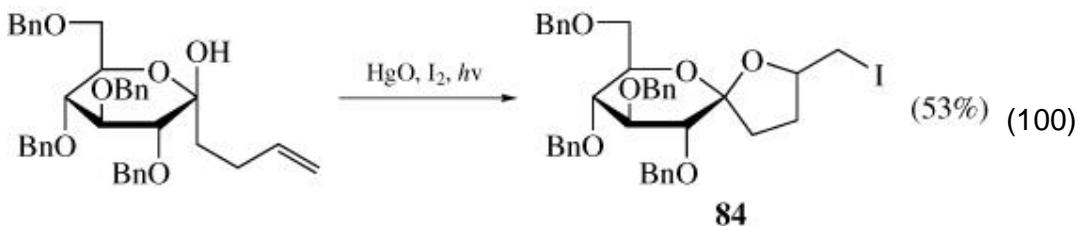
3.5. Radical/Radical Coupling Methods
In contrast to the methods discussed so far, radical/radical coupling methods are nonchain processes. Therefore, it is not sufficient to generate a small amount of radical to start the reaction; the intermediate radical must be generated in stoichiometric amounts. Control of selectivity is the basic problem in these methods. Radical recombinations usually have rates that are close to diffusion control. However, there are methods available that allow the preferred formation of cross-coupled products.

One example is the mixed Kolbe coupling reaction where one precursor is

employed in excess (Eq. 101). (167) Because the rate of radical formation from both precursors is similar, the concentration of the radical derived from the excess acid will always be higher than the concentration of the cyclic radical. Therefore, the

$$\text{(63\%)} \qquad \text{(101)}$$
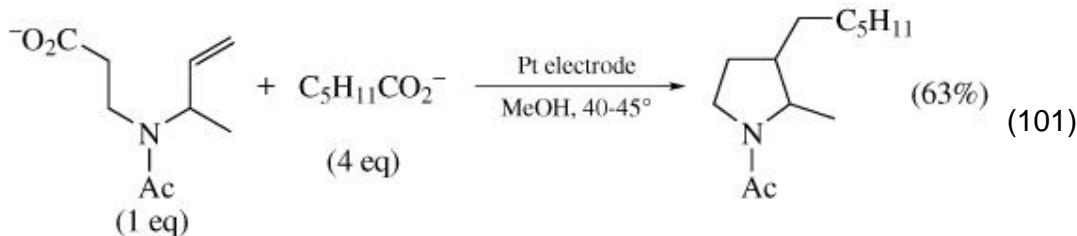
cyclic radical will preferentially give the cross-coupled products. However, this method is of only limited value and is probably restricted to examples where one of the acids is inexpensive.

A more general method for selective radical/radical coupling is the cyclization of organocobalt(III) complexes.

RCo(salen)py **85**
Alkylcobalt salen

RCo(salophen)py **86**
Alkylcobalt salophen

RCo(dmgH)$_2$py **87**
Alkylcobaloxime
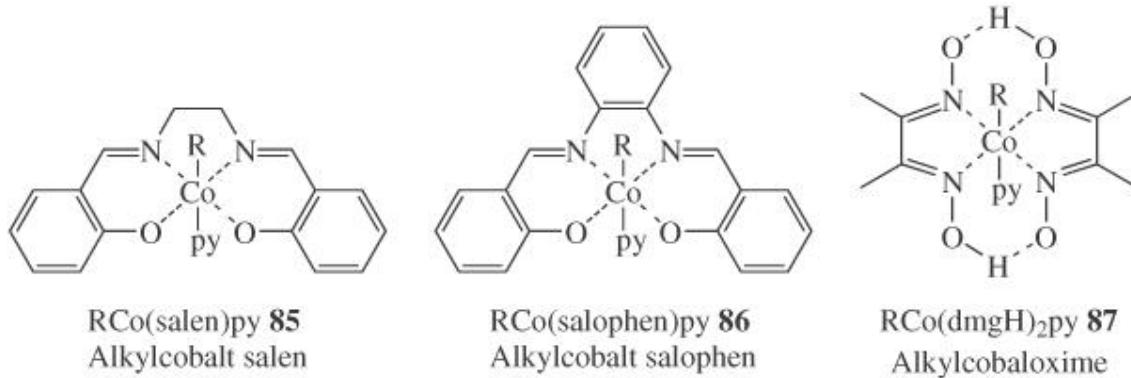
The alkyl- or acylcobalt(III) salen **85**, salophen **86**, or dimethylglyoximato complexes **87** are air-stable compounds that are readily prepared by substitution reactions of halides or tosylates with the strongly nucleophilic cobalt(I) anions. The carbon–metal bond in these complexes is weak and easily cleaves upon irradiation or thermolysis. Bond homolysis yields a carbon-centered radical **88** and a paramagnetic cobalt(II) complex **89**. (137) The bond cleavage is reversible and the substrate complex can be reformed by rapid radical recombination. However, the lifetime of the alkyl radical is usually long enough so that radical cyclization can take place prior to recombination of the alkyl radical and the cobalt(II) fragment. The cyclization reaction is usually terminated by formation of a double bond by β -hydride elimination of a cobalt hydride complex **90** (Eq. 102).

$$R^1Co(III)L \underset{85\text{-}87}{\overset{h\nu \text{ or heat}}{\rightleftharpoons}} \underset{88 \quad 89}{R^1 \bullet + Co(II)L} \xrightarrow{\text{cyclization}} R^2 \bullet + Co(II)L$$

$$R^2 \bullet + Co(II)L \rightleftharpoons \underset{90}{R^2 - Co(III)L} \xrightarrow[\text{elimination}]{\beta\text{-hydride}} \text{alkene}$$

(102)
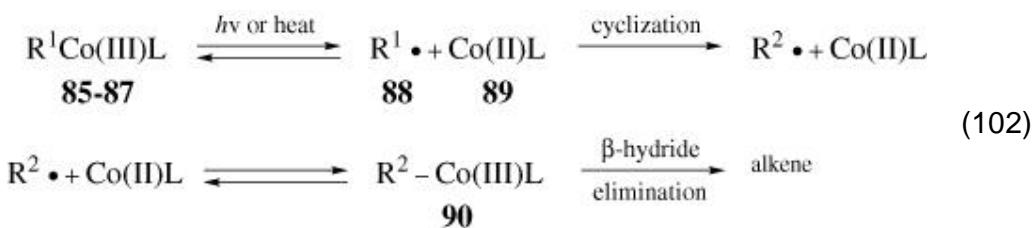
An example of a 6-exo cyclization of the alkylcobaloxime **91** that was prepared by nucleophilic opening of an epoxide is shown in Eq. 103. (168)

(103)
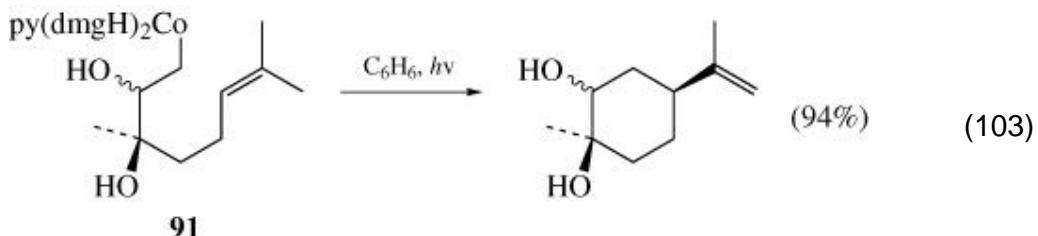
With substrates that preferentially react via a $S_{RN}1$ mechanism (e.g., aryl iodides), cyclization occurs in the course of the synthesis of the complex, and the cyclic alkylcobalt(III) complex is the sole reaction product. (169) The cobalt group can either be eliminated or converted into a wide variety of functional groups, like hydroxy, halogen, oxime, phenylthio, and phenylseleno (Eq. 104). (170)

(104)
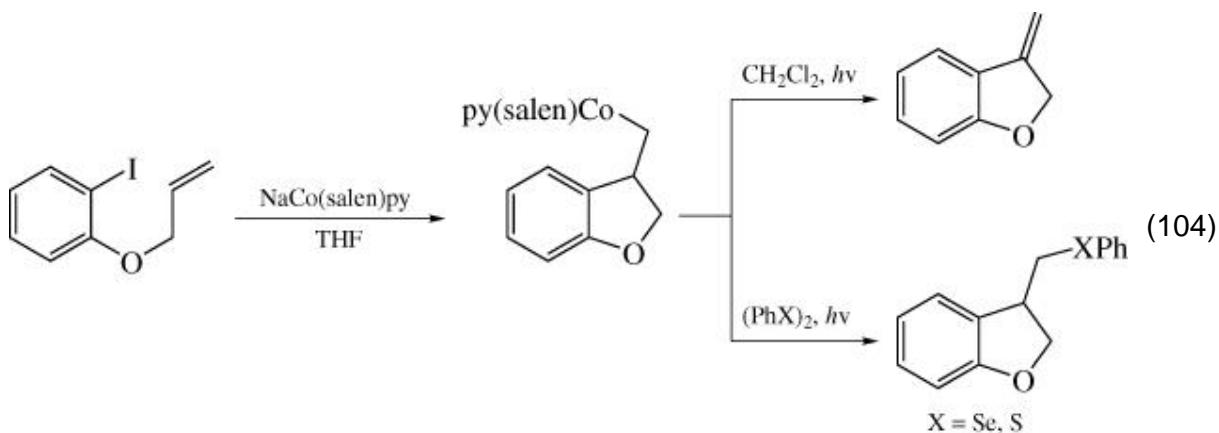
The retention of functionality in the product, either as a double bond or as the alkyl metal bond, is the main advantage of this method when compared to reductive cyclization methods.

A key feature for the success of the cobalt method is the relatively high concentration of the cobalt(II) complex **89** in the reaction mixture. Thus the desired cross-coupling of the alkyl radicals with cobalt(II) complex **89** is strongly favored over the unwanted cross-coupling of the alkyl radicals with themselves. (171)

In addition to the stoichiometric procedures, methods are available in which only catalytic amounts of cobalt complexes are used in the presence of a reducing agent (see Redox Methods).

3.6. Redox Methods
In redox methods, the initial radicals are generated and the cyclic radicals are trapped by electron-transfer processes. For a successful cyclization, both steps have to be selective. Therefore, substrates should be chosen so that the electronic properties of the initial and cyclic radical are different (e.g., the cyclic radical is more easily oxidized than the initial radical). This is usually achieved by incorporation of suitable substituents in the precursors. (154)

3.6.1. Reductive Methods
In reductive methods, the initial radical is generated by a one-electron transfer to the precursor. This method is suited for the cyclization of nucleophilic radicals because they are not easily reduced. However, a second electron transfer occurs after the cyclization, thereby removing the cyclic radical. Depending on the method employed, this either results in the formation of protonated (reduced) products or organometallic intermediates which can be trapped with electrophiles.

An example of this type of reaction is the titanium-promoted cyclization of epoxides. The reaction proceeds via reductive opening of the epoxide by titanium(III) chloride and subsequent cyclization of the β -hydroxy radical. The cyclic radical is then reduced to an organometallic intermediate that can be trapped with electrophiles like iodine or a proton (Eq. 105). (172, 173)

(105)
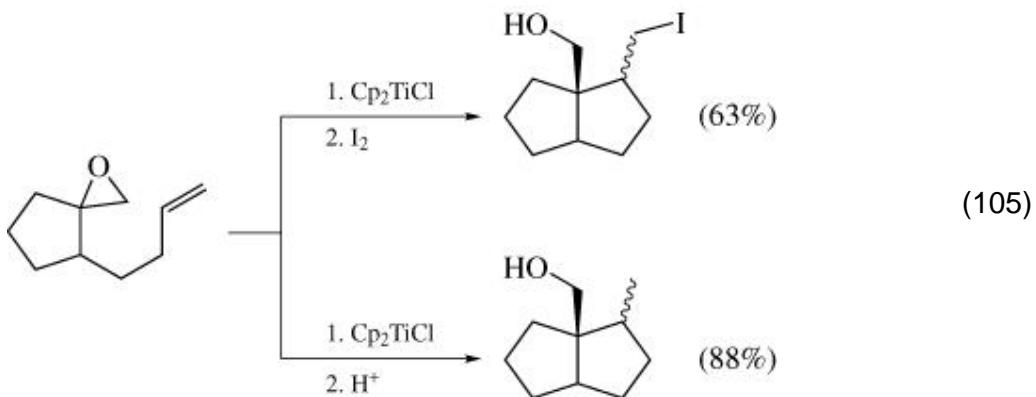
Similar transformations are possible with samarium(II) iodide. Precursors are usually aryl iodides or bromides from which the aryl radicals are generated by a single-electron transfer followed by loss of iodide. Again, the cyclic radical is reduced to an organometallic intermediate that can react with electrophiles. (174, 175) In Eq. 106 the samarium complex is trapped by addition to a ketone. (176)

(106)
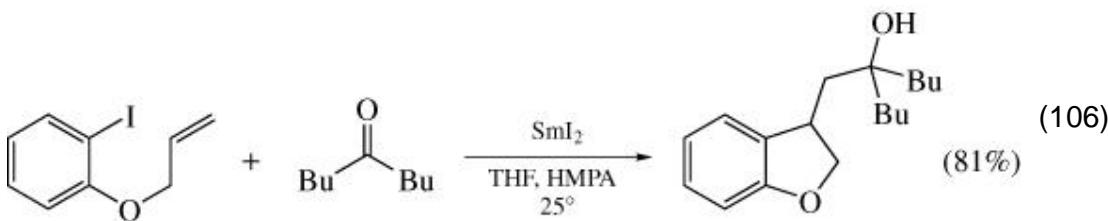
The reductive method can be employed further for the cyclization of unsaturated aldehydes and ketones to cycloalkanols. The reaction proceeds via reduction of the carbonyl group to a ketyl radical anion followed by intramolecular addition to a carbon–carbon multiple bond. Potential side reactions include overreduction of the carbonyl group to the alcohol and dimerization of two ketyl radicals to a pinacol. Furthermore, many functional groups have to be protected because they are not compatible with the strongly reductive conditions. For electron transfer, chemical reductants [e.g., samarium(II) iodide, metals in ammonia] or electrochemical techniques are usually employed. (5) Samarium(II) iodide is popular because it combines practical advantages (solubility in organic solvents) with high reducing power and excellent chemoselectivity (nitriles, esters, alkynes, and many other functional groups are tolerated). (177) In addition, high stereoselectivities are

often observed. (178) This is illustrated by the example in Eq. 107 in which the organometallic intermediate is trapped by acetone. (179)

$$\text{(107)} \qquad (75\%)$$
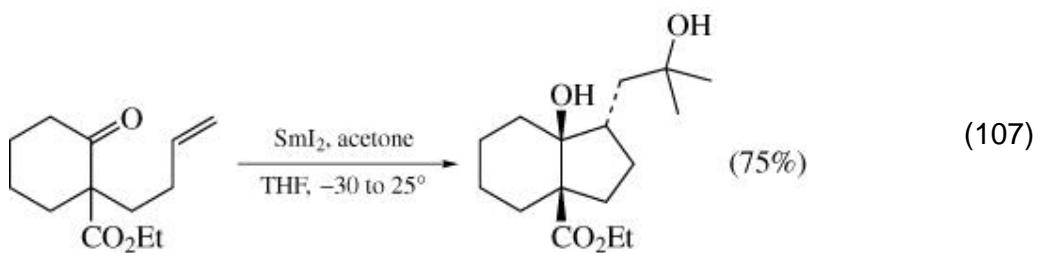
Furthermore, electron transfer can be induced photochemically under very mild reaction conditions. (180) Either hexamethylphosphoric triamide (HMPA) or triethylamine/acetonitrile can be employed as the electron donor. In a recent example, this method is used for the reduction of an α , β -unsaturated ketone (Eq. 108). Cyclization occurs exclusively at the β position of the carbonyl group. (181)

$$\text{(108)} \qquad (53\%)$$
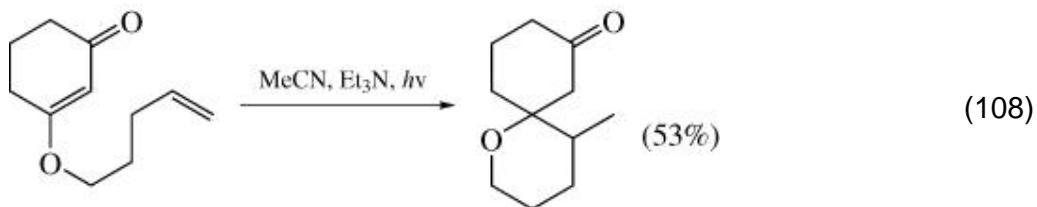
Another important class of reductive cyclizations is mediated by catalytic amounts of cobalt complexes in the presence of chemical or electrochemical coreductants. This type of reaction is closely related to the cyclization of organocobalt(III) complexes discussed in the preceding section on Radical/Radical Coupling Methods. The coreductant serves to recycle the nucleophilic Co(I) complexes which promote formation of the initial radical. The most common catalysts are vitamin B_{12} (182) or vitamin B_{12}-model systems like chlorocobaloxime **92**. (170) Either zinc or sodium borohydride can be employed as a chemical coreductant. Suitable precursors are alkyl or aryl bromides and iodides. The cobalt-catalyzed cyclization usually provides reduced products (Eq. 109). (183)

$$\text{(109)}$$
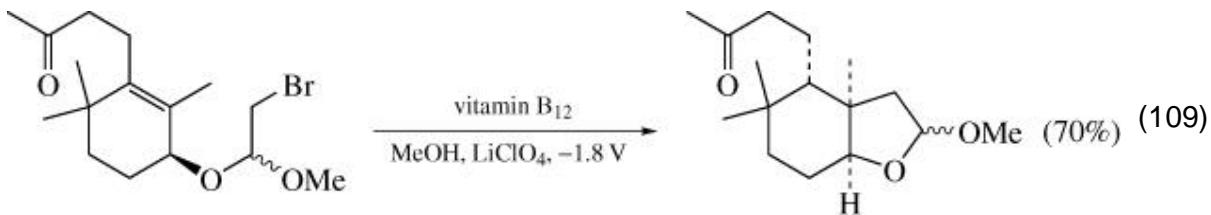
However, if suitable substrates and reaction conditions (184) are used, alkenes are formed by hydridocobalt elimination from an intermediate alkylcobalt(III) complex (Eq. 110). (185, 186)

$$\text{(110)}$$
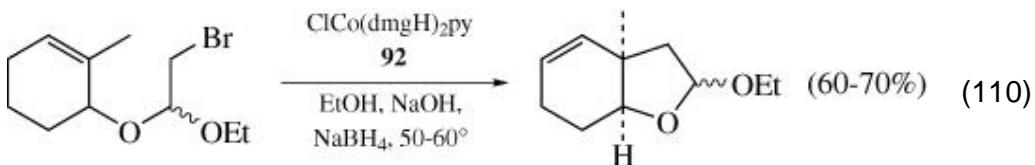
The possibility of retaining functionality in the product is an important advantage over other reductive radical cyclization methods. Furthermore, workup is often simplified because only catalytic amounts of metal byproducts have to be removed.

3.6.2. Oxidative Methods

Oxidative cyclization methods are usually applied to the cyclization of electrophilic radicals because these radicals are relatively inert to further oxidation. The cyclic radicals are oxidized to the cation followed by quenching with a nucleophile. Therefore, the product often possesses a higher degree of functionality than the starting material. The long lifetime of the initial radical makes oxidative methods ideally suited for conducting slow cyclizations. Although the oxidation can be conducted by electrochemical techniques (187) or by photoinduced electron transfer, (188) metal salts are usually applied in synthesis. The manganese(III)-promoted oxidation of enolizable dicarbonyl compounds is one of the most useful methods. The initial radical is chemoselectively generated by oxidation of the most acidic carbon–hydrogen bond. The cation formed by oxidation of the cyclic radical can be trapped intramolecularly by electrophilic substitution (189) or lactonization. (190) An example of the latter reaction is shown in Eq. 111. (191)

(61%)   (111)
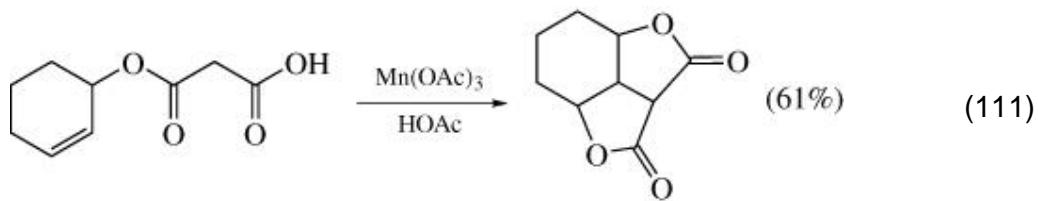
By addition of copper(II) salts to the reaction mixture, it is possible to obtain products that contain a double bond. The alkenes are probably formed by metal hydride elimination of an intermediate alkylcopper complex (Eq. 112). (192)

(41%)   (112)
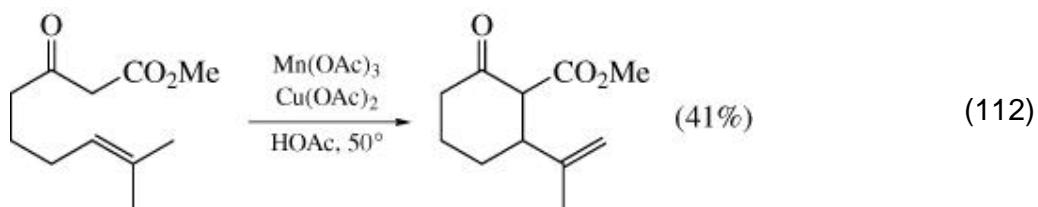
The ability to conduct slow 8-endo cyclizations with the manganese(III)-promoted reaction is demonstrated by the example in Eq. 113. (193, 194)

(47%)   (113)
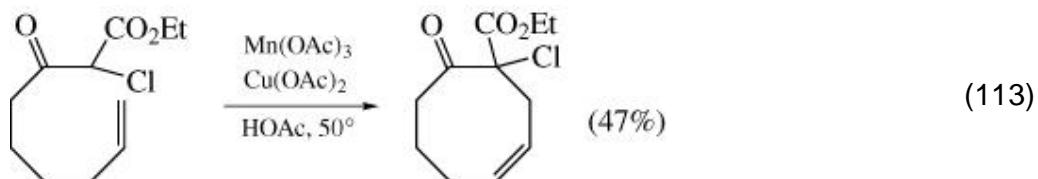
The main disadvantages of oxidative cyclizations are the limited range of possible substrates, the use of large amounts of metal salts (2–3 equiv), and the relatively low yields.

3.7. Sequential Reactions

In sequential radical reactions, two or more radical reactions are connected in a reaction series. This is possible because most of the radical reactions, like fragmentation, cyclization, or addition, generate a new radical that can serve as a precursor for a second radical transformation. Actually, all radical

cyclization methods are sequences of radical reactions, but here "sequential reactions" are defined as transformations in which a substrate undergoes two or more subsequent radical reactions, excluding steps that involve radical generation and radical removal. (4) The most interesting feature of these reactions is the possibility of constructing complicated structures in a single synthetic step. In general, all the restrictions that apply to single radical transformations are also valid for sequential reactions. Hence, all reactions have to be faster than radical recombination or reaction of the intermediate radicals with the solvent. In addition, the final radical, but not the intermediate radicals, must selectively be converted to a stable product. So far, inter- and intramolecular additions, intramolecular 1,5-hydrogen transfer reactions, and fragmentation reactions have been included in sequential radical reactions. The combination of two or more cyclization steps is the most prominent type of sequential reaction, and can be employed for the ready construction of polycyclic compounds. In principle, every method that is suitable for conducting radical cyclizations can be employed for tandem cyclization as well. Equations 114 and 115 present examples of tandem cyclizations conducted by the tin method (195) and by oxidation with manganese(III). (196)

(114)
(75%)

(115)
(68%)
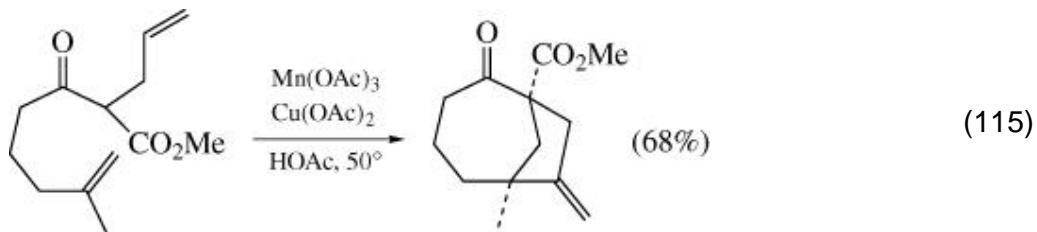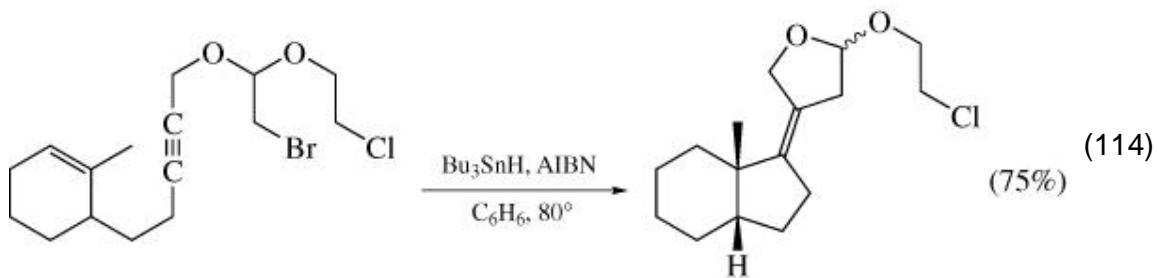
In another type of sequential reaction, 1,5-hydrogen abstractions are coupled with radical cyclizations. (197) The hydrogen shift makes it possible to use a carbon–hydrogen bond as a radical precursor for a cyclization. This can be important if the usual precursor in this position is difficult to prepare or is unstable. For a successful transformation the hydrogen transfer step should be rapid to compete with unwanted side reactions. Therefore, reactive radicals

like aryl, vinyl, or alkoxyl (198) radicals are generated in the initial step. In Eq. 116 an example is shown of the radical translocation reaction of an aryl iodide. (199)

$$\text{(83\%)} \qquad \text{(116)}$$
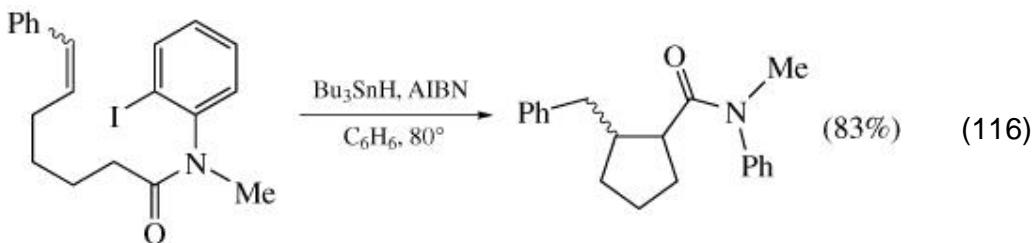
A useful class of sequential reactions is the combination of cyclization and fragmentation. (73) Depending on the structure of the substrate, the net result of this sequence is either a group migration (200) or a ring expansion. The latter reaction is especially useful for the formation of medium-sized rings which are not accessible by direct radical cyclizations. The ring expansion proceeds via radical cyclization to a carbonyl double bond followed by rapid β-bond cleavage of the alkoxy radical. The direction of the fragmentation is often controlled by substituents that make the final radical more stable than the starting radical. It is possible to expand rings by one, three, or four atoms. However, expansion by two atoms is not possible because the initial 4-exo cyclization is too slow. As the initial cyclization is often slow and reversible, syringe pump addition of tin hydride and fragmentation methods are suited for these sequences. Equation 117 shows an

$$\text{(73\%)} \qquad \text{(117)}$$
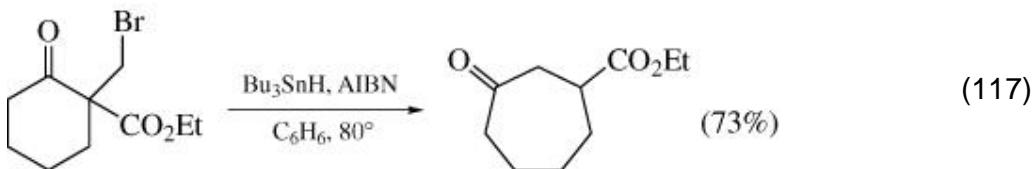
example of a one-carbon expansion reaction conducted by the tin method. (75) The ester group not only stabilizes the final radical but also accelerates the initial cyclization.

The example in Eq. 118 shows the formation of a 10-membered ring by a four-atom expansion of cyclohexenone derivative **93**. (76) Problems in this type of sequence

(118)
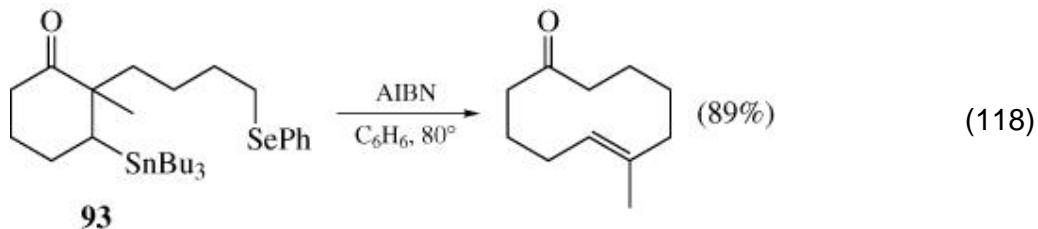
are often associated with direct reduction of the initial radical either by tin hydride or by an intramolecular 1,5-hydrogen transfer.

Sequences are also known where fragmentation precedes cyclization. In the most prominent method, the initial radical is formed by fragmentation of a cyclopropyl carbinyl radical. This sequence can be used for the generation of chiral radicals because the precursors can often be prepared in optically pure form by standard cyclopropanation methods. The cyclopropylcarbinyl radicals can be generated from α -cyclopropyl alcohols either by oxidation (103) or by the tin hydride method via thiohydroxamate **94** (Eq. 119). (201, 202) Further suitable precursors are

(119)
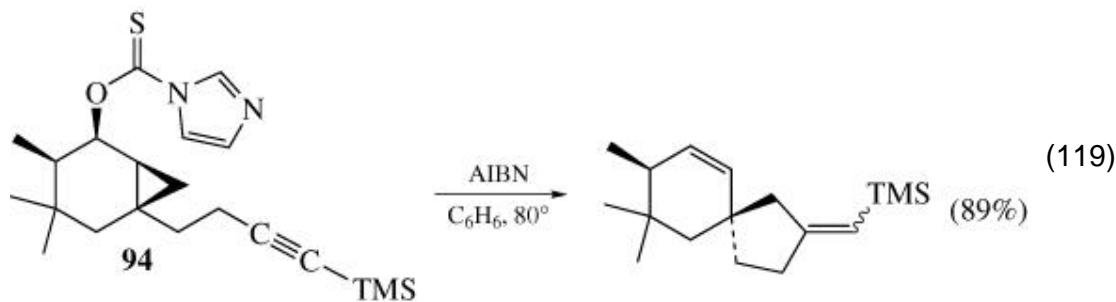
cyclopropyl ketones **95** that are reduced by samarium(II) iodide. An example of this strategy is shown in Eq. 120. (203)

(120)
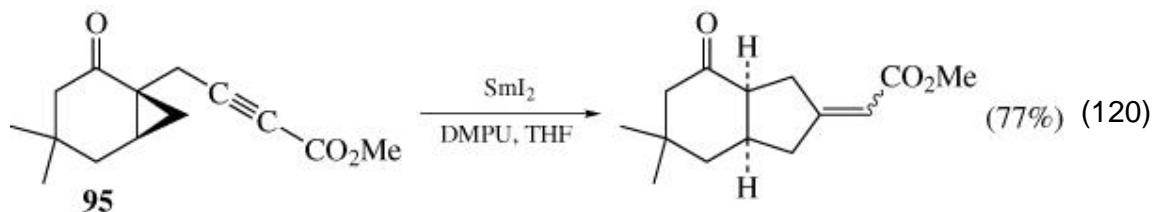
If an epoxide is used, this method allows the generation and cyclization of oxygen-centered radicals. (204)

The combination of inter- and intramolecular reaction steps has a great synthetic potential. For sequences where cyclization precedes addition, it is important that cyclization of the initial radical is faster than the competing intermolecular addition. Therefore, fast cyclization steps should be included in such a sequence. Furthermore, the addition step of the intermediate radical to the alkene acceptor has to be optimized, for example, by adjusting the concentration and the electronic properties of the alkene. An excess of activated alkene is often used to accelerate the intermolecular addition and thereby suppress reduction of the cyclic radical. Equation 121 shows an example of a cyclization/addition sequence

(121)
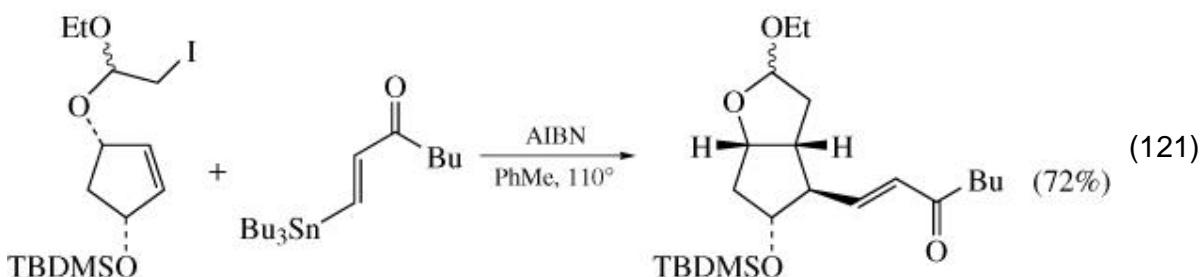
conducted by the fragmentation method. (205) In addition, there are examples that have been conducted by tin hydride (206, 207) or reductive methods. (184)

The reverse sequence, addition followed by cyclization, assembles a new ring from two isolated precursors. In this type of reaction, the main problem is differentiation of the initial and final radicals of the sequence. For a successful annulation it is necessary that the initial (but not the final) radical adds to the alkene and that the final (but not the initial) radical selectively abstracts hydrogen from tin hydride. Selectivity is usually achieved by the introduction of substituents or by generating different types of initial and final radicals. This concept is demonstrated by the example presented in Eq. 122. In this reaction, the electrophilic initial radical preferentially adds to the electron-rich alkene **96**, whereas iodine abstraction by the final vinyl radical is faster than the competing addition to another alkene molecule. The intermediate vinyl iodide **97** was not isolated but directly reduced with tin hydride. (208)

(122)
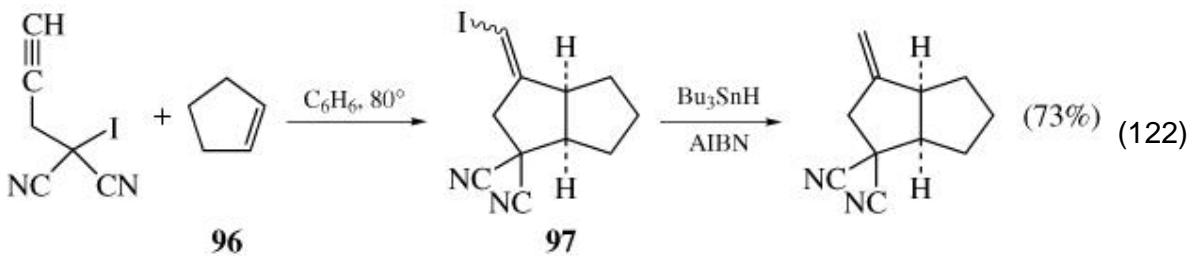
Addition/cyclization sequences can also be carried out by the tin hydride method, (69, 209) by oxidative methods, (210, 211) and by the thiohydroxamate method. (34) An example of the last reaction is shown in Eq. 123. (212)

In addition to sequences consisting of two radical reactions, it is possible to combine three radical reactions in one transformation. The sequence of the steps can differ, and combinations are known of fragmentation/hydrogen–transfer/cyclization, (213) addition/cyclization/addition, (214) cyclization/addition/cyclization, (215)

$$(123)$$

$$(64\%)$$
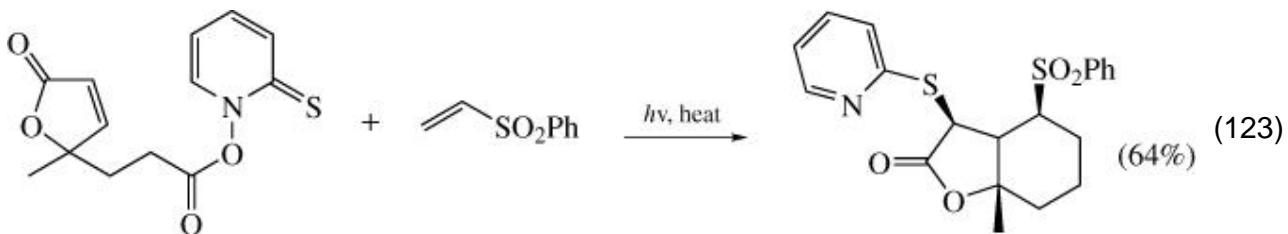
and fragmentation/ addition/cyclization reactions. An example of one of these sophisticated sequences is shown in Eq. 124. (216) The reaction is promoted by reversible addition of a thiyl radical **99** to the double bond of **98** followed by addition to alkene **100** and cyclization. The reaction is terminated by rapid β fragmentation of **101** that liberates the chain-carrying butylthio radical **99**.

$$\overset{\text{BuSSBu}}{\underset{C_6H_6,\ h\nu}{\longrightarrow}} \quad (81)$$
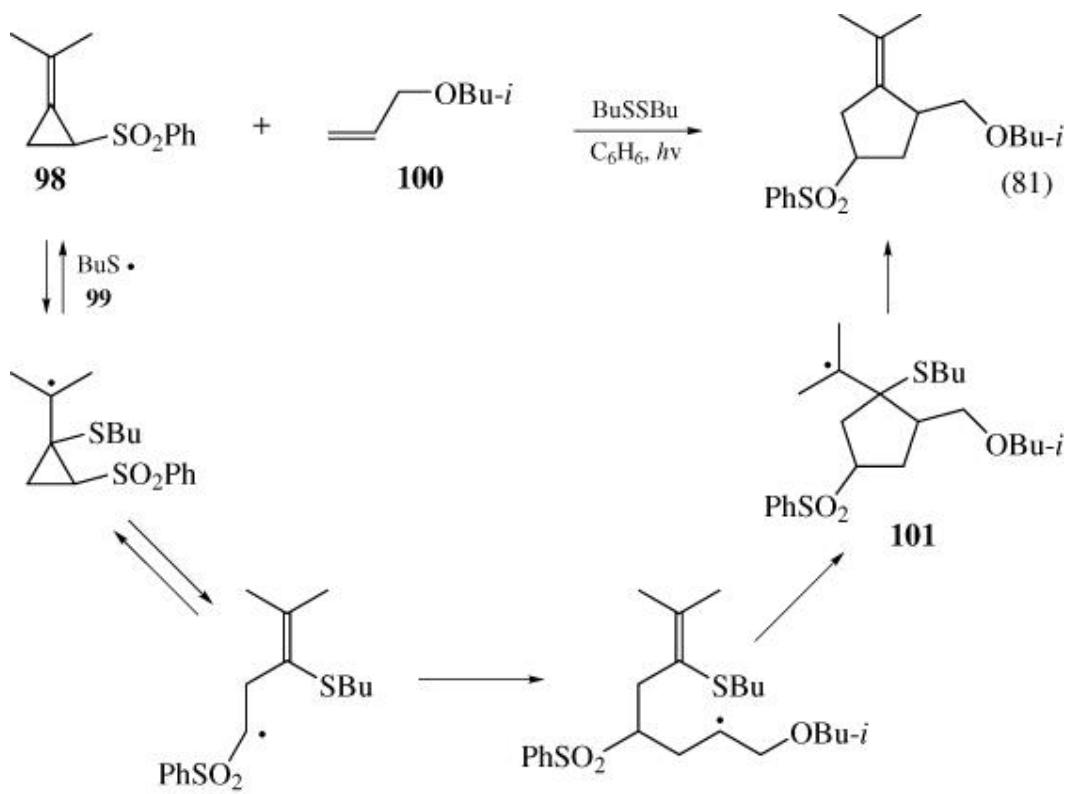
4. Comparison with Other Methods

There are too many cyclization methods in the literature for a complete comparison. For an overview of some methods see the review of C. and Y. Thebtaranonth. (216a)

Cationic cyclizations (216b) often lead to the thermodynamically controlled products. Sometimes Wagner–Meerwein rearrangements can occur. 5-Hexenyl cations cyclize in a 6-endo mode. Acidic conditions are used.

Radical reactions lead mainly to products of kinetic control (5-exo cyclization). The reaction conditions are neutral for several methods and various functional groups are tolerated. If organotin compounds are used, the removal of all tin residues can be a problem.

Anionic cyclizations occur under basic conditions and β elimination can be a competing reaction. 5-Hexenyl anions cyclize in a 5-exo mode, (216c,d) approximately 10^8 times slower than the corresponding radical cyclization. (216c) The intramolecular Michael addition was previously reviewed (216e) and is an alternative to radical cyclizations with activated olefins. Thermodynamically and kinetically controlled reactions are possible.

The metal-catalyzed cyclization reactions (mostly with palladium) (216a,f) often occur with high yield and under mild basic conditions. Substrates must usually be chosen to avoid β -hydride elimination.

These methods are compared in Table A. Included are some functional groups which can be used as precursors and functional groups which are tolerated under the reaction conditions.

Table A. Comparison of Cyclization Methods

	Cationic	Radical	Anionic	Palladium
Precursor	Cl, Br, I, OH, OR, OSO$_2$R, C = C, C = O, C(OR)$_2$	[Cl][a], Br, I, OH[b], OOR, SPh, SePh, NH$_2$[b], N = NR, N = C, NO$_2$,C = C, C ≡ C, C = O,	Cl, Br, I, SPh, SePh, SnR$_3$,C = C, H	[Cl][a], Br, I, OH, OAr, O$_2$CR, O$_2$COR, SO$_2$R, OP(O)(OR)$_2$,NO$_2$, C

Tolerated functional groups		CO_2H^b, anions, SnR_3, BR_2, HgX, CoL_n, H F, [Cl][a], OH, OR, SR, SO_2R, $NH_2, NR_2, CN, [C=O][a]$, $C(OR)_2, CO_2R$, SiR_3	OR^c, $C(OR)_2, SO_2R^c$, NR_2, $C=O^d$	$= C$, cyclopropyl, epoxide, H [OH][a], OR, $SO_2R, [NH_2][a]$, $NR_2, C=O$, $C(OR)_2, CO_2R$
Side reactions	Wagner–Meerwein rearrangement; hydride transfer	Dimerization; hydrogen abstraction	β-Elimination; addition to C = O	β-Elimination; isomerization
pH	Acidic	Neutral	Strongly basic	Mildly basic
Preferred regiochemistry of 5-hexenyl cyclization	6-endo	5-exo	5-exo	5-exo
Product control	Thermodynamic	Kinetic	Both possible	Both possible

[a]This group is sometimes useful.

[b]Two steps are needed.

[c] β-Elimination is possible in the precursor or the product.

[d]Aldol condensation is possible.

5. Experimental Conditions

Radical reactions require an inert atmosphere (nitrogen or argon). Normal bench/syringe technique is sufficient. Since there is little or no solvent dependence in radical reactions, all solvents (including water) can be used, as long as the reactants are soluble. As mentioned before attention must be paid to the half life time of the initiator. The concentrations of the reactants have to be adjusted well to optimize the expected reaction. (6, 7)

6. Experimental Procedures
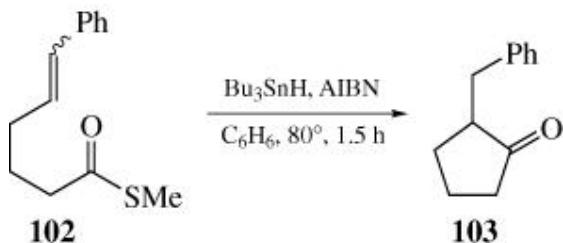
6.1.1. 2-(Phenylmethyl)cyclopentanone *(103) (Formation of a Carbocycle by the Tin Method) (34)*

A solution of **102** (84.6 mg, 0.316 mmol), tributyltin hydride (190 μL, 0.706 mmol), and AIBN (7.5 mg, 0.045 mmol) in benzene [CAUTION, SUSPECTED CARCINOGEN] (8 mL) was heated at reflux for 1.5 hours. After cooling, the solvent was evaporated, and the residue was purified by flash chromatography (10% EtOAc–hexanes) to provide 49.5 mg (90%) of **103** and 6-phenyl-5-hexenal (³18:1 by ^{1}H NMR integration). IR (thin film) 2961, 1737, 1160, 690 cm^{-1};^{1}H NMR(CDCl$_3$) δ 7.28–7.13 (m, 5H), 3.13 (dd, J = 13.7, 3.9 Hz, 1H), 2.51 (dd, J = 13.7, 9.4 Hz, 1H), 2.37–2.27 (m, 2H), 2.15–2.02 (m, 2H), 1.99–1.89 (m, 1H), 1.75–1.67 (m, 1H), 1.59–1.46 (m, 1H); high-resolution mass spectrum, calculated for C$_{12}$H$_{14}$O(M$^+$) m/z 173.0966, found m/z 173.0996; mass spectrum m/z 174 (M$^+$), 156, 146, 130, 117.
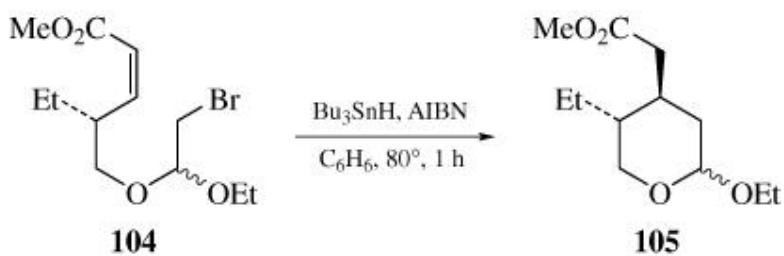
6.1.2. (–)-(4R,5R)-2-Ethoxy-5-ethyl-4-methoxycarbonylmethyl-3,4,5,6-tetra hydro-2H-pyran *(105) (Formation of a Heterocycle by the Tin Method) (93)*

A mixture of bromoacetal **104** (549 mg, 1.78 mmol), AIBN (30.3 mg, 0.185 mmol), and Bu$_3$SnH (0.65 mL, 2.42 mmol) in dry benzene (12 mL) was heated under reflux for 1 hour and then evaporated under reduced pressure. Silica gel column chromatography of the crude product with hexane–EtOAc

(92:8) as eluant gave tetrahydropyran **105** (395 mg, 97 %) as an oily mixture of two diastereomers. $[\alpha]_D^{24}-7.98°$ (c 0.43, CHCl$_3$); IR (CHCl$_3$):1732 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 4.77–4.89 (m, 0.6H), 4.66–4.69 (m, 0.4H), 3.40–4.44 (m, 4H), 3.68 (s, 3H), 2.61 (dd, J = 15.2, 4.2 Hz, 1H), 2.51 (dd, J = 15.2, 3.8 Hz, 1H), 0.73–1.06 (m, 3H); mass spectrum: m/z 215 (M$^+$–Me); Anal. Calcd for C$_{12}$H$_{22}$O$_4$: C, 62.6; H, 9.65. Found: C, 62.6; H, 9.7.
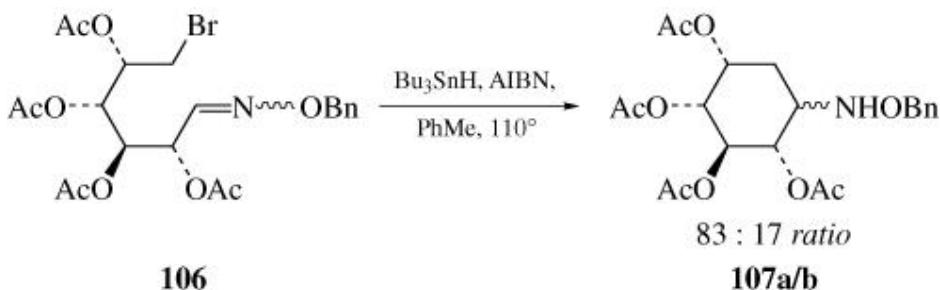
6.1.3. Radical Cyclization of Carbohydrate Derivatives (Tin Method) (217)
Bromide **106** (1.3 g, 2.5 mmol) and tributyltin hydride (2.4 equiv) were heated by dropwise addition of AIBN (cat.) in dry toluene at 110°. The reaction mixture was cooled and the solvent evaporated. The residue was dissolved in ether and 10% aqueous potassium fluoride solution was added, and the mixture was stirred for 18 hours. The organic phase was separated, dried, and evaporated. After chromatography (hexanes:EtOAc = 4:1) product **107a/b** was obtained in 52% yield (570 mg) as an 83:17 diastereomeric mixture. Recrystallization from hexane gave pure **107a**: mp 116–118° $[\alpha]_D^{24}$S(24,D) –72° (c 4.5, CHCl$_3$); IR (CHCl$_3$) 3200, 3080, 1755 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 7.34–7.26 (m, 5H), 5.44 (q, J = 3.1, 1H), 5.35 (t, J = 10 Hz, 1H), 5.21 (t, J = 10 Hz, 1H), 4.92 (dd, J = 10 and 3.2 Hz, 1H), 4.61 (s, 2H), 3.25 (ddd, J = 10.1, 12.4 and 4.2 Hz, 1H), 2.10, 2.03, 2.01, 1.98 (s, s, s, s, 4 × 3H), 1.88 (ddd, J = 3.0, 12.4 and 14.8 Hz, 2H); ^{13}C NMR(CDCl$_3$) δ 170.23, 170.05, 169.97, 169.91, 139.14, 128.67, 128.55, 128.14, 76.99, 71.87, 71.72, 71.20, 67.82, 56.87, 29.78, 21.01, 20.84, 20.75, 20.66; mass spectrum: m/z 438 (M$^+$); Anal. Calcd for C$_{21}$H$_{27}$NO$_9$: C, 57.66; H, 6.17; N, 3.20. Found: C, 57.27; H, 6.12; N, 3.50.
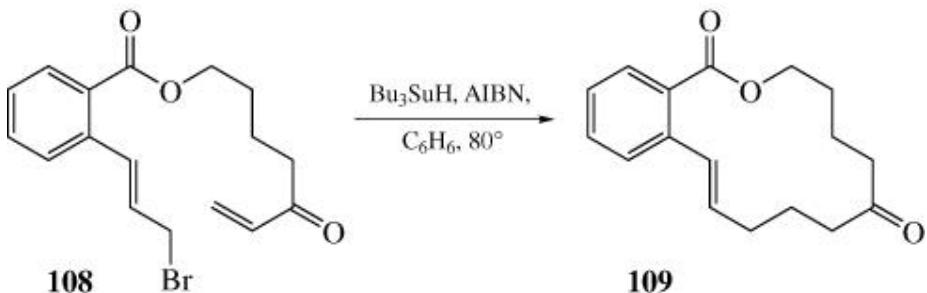
6.1.4. (11E)-3,4,5,6,9,10-Hexahydro-8H-2-benzooxacyclotetradecyne-1,7-dione *(109) (Macrocyclization Mediated by Tin Hydride) (127)*

A solution of tributyltin hydride (157 mg, 0.54 mmol) and AIBN (5 mg, 0.03 mmol)) in dry, degassed benzene (10 mL) was added over 8 hours via syringe pump to a solution of **108** (98 mg, 0.28 mmol) in dry, degassed benzene (100 mL) heated under reflux under an atmosphere of nitrogen. The cooled mixture was evaporated under reduced pressure and the residue was then dissolved in diethyl ether. The ether solution was stirred with 20% aq. KF for 24 hours and filtered, and the organic layer was separated, dried, and evaporated to leave a yellow oil. Purification by chromatography on silica gel using 25% Et$_2$O–hexanes as eluent gave 47 mg (61%) macrolide **109** as white needles, mp 78–80° (pentane); IR (CHCl$_3$) 2920, 1720, 1600, 1460, 1250, and 1075 cm^{-1};^{1}H NMR(CDCl$_3$) δ 7.78 (m, 1H), 7.60–7.15 (m, 3H), 6.88 (d, J = 16 Hz, 1H), 5.88 (dt, J = 16, 7 Hz, 1H), 4.50–4.20 (m, 2H), 2.65–2.10 (m, 6H), 2.04–1.50 (m, 6H); ^{13}C NMR(CDCl$_3$) δ 211.2 (s), 168.7 (s), 138.2 (s) 132.3 (d), 132.0 (d), 131.4 (d), 130.9 (d), 129.1 (s), 127.4 (d), 127.0 (d), 65.7 (t), 43.2 (t), 37.1 (t), 31.3 (t), 27.4 (t), 22.7 (t), 21.5(t); mass spectrum: *m/z* 272 (M$^+$); Anal. Calcd for C$_{17}$H$_{20}$O$_3$: C, 75.0; H, 7.4. Found: C, 75.1; H, 7.7.

6.1.5. (11E,3S)-14,16-Dimethoxy-3-methyl-3,4,5,6,9,10-hexahydro-8H-2-benzooxacyclotetradecyne-1,7-dione (Zearalenone) *(111) (Macrocyclization Mediated by a Silane Hydride) (127)*

A solution of tris(trimethylsilyl)silane (35 mg, 0.14 mmol) and AIBN (5 mg, 0.03 mmol) in dry toluene (2 mL) was added over 8 hours via syringe pump to a stirred solution of **110** (41 mg, 0.10 mmol) in dry, degassed toluene (35 mL) at 85° under nitrogen. The solution was heated at 85° for 2 hours and then cooled and evaporated to leave a residue which was purified by chromatography on silica gel using 50% Et$_2$O–hexanes as eluent to give 18 mg (55%) of zearalenone (**111**) as a white crystalline solid: mp 110–111° (Et$_2$O and hexane).

$[\alpha]_D^{24}$ +47.8° (*c* 1.0, CHCl$_3$); IR 2930, 1710, 1600, 1575 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 6.55 (d, 1H, *J* = 2 Hz), 6.30 (d, 1H, *J* = 2 Hz), 6.28 (d, 1H, *J* = 16 Hz), 6.05–5.90 (m, 1H), 5.46–5.06 (m, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.90–1.90 (m, 12H), 1.33 (d, 3H, *J* = 7 Hz); ^{13}C NMR δ 211.2 (s), 167.4 (s), 161.1 (s), 157.4 (s), 136.5 (s), 133.0 (d), 128.8 (d), 101.0 (d), 97.5 (d), 71.0 (d), 55.7 (q), 55.2 (q), 43.8 (t), 38.3 (t), 34.9 (t), 31.0 (t), 21.5 (t), 21.1 (t), 19.8 (q); high-resolution mass spectrum, calculated for C$_{20}$H$_{26}$O$_5$(M$^+$)*m/z*346.1780, found *m/z* 346.1776.

112   **113**   *cis : trans* 4 : 1
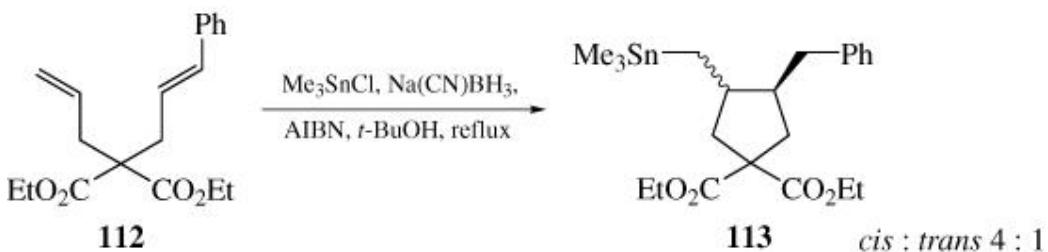
6.1.6. cis/trans-(1,1-Diethoxycarbonyl)-4-(trimethylstannylmethyl)-3-benzylcyclopentane (113) (Carbocyclization of a Diene with Tin Hydride) (218)

To a solution of **112** (1.3 g, 5.1 mmol) in 20 mL of anhydrous *tert*-butyl alcohol under argon, was added trimethyltin chloride (4 g, 10.0 mmol), sodium cyanoborohydride (0.95 g, 15.0 mmol) and AIBN (15 mg, 1.0 mmol). The solution was refluxed for 1 hour (until the diene had disappeared as monitored by TLC using KMnO$_4$ spraying agent). The solution was cooled to room temperature, quenched with 5% aqueous ammonia solution, stirred, and then concentrated under reduced pressure. The residue was dissolved in ether, washed three times with brine, dried (MgSO$_4$), and concentrated. Flash chromatography (3% EtOAc–hexanes) afforded 2.3 g (95%) of stannylated product **113** as an inseparable mixture in the form of a colorless oil (*cis*:*trans* = 4:1 by NMR). IR 3030, 3010, 2980, 2930, 1740, 1607, 1500, 1205, 760, 745, 695 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 7.14 – 7.32 (m, 5H), 4.09–4.26 (m, 4H), 2.97 (dd, *J$_{trans}$* = 13.9, 3.2 Hz, 2H), 2.79 (dd, *J$_{cis}$* = 12.7, 3.8 Hz, 2H), 2.21–2.46

(m, 2H), 1.97 (m, 4H), 1.17–1.27 m, 6H), 0.99 (d, J = 8.7 Hz, 2H); ^{13}C NMR δ 172.8(C = O*cis*),172.5(C = O *trans*), 141.3, 140.9, 128.9, 128.8, 128.1, 125.6, 125.5 (arom C's *cis* and *trans*), 61.1 (CH$_2$ from Et *cis* and *trans*), 58.5 (Cl *cis*), 57.7 (Cl *trans*), 50.3 (C3 *trans*), 45.7 (C3 *cis*), 43.8 (C4 *trans*), 43.0 (benzylic C *trans*), 41.6 (benzylic C *cis*), 40.7 (C4 *cis*), 39.7 (C2 *trans*), 39.4 (C5 *trans*), 37.3 (C5 *cis*), 34.8 (C2 *cis*), 14.9 (CH$_2$Sn *trans*), 13.9 (Me from Et *cis* and *trans*), 11.4 (CH$_2$Sn *cis*), – 9.6 (MeSn *trans*), – 9.8 (MeSn *cis*); high-resolution mass spectra, calculated for C$_{22}$H$_{34}$O$_4$Sn (M$^+$) *m/z* 482.1478, found *m/z* 482.1463.

114   →   **115a/b** 52 : 48 ratio
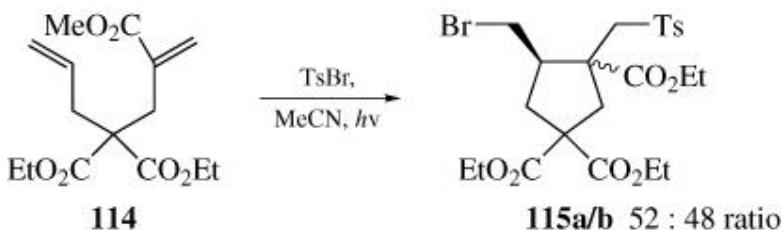
6.1.7. Diethyl 4-(Bromomethyl)-3-(methoxycarbonyl)-3-(tosylmethyl)-cyclopentane-1,1-dicarboxylate *(115a/b)* (Cyclization of a Diene with Tosyl Bromide) *(219)*

Irradiation (high-pressure mercury lamp) of a solution of diene **114** (1.5 g, 5 mmol) and tosyl bromide (1.18 g, 5 mmol) in 140 mL of acetonitrile for 24 hours, purification on silica gel using EtOAc–petroleum ether (15:85 to 40:60), gave 1.79 g (67%) of **115a/b**. The 52:48 ratio was determined by analytical HPLC (EtOAc:isooctane, 25:75; 2 mL/min). Anal. Calcd for C$_{22}$H$_{29}$BrO$_{28}$S : C, 49.54; H, 5.48; S, 6.01 Found: C, 49.49; H, 5.50; S, 5.90.

Product **115a**: ^{1}H NMR(CDCl$_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.30–4.14 (m, 4H), 3.73 (s, 3H), 3.60 (d, J = 13.7 Hz, 1H), 3.57 (dd, J = 9.8, 3.6 Hz, 1H), 3.38 (d, J = 15.2 Hz, 1H), 3.35 (d, J = 13.7, 1H), 3.11 (t, J = 9.8, 1H), 3.04 (d, J = 15.2, 1H), 2.73–2.60 (m, 2H), 2.45 (s, 3H), 2.48–2.39 (m, 1H), 1.27 (t, J = 7.1, 6H); ^{13}C NMR(CDCl$_3$) δ 172.6, 171.7, 171.0, 144.8, 137.6, 129.8, 127.6, 62.1, 61.7, 57.4, 56.7, 53.3, 52.8, 49.7, 39.5, 37.5, 31.0, 21.3, 13.7.

Product **115b**: ^{1}H NMR(CDCl$_3$) δ :7.77 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.31–4.14 (m, 4H), 4.06 (d, J = 13.8 Hz, 1H), 3.68 (s, 3H), 3.40 (dd, J = 10.3, 4.0 Hz, 1H), 3.34 (d, J = 14.9 Hz, 2H), 3.29 (d, J = 13.8 Hz, 1H), 3.03 (t, J = 10.3, 9.4 Hz, 1H), 2.89 (d, J = 14.9, 1H), 2.45 (s, 3H), 2.60–2.39 (m, 2H), 2.24 (t, J = 11.3, 1H), 1.29 (t, J = 7.1, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR(CDCl$_3$) δ 172.6, 171.6, 170.8, 144.9, 137.8, 129.9, 127.8, 63.3, 62.1, 61.7, 57.5, 53.8, 52.6, 51.7, 40.8, 37.9, 30.9, 21.6, 14.1, 13.9.
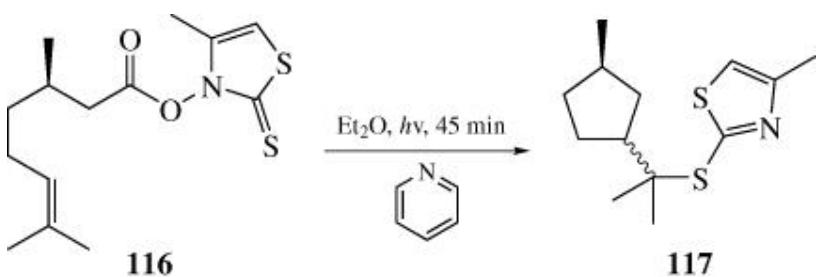
6.1.8. Photolysis of (R)-(+)-3-Citronoyloxy-4-methylthiazolin-2-(3H)-thione (116) [Cyclization by the Barton Method] (220)

A solution of ester **116** (1.55 g, 5.18 mmol) in ether (20 mL) was irradiated under nitrogen at room temperature with a 100-W medium pressure mercury lamp for 45 minutes. The solvent was then evaporated and the residue chromatographed on silica with pentane–ether (95:5) to give the cyclization product **117** as a 1:1 mixture of diastereomers. The mixture was a colorless analytically pure oil (1.08 g, 82%). IR (film) 3070, 1510, 1445, 1365, 1295, 1140, 1020 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 7.05 (m, 1H), 2.55 (m, 3H), 2.40–1.20 (m, 8H), 1.40 (s, 6H), 1.02, and 1.00 (2 d, J = 7.0 Hz ca. 1:1, 3H); mass spectrum: m/z 255 (M$^+$), 132, 131; Anal. Calcd for C$_{13}$H$_{21}$NS$_2$: C, 61.42; H, 8.28; N, 5.48; S, 25.10 Found: C, 61.1; H, 8.3; N, 5.65; S, 24.95%.
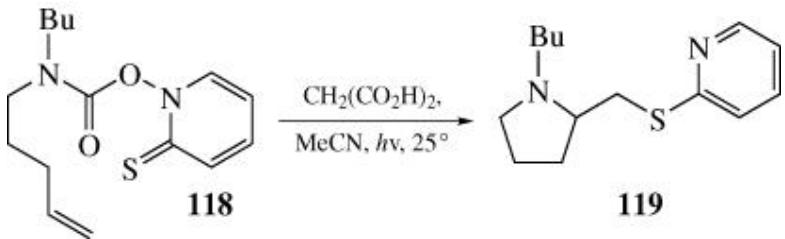
6.1.9. N-Butyl-2-[(2-pyridylthio)methyl]pyrrolidine (119) (Cyclization of an Aminyl Radical) (152)

Compound **118** (0.30 g, 1.0 mmol) and malonic acid (0.31 g, 3.0 mmol) were weighed into a round-bottomed flask containing a small stirring bar. The flask was sealed with a septum, wrapped with aluminium foil to exclude light, and purged with nitrogen. Acetonitrile (20 mL) was then added via syringe. The shield was removed, and the mixture was stirred and irradiated with a 100- or 150-W tungsten filament bulb from a distance of about 0.5 m. The reaction was monitored for disappearance of the PTOC carbamate **118** by TLC. When the reaction was judged to be complete, solvent was removed at reduced

pressure. The residue was partitioned between ether and 10% aqueous HCl. The aqueous portion was basified and extracted with several portions of ether. The combined ethereal extract was washed with saturated NaCl solution and dried (K_2CO_3). Purification by chromatography (silica gel, ether elution) gave 0.23 g (0.92 mmol, 92 %) of **119** as a heavy oil. ^{1}H NMR(CDCl$_3$) δ 8.37 (dd, 1H), 7.40 (dt, 1H), 7.13 (dd, 1 H), 6.90 (dt, 1H), 3.59 (dd, 1H), 3.13 (dt, 1H), 3.0–2.8 (m, 2H), 2.60 (m, 1H), 2.14 (m, 2H), 2.0–1.2 (m, 8H), 0.88 (t, 3H); ^{13}C NMR(CDCl$_3$) δ 160.0, 149.8, 136.2, 122.7, 119.6, 63.8, 54.8, 54.6, 34.4, 31.1, 30.4, 22.7, 21.0, 14.3; mass spectrum: *m/z* 139, 126, 96.

120   **121** *trans:cis* = 4.7:1
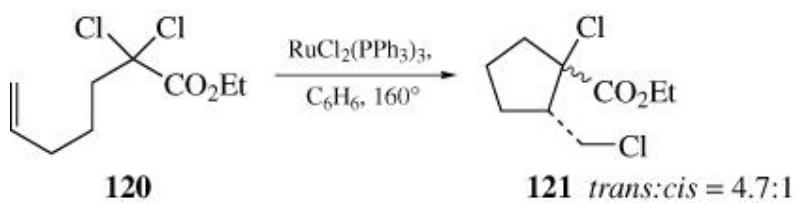
6.1.10. Ethyl cis/trans-1-Chloro-2-(chloromethyl)cyclopentane-1-carboxylate *(121) (Ruthenium-Catalyzed Cyclization; Atom Transfer Method) (221)*

General Procedure: Dichloro compound **120** and a transition metal catalyst (8.3 mol%) were placed in a resealable Pyrex^{TM} tube, and 1.0 mL of benzene was added. The mixture was degassed via three freeze/thaw cycles, and the tube was sealed under vacuum, placed in an oil bath, and heated at 155–160° for 22 hours. After cooling, the vessel was opened under argon. A small aliquot was passed through a plug of Florisil^{TM} and was analyzed by GLC to determine if the reaction was complete. If the starting dichloro compound **121** remained, the solution was degassed again and heated as before. Once the reaction was complete, hexane (3 mL) and benzene (2 mL) were added to the solution, and the mixture was filtered through a 3-cm plug of Florisil, which was washed with benzene (3 mL), and the solvent was removed in vacuo. Crude product mixtures were analyzed by GLC. Pure cyclic esters were isolated by preparative TLC, eluting once with 9:1 hexanes–EtOAc and once with 9:1 hexanes–methylene chloride.

trans-**121a**: (61%), bp 50–55° (<0.1 torr, bulb-to-bulb); IR (film) 2975, 2870, 1735, 1445, 1370, 1200, 1095, 1040, 920, 755 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 4.26 (q, *J* = 7.1 Hz, 2H), 3.82 (dd, *J* = 11.0, 6.4 Hz, 1H), 3.54 (dd, *J* = 10.8, 7.8 Hz, 1H), 2.87 (m, 1H), 2.49–1.59 (m, 6H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR(CDCl$_3$) δ 170.5, 77.2, 62.4, 51.6, 44.8, 41.9, 28.2, 21.0, 13.9; mass spectrum: *m/z* 226, 224, 189, 156, 153, 135, 115, 79, 41, 28; high-resolution mass spectrum, calculated for C$_9$H$_{14}$O$_2$Cl *m/z* 224.0371, found *m/z* 224.0372.

cis-**121b**: (13%), bp 50–55° (<0.1 torr, bulb-to-bulb); IR (film) 2975, 2870, 1735, 1445, 1370, 1325, 1265, 1200, 1080, 1035, 1020, 915, 860, 750 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 4.25 (q, J = 7.1 Hz, 2H), 3.71 (dd, J = 10.9, 4.3 Hz, 1H), 3.43 (dd, J = 10.9, 9.1 Hz, 1H), 2.77 (m, 1H), 2.57 (m, 1H), 2.32–1.61 (m, 5H) 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR(CDCl$_3$) δ 169.5, 74.4, 62.2, 55.0, 44.6, 40.0, 28.1, 21.1, 13.9; mass spectrum: m/z 226, 224, 189, 156, 153, 135, 115, 79, 41, 28; high resolution mass spectrum, calculated for C$_9$H$_{14}$O$_2$Cl m/z 224.0371, found m/z 224.0374.

122   123
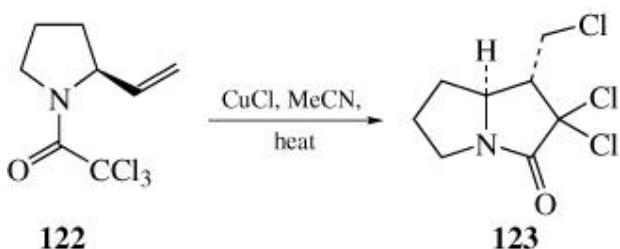
6.1.11. (1R,8S)-1-Chloromethyl-2,2-dichloro-3-oxohexahydropyrrolizidine (123) (Copper-Catalyzed Cyclization; Atom Transfer Method) (222)

A suspension of **122** (500 mg, 2.06 mmol) and recently recrystallized copper(I) chloride (194 mg, 1.96 mmol) in 14 mL of deoxygenated acetonitrile was heated in a sealed tube with a Teflon tap at 160° for 2 hours. After cooling, solvent was removed under reduced pressure and the residue purified by flash chromatography (hexanes–EtOAc = 4:1) to afford 467 mg (93%) of product

123 as a white solid mp 60–62°. $[\alpha]_D^{24}$ S(24,D) – 24°(c = 1.0, CH$_2$Cl$_2$); IR 2972, 1918, 1413, 843 cm^{-1};^{1}H NMR(CDCl$_3$) δ 3.98 (dd, J = 11.3, 4.2 Hz, 1H), 3.86 (dd, J = 11.3, 10.3 Hz, 1H), 3.68 (m, 1H), 3.55 (m, 1H), 3.28 (ddd, J = 12.1, 8.9, 3.2 Hz, 1H), 2.76 (m, 1H), 2.17 (m, 2H), 1.60 (m, 1H); mass spectrum: m/z 247, 245, 243, 241, 206. Anal. Calcd for C$_8$H$_{10}$Cl$_3$NO : C, 39.62; H, 4.16; N, 5.78. Found: C, 39.67; H, 3.98; 5.53.

124   125
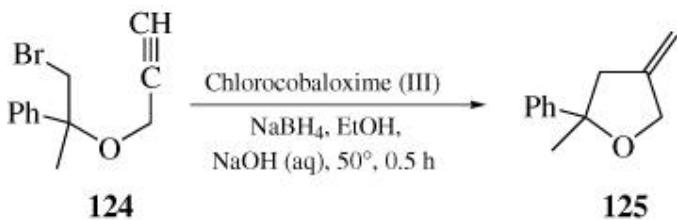
6.1.12. 2-Methyl-2-phenyl-4-methylenetetrahydrofuran *(125)* *(Cobalt-Mediated Cyclization; Radical/Radical Coupling) (223)*

To a solution of bromide **124** (2.53 g, 10 mmol) in ethanol (50 mL) were added aqueous sodium hydroxide (10 N, 1 mL) and sodium borohydride (380 mg, 10 mmol). The solution was warmed to 50° under nitrogen, and powdered chlorocobaloxime(III) (240 mg, 0.6 mmol) was added in portions over 1 hour. The temperature of the mixture was kept at 50–60°. After the addition, the mixture was stirred for 30 minutes at the same temperature. Most of the ethanol was removed under reduced pressure, and saturated NaCl (50 mL) was added. The mixture was extracted with pentane–ether (4:1) several times. The extracts were washed with saturated NaCl and dried (Na_2SO_4). After evaporation of the solvents, the residue was distilled under reduced pressure to give **125** (1.27 g, 73%); bp 62–63° (0.5 mm Hg). IR (CCl_4) 1671, 1044, 884, 700 cm^{-1};^{1}H NMR(CCl_4) δ 7.50–7.20 (m, 5H), 4.97 (t, J = 2 Hz, 1H), 4.87 (t, J = 2 Hz, 1H), 4.42 (broad t, J = 15 Hz, 2H), 2.91 (broad d, J = 16 Hz, 1H), 2.70 (broad d, J = 16 Hz, 1H), 1.48 (s, 3H); HRMS, calcd for $C_{12}H_{14}O$ M$^+$): *m/z* 174.1043, found *m/z* 174.1041.
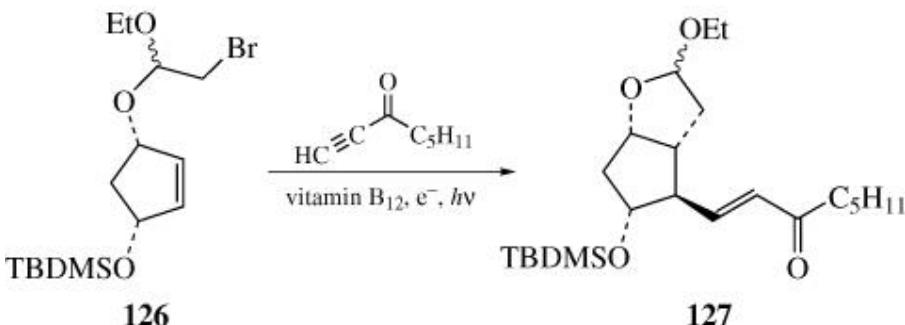
6.1.13. trans-1-[(2R/S,3aR,4R,5R,6aS)-5-([[(1,1-Dimethylethyl)-dimethylsilyl]oxy)-2-ethoxyhexahydro-2H-cyclopenta[b]furan-4-yl]octen-3-one *(127)* *(Reductive Cyclization Catalyzed by Vitamin B$_{12}$) (224)*

The cathode compartment of an electrochemical cell containing C-felt (2.77 g) as cathode material was charged with a solution of vitamin B$_{12}$ (250 mg, 0.18 mmol) in 0.3 M LiClO$_4$/DMF (250 mL). The anode compartment was charged with 0.3 M LiClO$_4$/DMF (ca. 50 mL). The B$_{12}$ was reduced to Co(I) at a constant cathode potential of –1.4 V (vs. SCE) until the initial current of about 50 mA had diminished to a stable background level and the color had changed from red to dark green. On reducing the potential to –0.9 V a stable background level of approximately 3.5 mA was observed. Keeping the potential at –0.9 V, 1-octyn-3-one (3.72 g, 30.0 mmol) was added, followed by bromoacetal **126** (3.65 g, 10.0 mmol) after 15 minutes. Thereby the color changed to dark red and the current remained at a low level. After switching on

the 250-W halogen lamp the current rose to 30 mA and the temperature to 40–41°, which was maintained throughout the reaction. Additional alkyne was added after 5 hours (2.48 g, 20.0 mmol) and again after 25 hours (1.24 g, 10.0 mmol). After 44 hours the current had diminished to a constant background level of 9 mA, and 1543 Cb e^- (16.0 mmol) had been consumed. The solution was poured into ice water (750 mL) and extracted with Et_2O(6 × 100 mL). The organic solution was washed with brine (3 × 100 mL), dried (Na_2SO_4), and the solvent removed. Excess alkyne was removed by bulb-to-bulb distillation (45° oven temperature/5 × 10^{-2} mbar) and the residual dark brown liquid (8.86 g) was filtered through silica gel (70 g; low-boiling petroleum ether/Et_2O 8:2). Flash chromatography of the crude product (219 g silica gel; low-boiling petroleum ether/Et_2O 19:1 to 8:1) afforded two main fractions. The latter was the desired product **127**: 3.5 g of a yellow liquid comprising four isomers of **127** (containing at least 65 % product by GC). For *cis-trans* isomerization the latter fraction was dissolved in hexanes (50 mL) containing I_2 (90 mg), washed with brine containing a small amount of sodium thiosulfate (2 × 25 mL), and brine (25 mL), dried (Na_2SO_4), and the solvent removed. Flash chromatography (150 g; low-boiling petroleum ether–Et_2O 19:1 to 8:2) of the remaining dark liquid (3.36 g) afforded essentially pure product [2 diastereomers, 1.07 g (26 %) and 0.85 g (21 %)] as slightly yellow oils (assignment of configuration was based on NOE experiments). For elemental analysis a sample was distilled in a glass tube at 150° (oven temperature/5 × 10^{-3} mbar). Anal. Calcd for $C_{23}H_{42}O_4Si$: C, 67.27; H, 10.31. Found: C, 67.27; H, 10.23; IR (neat) 3450, 2960, 2930, 2860, 2250, 1695, 1680, 1630, 1465, 1405, 1380, 1360, 1250, 1115, 1050, 1005, 910, 865, 835, 775, 730, 670, 645 cm^{-1};^{1}H NMR($CDCl_3$) δ 6.64 (dd, J = 15.83, 8.05 Hz, 1H), 6.09 (dd, J = 15.84, 0.96, 1H), 5.19 (d, J = 4.91 Hz, 1H), 4.42 (ddd, J = 7.02, 7.02, 4.20 Hz, 1H), 3.89 (ddd, J = 8.15, 8.15, 8.15 Hz, 1H), 3.67 (dqd, J = 9.61, 7.11, 0.76, 2H), 3.48–3.34 (m, 2H), 2.48 (t, J = 7.45, 1H), 2.45–2.25 (m, 3H), 2.01 (ddd, J = 13.53, 8.82, < 1 Hz, 1H), 1.84 (ddd, J = 13.48, 4.83, 4.83 Hz, 1H), 1.72 (ddd, J = 13.48, 8.86, 4.34 Hz, 1H), 1.65–1.50 (m, 1H), 1.35–1.10 (m, 2H), 1.15 (td, J = 7.07, 0.77, 3H), 0.95–0.70 (m, 1H), 0.82 (s, 9H), – 0.02 (s, 6H); ^{13}C NMR($CDCl_3$) δ 146.2, 130.8, 105.1, 79.5, 78.1, 62.6, 57.0, 44.3, 41.0, 40.4, 38.4, 31.5, 25.7, 24.0, 22.5, 18.0, 15.2, 13.9,–4.5,–4.7; mass spectrum: *m/z* 365, 354, 353, 309, 308, 307, 281, 234, 233, 199, 189, 187, 178, 161, 153, 151, 136, 135, 133, 131, 129, 117, 107, 105, 101, 99, 91, 81, 79, 75, 73, 72, 71, 59, 55, 44, 43, 41.

128 → 129 (reagents: NaC$_{10}$H$_8$, THF, rt, 3 h)
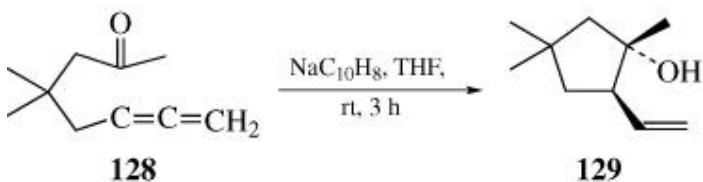
6.1.14. trans-2-Ethenyl-1,4,4-trimethylcyclopentanol (129) (Reductive Cyclization with NaC₁₀H₈) (225)

General Procedure: To a solution of dry recrystallized naphthalene (1.92 g, 15.0 mmol) in dry tetrahydrofuran (20 mL), stirred under nitrogen at room temperature, was added freshly cut sodium (580 mg, 25.2 mmol) in small pieces. The resulting green solution was then stirred at room temperature for 3 hours. This routinely gave a 0.6 M solution of the reagent. The solution of sodium naphthalenide (0.6 M, 2.8 mL, 1.68 mmol) was added dropwise under nitrogen to a well-stirred solution of **128** (304.2 mg, 2.0 mmol) in dry tetrahydrofuran (11 mL) at room temperature until a faint green end point was reached. The coloration discharged in about 3 minutes after turning off the nitrogen. The mixture was poured into water (30 mL) and then extracted with ether (3 × 25 mL). The combined ether extracts were washed with dilute hydrochloric acid (30 mL), followed by water until they were neutral. Evaporation of the dried extracts gave the crude product, which was purified by column chromatography on silica gel using ether hexane (1:1) as eluant, giving 97.1 mg (55.8%) of the desired alcohol **129** (eluted second) and 132.6 mg (22.1%) of recovered starting material (eluted first). IR 3370, 1540 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 5.84 (m, 1H), 5.08 (m, 2H), 2.69 (m, 1H), 2.20–0.69 (m,5H), 1.16 (s, 3H), 1.14 (s, 3H), 1.06 (s, 3H); ^{13}C NMR(CDCl$_3$) δ 138.1 (d), 115.6 (t), 81.01, 56.04 (t), 55.0 (d), 45.4 (t), 37.8, 32.1 (q), 31.6 (q), 25.1 (q); high resolution mass spectrum, calculated for C$_{10}$H$_{18}$O *m/z* 154.1357, found *m/z* 154.1351.

130   SmI$_2$, THF, HMPA, *t*-BuOH   **131** diastereomeric ratio >150:1
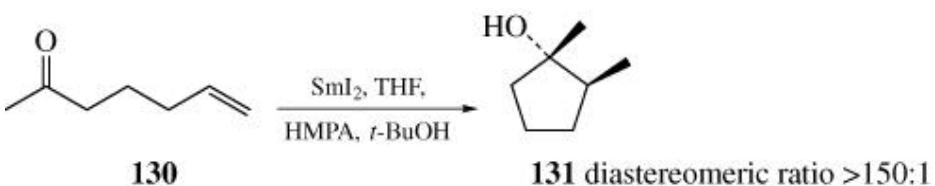
6.1.15. (1R*,2R*)-Dimethylcyclopentan-1-ol (131) (Reductive Cyclization with Samarium(II) Iodide) (178)

General Procedure for Preparation of SmI₂/THF/HMPA: Samarium metal (0.30 g, 2.0 mmol) was added under a flow of argon to an oven-dried round-bottomed flask containing a magnetic stirring bar and septum inlet. The flask and samarium were gently flame dried and cooled under argon. To the samarium was added 13 mL of tetrahydrofuran followed by methylene iodide (0.482 g, 1.8 mmol), and the mixture was stirred at room temperature for 1.5 hours. HMPA [CAUTION, SUSPECTED CARCINOGEN] (2.51 mL, 14.5 mmol) was added, and the resulting purple solution was stirred 10 minutes before

addition of the olefinic ketone.

General Procedure for Cyclization of Olefinic Ketones: To the SmI_2 solution described above was added olefinic ketone **130** (0.116 g, 1.04 mmol) and *t*-BuOH (0.160 g, 2.16 mmol) in 14 mL of THF over a 15-minute period. Upon completion, the reaction was quenched with saturated aqueous $NaHCO_3$ and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Final purification involved filtering through a short column of Florisil to remove residual HMPA. Kugelrohr distillation gave 0.102 g (86%) of desired product **131**: bp 60° (25 mm Hg). IR (CCl_4) 3419, 2940, 2856 cm^{-1};^{1}H NMR($CDCl_3$) δ 1.96–1.48 (m, 6H), 1.82 (br s, 1H), 1.20–1.12 (m, 1H), 1.09 (s, 3H), 0.82 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR($CDCl_3$) δ 80.90, 44.67, 40.06, 31.73, 22.71, 20.45, 15.40. High resolution mass spectrum, calculated for $C_7H_{14}O$ *m/z* 114.1045, found *m/z* 114.1051; Low resolution mass spectrum *m/z* 114, 85, 71, 58.
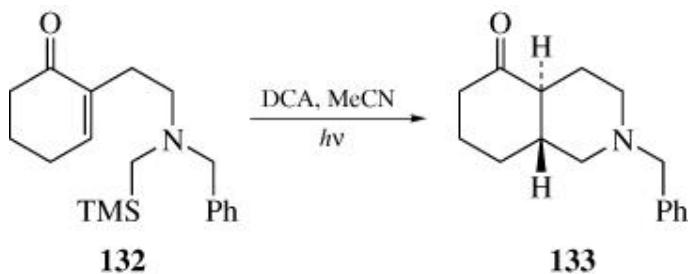
6.1.16. Photosensitized Reductive Cyclization of Aminoethylcyclohexenones (*226*)

Solutions of the (aminoethyl)cyclohexenones (2 mmol) in MeOH (with and without added MeCN) containing 9,10-dicyanoanthracene (DCA) (ca. 1×10^{-4} M) were irradiated with uranium glass-filtered light. Irradiations were monitored by GLC and UV and terminated when >95% of starting material was consumed. The photolysates were concentrated in vacuo and filtered to remove DCA. The filtrates were subjected to an acid–base extraction procedure to separate the amine products. The amine-containing fractions were subjected to chromatographic (flash column) separation to provide the photoproducts.

Irradiation of N-Benzyl-N-trimethylsilylmethylaminoethylcyclohexenone (**132**): A solution of **132** (1 mmol) in MeCN containing DCA (6.6×10^{-2} mmol) was irradiated for 4 hours (78% conversion). Product yields were determined by GC with triphenylene as internal standard. Workup followed by preparative TLC (silica gel, 1:10 EtOAc–hexanes) separation afforded cyclized products.

133: IR 2930, 2870, 2800, 2760, 1710, 1495, 1450, 1440, 1465, 1310, 1270, 1165, 1070, 1025, 985 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 7.33–7.21 (m, 5H), 3.52 and 3.45 (q, J = 13.2 Hz, 2H), 2.97 (br d, J = 11.3 Hz, 1H), 2.89 (br d, J = 10.5 Hz), 2.36 (m, 1H), 2.29 (ddd, J = 13.8, 13.5, 6.6 Hz, 1H), 2.05 (m, 1H), 1.93 (ddd, J = 12.5, 11.3, 2.7 Hz, 1H), 1.91 (ddd, J = 11.7, 11.6, 3.4 Hz, 1H), 1.80 (m, 2H), 1.78 (dd, J = 10.4, 10.5 Hz, 1H), 1.74–1.64 (m, 3H), 1.60 (dddd, J = 13.1, 12.5, 11.7, 3.9 Hz, 1H), 1.38 (dddd, J = 13.7, 13.6, 13.5, 3.8 Hz, 1H); ^{13}C NMR(CDCl$_3$) δ 221.3, 138.3, 129.0, 128.2, 127.0, 63.0, 60.0, 53.4, 53.3, 43.3, 41.5, 29.6, 26.2, 24.7. MS m/z: 243, 201, 159, 146, 134, 113, 91; HRMS m/z 243.1620 (C$_{16}$H$_{21}$NO requires 243.1623).

134   135
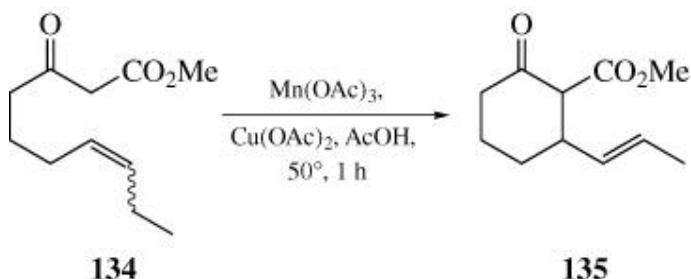
6.1.17. Methyl trans-2-Oxo-6-[1E-propenyl]cyclohexanecarboxylate (135) [Oxidative Cyclization with Manganese) (192)

To a solution of Mn(OAc)$_3$·2H$_2$O (1.376 g, 5.10 mmol) and Cu(OAc)$_2$ (0.510 g, 2.55 mmol) in 18 mL of glacial acetic acid was added a solution of **134** (0.505 g, 2.55 mmol) in 7 mL of glacial acetic acid to give an opaque brownish green solution containing some undissolved Mn(OAc)$_3$·2H$_2$O. The mixture was stirred for 1 hour at 50° at which time the solution was light blue and contained a white precipitate. Water was added to give a single cloudy phase in which the white precipitate had dissolved. The solution was extracted with five 15-mL portions of methylene chloride. The combined organic layers were washed with saturated aqueous sodium bicarbonate solution until neutral and then with water. The aqueous layer was back extracted with two 15 mL-portions of methylene chloride. The combined organic layers were dried over MgSO$_4$, and the solvent was removed in vacuo to provide 0.512 g of crude cyclized product **135**. Flash chromatography on silica gel (3:1 hexanes–Et$_2$O) gave 0.365 g (71%) of **135** as a 1.3:1 mixture of keto and enol tautomers. The keto and enol tautomers were partially separated by flash chromatography but equilibrated at 25° after 15 days: IR (neat) 1745, 1715 cm^{-1}; Anal. Calcd for C$_{11}$H$_{16}$O$_3$: C, 67.32; H, 8.22. Found: C, 66.90; H, 8.33%.

Keto tautomer: ^{1}H NMR (CDCl$_3$) δ : 5.47–5.08 (m, 2H), 3.63 (s, 3H), 3.12 (d, J = 12.0 Hz, 1H), 2.75 (dddd, J = 12.0, 12.0, 8.0, 4.0 Hz, 1H), 2.35–2.32 (m,

1H), 2.29–1.57 (m, 5H), 1.54 (d, J = 3.7 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 205.2, 169.5, 131.7, 126.2, 62.9, 51.6, 44.3, 40.6, 34.1, 24.6, 17.7. Enol tautomer: ^{1}H NMR (CDCl$_3$) δ : 12.32 (enolic H), 5.47–5.08 (m, 2H), 3.63 (s, 3H), 3.15–3.05 (m, 1H), 2.41–2.36 (m, 1H), 2.29–1.57 (m, 5H), 1.54 (d, J = 3.7 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 172.8, 134.1, 124.5, 99.7, 51.0, 39.6, 30.4, 28.8, 28.0, 16.8, one carbon was not observed.

136   137
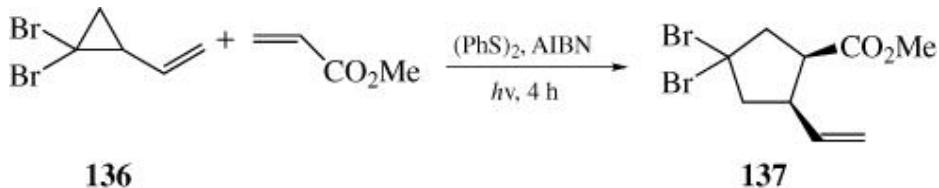
6.1.18. cis/trans Methyl 3,3-Dibromo-5-ethenyl-r-1-cyclopentanecarboxylate (137) (Sequential Reaction) (227)

A solution containing **136** (50 mg, 0.22 mmol), methyl acrylate (0.3 mL, 3.32 mmol), phenyl disulfide (8 mg, 0.04 mmol), and AIBN (36 mg, 0.22 mmol) was irradiated for 4 hours with a 300-W sun lamp. Purification of the residue by flash chromatography using Et$_2$O–hexanes (5:95) as eluent yielded 51 mg (74%) of cyclopentane **137** (diastereomer ratio = 9:1) as a clear oil. Partial separation of the two diastereomers was achieved by careful flash chromatography using Et$_2$O–hexanes (3:97) as eluent.

cis: IR (neat) 1715 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ5.68 (ddd, J = 17.1, 10.1, 8.1 Hz, 1H), 5.12 (d, J = 17.0 Hz, 1H), 5.07 (d, J = 10.0 Hz, 1H), 3.65 (s, 3H), 3.36 (m, 2H), 3.14 (dd, J = 14.5, 9.0 Hz, 1H), 3.01 (m, 1H), 2.93 (ddd, J = 14.2, 4.3, 2.3 Hz, 1H), 2.63 (dd, J = 14.2, 9.9 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 172.5, 135.3, 117.5, 62.2, 56.0, 53.5, 51.8, 46.3, 44.2; MS *m/z* 312, 233, 173; HRMS calcd for C$_9$H$_{12}$O$_2$Br$_2$, 311.9184; found, 311.9156.

trans: IR (neat) 1715 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.59 (ddd, J = 17.4, 10.2, 7.6 Hz, 1H), 4.91 (dt, J = 17.0, 1.2 Hz, 1H), 4.83 (dd, J = 10.1, 1.2 Hz, 1H), 3.25 (s, 3H), 3.16 (ddd, J = 17.4, 8.6, 7.7 Hz, 1H), 3.02 (ddd, J = 14.6, 7.9, 1.4 Hz, 1H), 2.72 (dt, J = 14.0, 1.3 Hz, 1H), 2.70 (dt, J = 14.0, 1.3 Hz, 1H), 2.60 (heptet, J = 8.6 Hz, 1H), 2.32 (ddd, J = 14.5, 8.6, 1.1 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 173.3, 138.6, 116.0, 61.4, 56.9, 54.4, 52.2, 48.5, 45.5; MS *m/z* 281, 233, 173; HRMS calcd for C$_8$H$_9$O$_2$Br$_2$(M$^+$ – OMe) *m/z* 280.9000; found, *m/z* 280.8993.

138   **139**
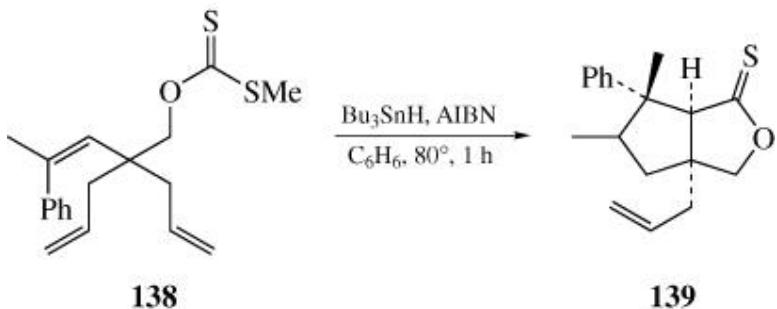
6.1.19. 7,8-Dimethyl-8-phenyl-5-(2-propenyl)-3-oxabicyclo[3.3.0]octane-2-thione *(139) (Tandem Radical Cyclization of Homoallylic Xanthates; Sequential Reaction) (651)*

A mixture of **138** (0.225 g, 0.68 mmol), tributyltin hydride (0.224 g, 0.77 mmol), and AIBN (0.011 g, 0.066 mmol) in 35 mL of thiophene-free degassed dry toluene was heated at 80° with stirring for 1 hour under an argon atmosphere. The solvent was removed under reduced pressure. The pale yellow oil was purified by flash chromatography on silica gel (benzene) to give 0.138 g (71%) of the product **139**; mp 87–88°; IR (CHCl$_3$) 3050, 1640, 1270, 1180, 1030 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.43–7.23 (m, 5H), 5.86–5.77 (m, 1H), 5.26–5.21 (m, 2H), 4.60 (d, J = 10.0 Hz, 1H), 4.44 (d, J = 10.0 Hz, 1H), 3.58 (s, 1H), 2.39 (d, J = 7.2 Hz, 2H), ddq, J = 12.9, 12.9 and 7.0 Hz, 1H), 2.10 (dd, J = 12.9, 7.0 Hz, 1H), 1.74 (dd, J = 12.9 and 12.9 Hz, 1H), 1.29 (s, 3H), 0.77 (d, J = 6.7 Hz, 3H); ^{13}C NMR (CDCl$_3$) INEPT δ 221.8 (C), 144.5 (C), 132.7 (C), 128.0 (CH), 126.8 (CH), 126.5 (CH), 126.4 (CH), 120.2 (CH$_2$), 88.0 (CH$_2$), 78.6 (CH), 53.6 (C), 50.4 (C), 47.8 (CH), 45.0 (CH$_2$), 43.8 (CH$_2$), 14.0 (CH$_3$), 12.7 (CH$_3$); high resolution mass spectra for C$_{18}$H$_{22}$OS (M$^+$), calculated for m/z 346.1776, found m/z 346.1780.

7. Tabular Survey

The computer search of Chemical Abstracts covers the literature from 1964 to the end of 1993.

The tabular organization of the radical cyclization reactions starts with monocyclic rings followed by bicyclic and oligocyclic ring systems. Furthermore, each of these tables is divided into ring systems containing only carbon atoms and rings containing one or more heteroatoms. Within each table the compounds are listed according to ring size. Order of entry is determined by total carbon number of the substrate(s) and then total hydrogen number.

The reaction conditions include the type of mediator, solvent, and temperature (°C) if provided in the literature. Yields are given in parentheses and are based on either isolation or GC analyses. A dash (—) indicates that no yield was reported. Numbers not in parentheses are product ratios. When a reaction has been reported in more than one publication, the conditions producing the highest yield are given, and the reference to that paper is listed first.

The following abbreviations are used in the tables:

Ac	acetyl
ACN	azobiscyclohexylnitrile
AIBN	azobisisobutyronitrile
B_{12}	Vitamin B_{12}
BOC	*tert*-butoxycarbonyl
BOM	benzyloxymethyl
Bn	benzyl
BPO	benzoyl peroxide
bpy	bipyridine
Bu	butyl
Bz	benzoyl
Cbz	benzyloxycarbonyl
Cp	cylopentadienyl
CHD	cyclohexadiene
DBA	di-*tert*-butylamino
DCA	dicyanoanthracene
DCN	dicyanonaphthalene
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone

DIPHOS	1,2-bis(diphenyphosphino)ethane
DMF	*N,N*-dimethylformamide
dmgH	dimethyl glyoximate
DMP	dimethylpyrrolidinium
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone
DPDC	diisopropylperoxy dicarbonate
DPPE	2-(diphenylphosphino)ethyl
Glu	glucose
HMPA	hexamethylphosphoric triamide
Im	imidazole
IBDA	iodosobenzene diacetate
MEM	2-methoxyethoxymethyl
Mes	mesityl
MOM	methoxymethyl
Ms	methanesulfonyl (mesylate)
NBS	*N*-bromosuccinimide
NIS	*N*-iodosuccinimide
pic	2-pyridinecarboxylate
Piv	pivaloyl
PMB	*p*-methoxybenzyl
PTOC	[(1*H*)-pyridine-2-thione]oxycarbonyl
py	pyridine
pytos	pyridinium tosylate
salen	*N,N*¢-1,2-ethylenebis(salicylidimine)
salophen	*N,N*¢-1,2-phenylenebis(salicylidimine)
TBAF	tetrabutylammonium fluoride
TBAI	tetrabutylammonium iodide
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
thexyl	dimethyl-(2,3-dimethyl-2-butyl)
TMS	trimethylsilyl
TMTHF	tetramethyltetrahydrofuran
Tf	trifluoromethanesulfonate (triflate)
THF	tetrahydrofuran
THP	tetrahydropyran
TMP	2,2,6,6-tetramethylpiperidin-1-yl
Tol	toluene

Tr   trityl = triphenylmethyl
Ts   *p*-toluenesulfonyl
p-TSA   *p*-toluenesulfonic acid

Table I. Monocyclic Rings Containing Only Carbon

View PDF

Table II. Monocyclic Rings Containing One or More Heteroatoms

View PDF

Table III. Bicyclic Rings Containing Only Carbon

View PDF

Table IV. Bicycic Rings Containing One or More Heteroatoms

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Table V. Oligocyclic Rings Containing Only Carbon

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Table VI. Oligocyclic Rings Containing One or More Heteroatoms

[View PDF]

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7	A. 3-Membered Rings		
[structure] + Cl_3CSO_2Cl	Zn-Cu, CCl_4, 150°	[structure] (65)	229
C_{12}			230
[structure] $Fe(CO)_2(Cp)$	CBr_4, CH_2Cl_2	$R = CBr_3$ (65)	
	$ArSO_2I$, CH_2Cl_2	$R = ArSO_2$ (70)	
	Cl_3CSO_2Cl, CH_2Cl_2	$R = CCl_3$ (65)	
C_{17}			
[structure] $Co(dmgH)_2py$	Cl_3CSO_2Cl, CH_2Cl_2, $h\nu$	Cl_3C [structure] (75)	138
	TsI, CH_2Cl_2, 40°	Ts [structure] (60)	139
C_{18}			
[structure] $Co(dmgH)_2py$	Cl_3CBr, CH_2Cl_2, 55°	Cl_3C [structure]	231
		R^1	
		H (26)	
		Me (66)	
		Ph (43)	
[structure] $Co(dmgH)_2py$	Cl_3CBr, CH_2Cl_2, $h\nu$	Cl_3C [structure] (85)	138
[structure] $Co(dmgH)_2py$	Cl_3CBr, CH_2Cl_2, $h\nu$	Cl_3C [structure] (82)	138

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₂₃	Br₂CHCN, CH₂Cl₂, 55°	R¹ R² Me H (61) Ph CN (87)	231
	p-MeC₆H₄SO₂I, CH₂Cl₂, 40°	(72)	139
	PhMe, heat	R¹ R² PhCH₂ H (47) PhCH₂ Me (43) n-C₁₀H₂₁ H (60)	11
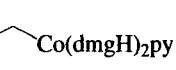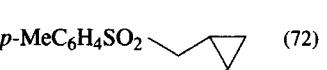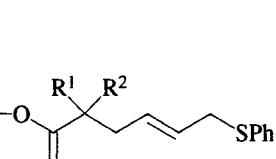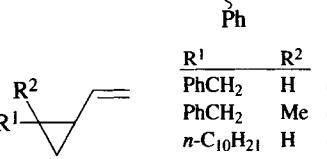
B. 4-Membered Rings

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₈	Bu₃SnH, AIBN, C₆H₆, 80°	(45)	232
C₁₂	Bu₃SnH, AIBN, C₆H₆, 80°	(72)	12
C₁₃	Bu₃SnH, AIBN, PhMe, 110°	(74)	233
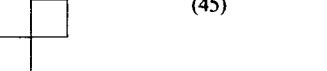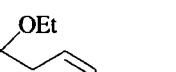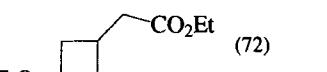
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
		C. 5-Membered Rings	
C₆	1. SmI₂, HMPA 2. ArCHO	(80) Ar = p-MeOC₆H₄	234
	AIBN, C₆H₆, 80°	I + II	
	Bu₃SnH, (TMS)₃SiH	I (34) + II (6) I (41) + II (11)	235 236
	(Bu₃Sn)₂, C₆H₆, 70-75°, hν	R¹ R² H H (77) Me H (87) E:Z = 3.3:1 Me Me (95) E:Z = 15:1	237
	1. MgI₂ 2. Bu₃SnH, AIBN, C₆H₆, 80°	R¹ R² H H (30) H OH (53) OH H (35)	238
	Bu₃SnH, AIBN, xylene, 130°	(92) + (1)	239

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(allyl–HgBr)	I_2, dioxane	(iodomethyl cyclopentane) (62)	240
C_7 OHC ... CN	Bu_3SnH, AIBN, C_6H_6, 80°	I + II; I + II (73) I:II = 52:48	115
Cl, Cl, CF_3, HO ...	Bu_3SnH, AIBN, 65°, 8 h	CF_3, Cl, HO ... (78)	241
O=CH ... CN *E:Z* = 65:35	1. Bn_2NH, benzotriazole 2. SmI_2, THF, 25°	Bn_2N ... CN (63) *cis:trans* = 67:33	242
Z + R,R,X	Bu_3SnH, AIBN, C_6H_6, 80°	R, Z, Z ...	243

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Z	X	R	time (h)	Yield
CN	Br	H	5	(58)
CN	I	Me	4	(65)
CO_2Et	I	Me	3	(75)
COMe	I	Me	4	(75)
CHO	I	Me	1.5	(60)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(hept-6-en-2-one)	SmI_2, THF, HMPA	HO ... (86)	178
	Hg cathode, DMF, $Bu_4N^+BF_4^-$, $DMP^+BF_4^-$	" (100)	244, 245
	Carbon rod cathode, MeOH, dioxane, Et_4NOTs	" (98)	246, 245
H–C≡C ... O (ynone)	Hg cathode, DMF, $Bu_4N^+BF_4^-$, $DMP^+BF_4^-$	HO ... (85)	244
Cl, Cl, CO_2Et	$RuCl_2(PPh_3)_3$, C_6H_6, sealed tube, 150°, 22 h	Cl, CO_2Et, H, Cl (61) + Cl, CO_2Et, H, Cl (13)	221

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	K$_3$Fe(CN)$_6$, N$_2$, NaOMe, MeOH	I + II (71) I : II = 60 : 40	247
	(Bu$_3$Sn)$_2$, C$_6$H$_6$, 70-80°, *hv*		248

R^1	R^2	R^3	
H	H	Me	(71)
H	H	TMS	(41)
H	Me	H	(65) E:Z = 77:23
Me	Me	H	(60) E:Z = 93:7
Me	Me	Me	(54) E :Z = 79:21
Me	Me	TMS	(45) E:Z = 19:81

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
+ CO	Bu$_3$SnH, AIBN, CO (75-90 atm), C$_6$H$_6$, 80°		249

R^1	R^2	R^3	X	
Me	Me	H	Br	(65)
Me	Me	Me	Br	(77)
H	Ph	H	Br	(62)
H	CO$_2$Et	H	I	(60)

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(27) + (46)	16
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(48) + (18)	16
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(16) + (53)	16
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 65°	+ 40:60	249a
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 70°	(88) + (3)	239
	AIBN, *n*-C$_6$H$_{14}$, 74°	(75)	250
	(Bu$_3$Sn)$_2$, C$_6$H$_6$, sun lamp, 80°	" (72)	106

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_8

C_6H_6, 80°, 10 h

I + **II**

I : II = 80 : 20   I + II (84)

251

$(Me_3Sn)_2$, hv

I + **II**
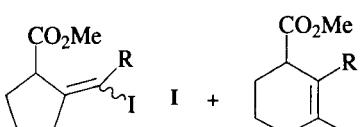
R = H   I + II (85)   I : II = 95 : 6
R = TMS   I + II (81)   I : II = 97 : 3

156

Bu_3SnH, AIBN,
C_6H_6, 80°

I + **II**
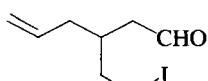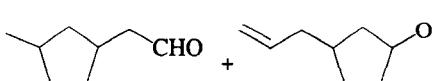
I + II (84)   I:II = 3:1

41, 40

Ph_3SnH, AIBN,
C_6H_6, 80°

I, II

27

R^1	R^2	R^3		I + II	I:II
Me	Me	Me		(75)	78:22
Me	H	H		(50)	80:20
Me	Me	$(CH_2)_2CH=CMe_2$		(78)	79:21
n-C_5H_{11}	H	Ph		(87)	63:37

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

 OHC...CO₂Me

$VCl_3(THF)_3$, Zn,
CH_2Cl_2, 25°

I + **II**

I + II (68)   I:II = 24:1

252

Bu_3SnH, AIBN,
C_6H_6, 80°
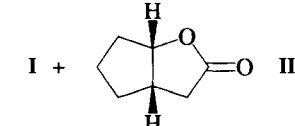
I + **III**

I + III (81)   I:III = 52:48

115
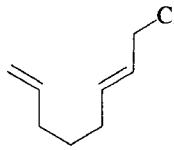
$(PhSe)_2$, DCN,
MeCN, hv,
(>280 nm)

(70)

253

$(Me_3Sn)_2$, AIBN,
C_6H_6

I + **II**

156

R		I cis:trans	II cis:trans	
MeO	16 h	57:43	34:66	(83)
t-BuO	hv, 10 min	47:53	31:69	(74)
Ph	hv, 10 min	28:72	30:70	(68)
t-Bu	hv, 10 min	35:65	33:67	(63)

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°		254

R^1	R^2	R^3	R^4	
Me	Me	Me	Me	(77)
H	Me	Me	Me	(74)
Et	Me	Me	Me	(91)
Me	Me	H	H	(37)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(*t*-BuO)$_2$, PhCl, 132°	(61)	255
	Cp$_2$TiCl, H$^+$	(94) isomeric ratio = 1:1	172
	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	(83)	16
	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	" (83)	16

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN PhMe, 100°	(74) + (4)	239
	Bu$_3$SnH, AIBN PhMe, 100°	(92) + (4)	239
	(Bu$_3$Sn)$_2$, AIBN, C$_6$H$_6$, 80°, *hv*	(75)	106
	K$_3$Fe(CN)$_6$, NaOMe, MeOH	I + II I + II (93) I:II = 40:60	247
	K$_3$Fe(CN)$_6$, NaOMe, MeOH	I + II I + II (93) I:II = 50:50	247

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO₂C, MeO₂C (with I and alkyne/ene) + R¹/R² alkene	(Bu₃Sn)₂, C₆H₆, *hv*	MeO₂C, MeO₂C cyclopentane with =CHI, R¹, R²	256

R¹	R²	
H	Ph	(59) *E:Z* = 3:1
H	CH₂TMS	(74) *E:Z* = 3:1
Et	Et	(77) *E:Z* = 4.4:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO₂C, MeO₂C (with I and allyl) + R¹/R² alkene	(Bu₃Sn)₂, C₆H₆, *hv*	MeO₂C, MeO₂C cyclopentane with CH₂I, R¹, R²	256

R¹	R²	
H	Ph	(70) *E:Z* = 1:1.4
H	CH₂TMS	(71) *E:Z* = 4.6:1
Et	Et	(72)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(butenyl 1,3-oxathiolan-5-one)	Bu₃SnH, AIBN C₆H₆, 80°	I (2-methylcyclopentanol) + II (2-methylcyclopentanol) I:II = 3:2 I + II (74)	116

C₉

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
Br, Br (1,1-dibromo-2-vinylcyclopropane) + CO₂Me (methyl acrylate)	(PhS)₂, AIBN, *hv*	Br, Br cyclopentane with CO₂Me and vinyl (74) *cis:trans* = 9:1	227

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
Cl, Cl (1,1-dichloro-2-vinylcyclopropane) + CN (crotononitrile)	(PhS)₂, AIBN, *hv*	Cl, Cl cyclopentane with CN, vinyl (73) 19:5:5:1 major isomer is shown	227

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
O with ≡CH and R¹/R² alkene (enynone)	Bu₃SnH, AIBN C₆H₆, 80°	cyclopentanone with =CHSnBu₃ and CH(R¹)(R²)	257
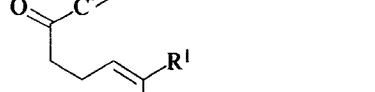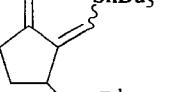
R¹	R²	
Me	Me	(91)
Ph	H	(92)
CO₂Et	H	(88)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
Br (4-(bromoethyl)-1,6-heptadiene)	Bu₃SnH, AIBN C₆H₆, 80°	methyl allyl cyclopentane (80 - 100)	258

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R¹/R² diallyl	TsBr, MeCN, *hv*, 20°	I (CH₂Br, Ts, R¹, R²) + II (CH₂Br, Ts, R¹, R²) + III (CH₂Br, Ts, R¹, R²)	259

R¹	R²	
CO₂Me	H	I:II:III = 69:19:12 (70)
Ph	CO₂Me	I:II:III = 73:27:0 (76)

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
CO₂Et structure, X = Br, X = OC(S)SMe	Bu₃SnH, AIBN C₆H₆, 80°	(cyclopentane-CH₂CO₂Et) (75) (68)	17
diene-iodo-OH structure	Bu₃SnH, O₂, PhMe	(cyclopentyl products) (38) + (24)	260
OHC—(chain)—CO₂Et	1. Benzotriazole, pyrrolidine (N–H) 2. SmI₂, THF, 25°	(pyrrolidine-cyclopentane-CH₂CO₂Et) (70)	242
ketone-allene structure	Na, THF, ultrasound NaC₁₀H₈, THF	I + II I:II = 70:30 (44) I:II = 74:26 (44)	261

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
EtO₂C—CHI—(chain)—alkene	Cr(OAc)₂, THF, rt	I + II + III (83) I:II:III = 63:32:5	262
Cl₂C(CO₂Et)—(chain)—C≡CR	RuCl₂(PPh₃)₃, cumene, 160°	R H (70) Me (83)	221
R¹C(O)—C(R²)(C(O)Y)—allyl	SmI₂, THF, 25°	main isomer	263

R¹	R²	Y	Diastereoselectivity	
Me	Me	OEt	25:1	(75)
Et	Me	OEt	30:1	(66)
i-Pr	Me	OEt	30:1	(63)
Me	Et	OEt	200:1	(51)
Me	H	OMe	20:1	(60)

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{10}$			
(β-keto ester, CO$_2$Me, alkene chain)	Mn(OAc)$_3$, Cu(OAc)$_2$, HOAc, 50°	(cyclopentanone CO$_2$Me propenyl) (36)	192
(dienoate, I, CO$_2$Me)	Bu$_3$SnH, O$_2$, PhMe	(cyclopentyl CHOH CH=CH CO$_2$Me) (69)	260
(EtO xanthate, S, O, pentenyl)	C$_7$H$_{16}$, reflux, *hv*	(cyclopentyl CH$_2$ S C(=S) OEt) (87)	264
(epoxide alkene I)	Ph$_3$SnH, Et$_3$B, C$_6$H$_{14}$, C$_6$H$_6$, 25°	(cyclopentyl CH=CH C(OH)Me$_2$) **I** + (cyclopentylidene CH$_2$ C(OH)Me$_2$) **II** **I + II** (48) **I:II = 3:2**	265
(allene Br, C=C=C=C)	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	(dimethyl cyclopentene C≡C) (43)	266

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(EtO$_2$C, NC, alkene)	CuCl$_2$, DMF, 80°	(EtO$_2$C, NC, cyclopentane CH$_2$Cl) (67)	267

(R^2, Br, R^3, Me, Si, Me, O, R^1)

1. Ph$_3$SnH, AIBN C$_6$H$_6$, 80°
2. H$_2$O$_2$

(cyclopentene R^2, R^3, CH$_2$OH, R^1 OH) **I** + (cyclohexene R^2, R^3, CH$_2$OH, OH, R^1) **II** 215

R^1	R^2	R^3		I + II	I:II
H	H	Me		(65)	100:0
H	n-C$_5$H$_{11}$	Me		(79)	90:10
H	H	H		(60)	100:0
H	n-C$_5$H$_{11}$	H		(67)	100:0
n-C$_5$H$_{11}$	H	Me		(75)	100:0
H	Ph	Me		(80)	42:58

(O, SMe, R^2, SMe, Br, R^1, R^1) | Bu$_3$SnH, AIBN C$_6$H$_6$, 80° | (O, SMe, R^2, SMe cyclopentanone, R^1, R^1) |

R^1	R^2	
Me	H	(42)
H	Ph	(54)
H	Me	(95)

268

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN C₆H₆, 80°	I + Bicycle	269

Y	Bicycle
CO₂Me	I + II (85) I:II = 2.1:1
CN	I + II (94) I:II = 3:1
COMe	I + II (93) I:II = 3.5:1

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

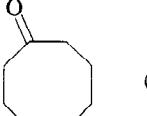| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(PhS)₂, AIBN, C₆H₆, 80°	I + II + III + IV	270

R	Y	I : II : III : IV
Et	CO₂Me	3.3 : 2.0 : 1.0 : 4.2 (80)
Bn	CO₂Me	2.8 : 1.6 : 1.0 : 3.5 (63)
Bn	CO₂Bu-*t*	4.2 : 1.1 : 1.0 : 2.4 (60)
Bn	O₂CBu-*t*	2.0 : 1.3 : 1.0 : 2.1 (43)
CH₂C₆H₄OMe-*p*	CO₂Me	1.8 : 1.3 : 1.0 : 2.6 (74)
CH₂C₆H₄CF₃-*p*	CO₂Me	3.1 : 1.8 : 1.0 : 3.7 (80)
TBDMS	CO₂Me	3.8 : 2.3 : 5.1 : 1.0 (78)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
OHC ... CO₂Et	VCl₃(THF)₃, Zn, CH₂Cl₂, 25°	(77)	252
OHC ... CO₂Me	VCl₃(THF)₃, Zn, CH₂Cl₂, 25°	(67)	252

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			225
	Hg cathode, DMF (55) NaC$_{10}$H$_8$ (56)		
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 60°, 1 h	(36) + (10)	271
	Ph$_2$SnH$_2$, BPO, C$_8$H$_{18}$, 110°	(62)	272
	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	(63)	273
	CrCl$_2$, DMF, 25°	(85)	274

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et$_3$B, C$_6$H$_{14}$, 25°	(68)	275
C$_{11}$	Ph$_3$SnH, Et$_3$B, C$_6$H$_{14}$, 25°	 **I** + **II** (62) **I:II** = 18:82	265
	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	(99)	276
	Zn, AcOH (77) Bu$_3$SnH, AIBN (68)		277
	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	 **I** + **II** (90) **I:II** = 8:1	116

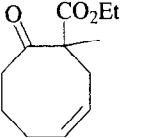TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
RO$_2$C, CO$_2$R (diallyl)	A: TsBr, MeCN, *h*v, 25° B: TsBr, PhCl, 135°	Ts—Br ring (RO$_2$C, CO$_2$R) **I** + Ts—Br ring (RO$_2$C, CO$_2$R) **II**	278

R		I + II	I:II	
Me	A	(85)	90:10	
	B	(76)	81:19	
Et	A	(85)	93:7	
	B	(85)	79:21	
t-Bu	A	(87)	93:7	

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO$_2$C, CO$_2$Me (diallyl)	EtSH, (PhS)$_2$, C$_6$H$_6$, *h*v	PhS—R ring (MeO$_2$C, CO$_2$Me) R = H or SPh *cis:trans* = 6:1 (92)	279
	TsNa, Cu(OAc)$_2$, AcOH, 90°	Ts— ring with =CH$_2$ (MeO$_2$C, CO$_2$Me) (51)	280
(diallyl diketone, O O)	TsSePh, AIBN, CHCl$_3$, 61°	Ts—SePh ring (O O) (95) 8.3:1	281

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

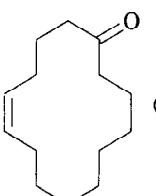| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R R (diallyl)	A: (PPh$_3$)$_2$ReCl$_3$, CCl$_4$, reflux B: (PPh$_3$)$_3$RuCl$_2$, CCl$_4$, reflux	CCl$_3$—Cl ring (R R) **I** + CCl$_3$—Cl ring (R R) **II**	282

R		I + II	I:II	
CO$_2$Et	A	(74)	5:1	
	B	(86)	—	
COPh	A	(73)	4.2:1	
	B	(84)	3.2:1	
COMe	B	(65)	—	

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO, CO$_2$Et (diene)	1. Hg(OAc)$_2$, MeOH 2. NaBH$_4$	MeO OMe ring with CO$_2$Et (90) *cis:trans* = 4:1	131, 283
Br, MeO$_2$C, CO$_2$Me	Bu$_3$SnH, AIBN C$_6$H$_6$, *h*v, heat	ring **I** (MeO$_2$C, CO$_2$Me) + cyclohexane **II** (MeO$_2$C, CO$_2$Me) I + II (87) I:II = 3:1	24
MeO$_2$C, I, MeO$_2$C (alkene chain)	1. (Me$_3$Sn)$_2$, *h*v 2. Bu$_3$SnH	MeO$_2$C, CO$_2$Me ring with ethyl (84)	18

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

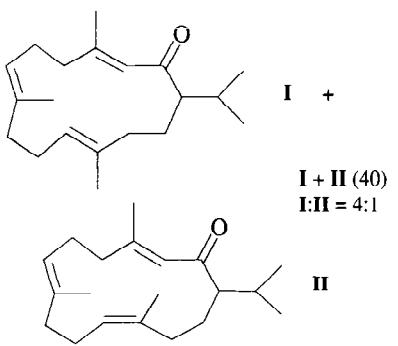| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R OOH (cyclohexane with allyl chain)	FeSO$_4$, AcOH	**I** + **II**	284

R

Me
Et
Ph

	I	**II**
	(38)	(30)
	(28)	(18)
	(32)	(7)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
EtO$_2$C, Cl, Cl (diene)	(PPh)$_3$RuCl$_2$, *t*-BuPh, 150-155°	CO$_2$Et...Cl (53) + Cl...CO$_2$Et (22)	221
(isopropenyl dithiolane chain)	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°, 24 h	O~SH **I** + O~SH **II**	285

I:II = 65:35, (—)

O ...CO$_2$Et (ketoester with butenyl)	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 50°	O (cyclopentanone) ...CO$_2$Et (39)	192

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
O ...CO$_2$Me	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 60°	O CO$_2$Me (27) + O CO$_2$Me (20) ...OAc	271
Cl, Br, CO$_2$Et	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	Cl...CO$_2$Et (66) 70:30 stereochemistry unknown	17
OHC ... C$_5$H$_{11}$	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	C$_5$H$_{11}$ **I** + C$_5$H$_{11}$ **II** OH / OH	115

I + II (32)   I:II = 66:34

R^1 O O Y R^2 (with allyl)	SmI$_2$, *t*-BuOH, THF, -78°	R^1 OH O R^2 Y	286

R^1	R^2	Y		Diastereoselectivity
Me	Me	OEt	(75)	25:1
Et	Me	OEt	(66)	30:1
i-Pr	Me	OEt	(63)	30:1
H	H	NEt$_2$	(78)	>200:1

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{12}

X			
Br	Bu₃SnH, AIBN C_6H_6, 80°	(93)	276
I	$CrCl_2$, DMF, 25°	(96)	274

Bu₃SnH, AIBN C_6H_6, 80°   287

Z		
S(O)Ph	(69)	
SO₂Ph	(70)	
POPh₂	(79)	
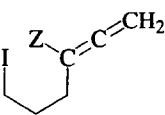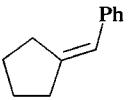
(PhS)₂, AIBN, *hv*
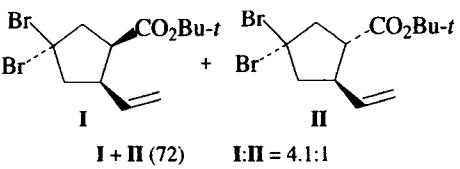
I + II (72)   I:II = 4.1:1   227
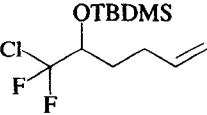
Bu₃SnH, AIBN C_6H_6, 80°, 10 h   (59)   288

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

PhSH, 60°   289

R¹	R²	
H	OBu-*n*	(82)
H	OTMS	(65)
OEt	OEt	(79)
Me	OAc	(74)
H	CH₂TMS	(63)

(PhS)₂, C_6H_6, *hv*   290

R¹	R²	
Me	Ts	(73)
Me	Cl	(73)
Cl	Cl	(47)

PhSH, 60°   289

E	R¹	R²	
CO₂Et	H	CO₂Me	(76)
CO₂Et	Me	OAc	(77)
COPh	H	CO₂Me	(63)
COPh	Me	OAc	(71)

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
OHC … Ph	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	I + II **I + II** (80) **I:II** = 53:47	115
HC≡C … R^1, NC, CN, R^2 R^1 R^2 Bu H *n*-Pr *n*-Pr Ph Me *i*-Pr Me	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	 (59) (86) (82) (76)	291, 208
p-O$_2$NC$_6$H$_4$ … Cl	CuCl, DMSO, 80°, ligand	I + II	292

ligand	I	II	I + II
bipyridyl	*trans:cis* = 71:29	*trans:cis* = 74:26	(90)
phenanthroline	*trans:cis* = 70:20	*trans:cis* = 71:29	(95)

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO$_2$C, MeO$_2$C … I … CN	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	(87) MeO$_2$C, CO$_2$Me, CN	197
Br … CH≡C … MeO$_2$C, CO$_2$Me	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	(62) MeO$_2$C, CO$_2$Me	293
Br … MeO$_2$C, CO$_2$Me	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	I, II + MeO$_2$C, MeO$_2$C III **I, II + III** (80)	293
I, Pr-*i* … NC, CN	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	CN, Pr-*i* I + CN, Pr-*i* II NC NC **I + II** (52) **I:II** = 20:1	294

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(structure)	Bu₃SnH, AIBN C₆H₆, 80°	**I** + **II** I + II (82) I:II = 2.9:1	294
(structure) R = Me, Et	TsBr, MeCN, *hv*	**I** + **II** R: Me (70-80) 57:43 Et (70-80) 63:37	278
(structure)	TsNa, Cu(OAc)₂, AcOH, 90°	(73)	280
(structure)	Bu₃SnH, AIBN C₆H₆, 80°	**I** + **II** I + II (60) I:II = 95:5	17

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(structure)	Bu₃SnCl, AIBN, Na(CN)BH₃, *t*-BuOH, 80°	**I** + **II**	197, 295

R¹ / R² I+II I:II
Me / Me (65) —
OMe / Me (82) 14:86
OTBDMS / H (66) 40:60
CO₂Me / H (60) 82:18
S(CH₂)₃S (96) —
O(CH₂)₃O (56) —

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(structure)	Mn(OAc)₃, EtOH	(40)	296
(structure)	Mn(OAc)₃, Cu(OAc)₂, AcOH, 50°	**I** + **II** I + II (67) I:II = 7:3	192

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	(42)	266
+ HC≡CR^3	(PhS)$_2$, AIBN, *hv*	I + II	297

R^1	R^2	R^3		I : II	I + II
CO$_2$Bu-*t*	H	H	C$_6$H$_6$, 80°	1.9:1	(50)
CO$_2$Bu-*t*	Me	Me	AlMe$_3$, PhMe, -30°	3.8:1	(53)
OBn	H	H	C$_6$H$_6$, 80°	1.7:1	(50)

C$_{13}$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN C$_6$H$_6$, 80°	(91)	298

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Hg(OAc)$_2$, AcOH 2. NaBH(OMe)$_3$	(70)	299
	Bu$_3$SnH, AIBN,	(95)	300
	Ph$_2$PH, AIBN, C$_6$H$_6$, 80°	(36)	301
	TsSePh, AIBN, C$_6$H$_6$, 80°	(96)	302
	A. TsSePh, AIBN, CHCl$_3$, 61° B. TsSePh, CHCl$_3$, *hv*	A. (98) 7.2:1 ratio B. (89) 8.7:1 ratio	281
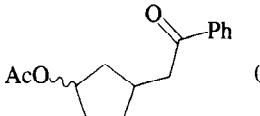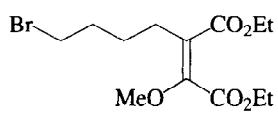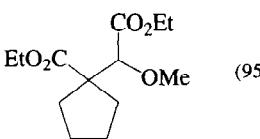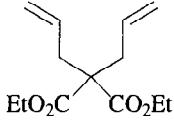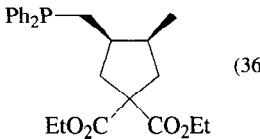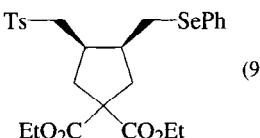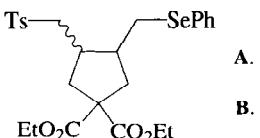
TABLE I. MON OCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
EtO_2C CO_2Et	I CO_2Et $Cr(OAc)_2$, THF, 25°	EtO_2C ... I (88) EtO_2C CO_2Et	262
R^1 R^2	$(R^3)_3SiH$, $(t\text{-}BuO)_2$, 140°	$(R^3)_3Si$ R^1 R^2 R^1 R^2 R^3: CO_2Et CO_2Et Cl (84); Ph OMe Et (60)	303
EtO_2C CO_2Et R R; R: H, Me	$(PhSe)_2$, C_6H_6, $h\nu$, 40°	$PhSe$ R R ~SePh EtO_2C CO_2Et (70) (84)	304
EtO_2C CO_2Et	Bu_3SnH, AIBN, C_6H_6, 80°	~$SnBu_3$ EtO_2C CO_2Et (—)	25

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
Ts $CClF_2$ OH	Bu_3SnH, C_6H_6, $h\nu$, 35°	Ts ...F F OH (62) + Ts ...F F OH (11)	305
$p\text{-Tol}$ S $CClF_2$ O OH 2S, 3R, R_S	Bu_3SnH, AIBN C_6H_6, $h\nu$ (350 nm), 35°	$p\text{-Tol}$ S F O OH Cl (75) 5.8:5.4:1:1 ratio of isomers	306
Ph ~~~ O SeMe	Bu_3SnH, AIBN C_6H_6, 80°	Ph O (90)	34
EtO_2C CO_2Et	Ph_2PH, AIBN, C_6H_6, 80°	~~PPh_2 EtO_2C CO_2Et (74)	301
MeO_2C CO_2Me	$B(SePh)_3$, AIBN	~$SePh$ MeO_2C CO_2Me (40) + $SePh$ ~$SePh$ MeO_2C CO_2Me (21)	307

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			308
	Hg cathode, CH$_2$(CO$_2$Me)$_2$ *n*-Bu$_4$NBr, MeCN	*trans:cis* = 7.5:1 (66)	
	Hg cathode, CeCl$_3$ CH$_2$(CO$_2$Me)$_2$ *n*-Bu$_4$NBr, MeCN	*trans:cis* = 14.8:1 (73)	
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 I:II I + II 84:16 (72) 86:14 (40) > 95:5 (82) > 95:5 (94)	81
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(>80)	309
	Cp$_2$TiCl, H$^+$	*cis:trans* = 85:15 (68)	172
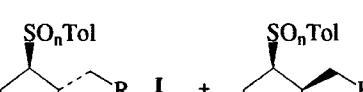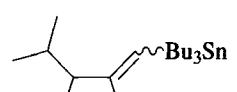
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Hg cathode, CH$_2$(CO$_2$Me)$_2$ *n*-Bu$_4$NBr, MeCN	 I + II (89)	310
C$_{14}$ 	AIBN, C$_6$H$_6$, 80°	 (69) (19)	251
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 55°, 3 d	(65)	311
	Bu$_3$SnH, AIBN, PhMe, 110°	(89)	233
	(TMS)$_3$SiH, C$_6$H$_6$, AIBN, 70°	 I + II (78) I:II = 4.6:1	312
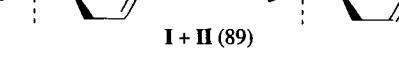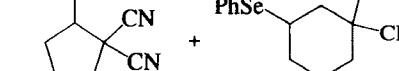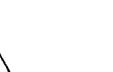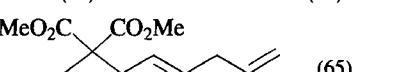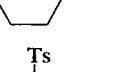
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et₂O, *hv*	(82)	220
	Bu₃SnH, AIBN, C₆H₆, heat	(75)	313
	A. (PhS)₂, AIBN, *hv* B. Ph₃SnH, AIBN	I + II + III	314

	R	I	II	III	
A	H	(82)	(10)	(—)	Double bond
B	H	(81)	(8)	(3)	isomerizes
A	Me	(83)	(< 2)	(—)	
B	Me	(85)	(< 2)	(5)	

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(88)	313
	NaC₁₀H₈, THF, rt	(50) 6 : 1 mixture	315
	Bu₃SnH, AIBN, C₆H₆, heat		243

R	X	Z	
Me	I	CN	(67)
Ph	I	CN	(75)
Ph	Br	CN	(70)
Ph	I	CO₂Et	(53)
Ph	Br	CO₂Et	(45)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	BPO, CCl₄ (93) TsNa, AcOH, H₂O (95)		316, 316a

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu₃SnH, AIBN, C₆H₆, heat → 317

R^1	R^2	
MOM	n-C₆H₁₃	(96)
MOM	Ph	(91)
MOM	BzOCH₂	(84)
TBDMS	BnCH₂	(60)

Mn(OAc)₃, Cu(OAc)₂, AcOH → 211

R	
n-Bu	(35)
OAc	(40)
CH₂TMS	(89)

Bu₃SnH, AIBN, C₆H₆, 80° → (45) 266

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu₃SnH, AIBN, C₆H₆, 80° → 318

R^1	R^2	R^3	I	II
H	H	H	(32)	(27)
Ph	H	H	(37)	(20)
Me	Me	H	(30)	(22)
H	H	Me	(31)	(—)

SmI₂, THF → 179

R^1	R^2		diastereomeric ratio
Me	Me	(79)	31:1
Et	Et	(73)	65:1
i-Pr	i-Pr	(32)	>200:1
(CH₂)₅		(58)	200:1
(CH₂)₄		(60)	60:1
CH(Me)(CH₂)₄		(75)	1:1
(CH₂)₂CH(Bu-t)(CH₂)₂		(61)	10:1
Me	(CH₂)₃Cl	(65)	1:1
Me	(CH₂)₃NEt₂	(33)	1:1
H	n-Pr	(55)	17:17:1:1

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°, 10 h	X: OTBDMS (1:1) (81); NBn$_2$ (28)	288
	Bu$_3$SnH, AIBN, PhMe, 110°	(60)	319
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(67)	320
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 50°	(70)	321
	Heat	(55)	243

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TsCl, BPO, PhMe, 100° *or* (Bu$_3$Sn)$_2$, C$_6$H$_6$, hv, 25°		322 323

R^1	R^2		isomer ratio
OAc	Me	(77)	3.5:1
OBn	Me	(73)	—
CH$_2$OBn	Me	(81)	1.2:1
CH$_2$OBn	H	(61)	2.4:1
(CH$_2$)$_2$OBn	Me	(73)	1.1:1
CH$_2$Cl	Me	(78)	1.2:1
C$_6$H$_{13}$	H	(75)	2.5:1

C$_{15$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II (97) I : II = 2.9 : 1	294
	BPO, CCl$_4$ (80); TsNa, AcOH, H$_2$O (80)		316, 316a

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu₃SnH, AIBN, C₆H₆, 80°

n	X	R¹	R²		I:II	I + II
2	Cl	CO₂Et	H	E-alkene	30:70	(81)
2	Cl	CO₂Et	H	Z-alkene	50:50	(73)
1	Cl	CO₂Et	H	E-alkene	25:75	(70)
1	Cl	CO₂Et	H	Z-alkene	30:70	(88)
2	Br	H	CO₂Et		30:70	(70)
1	Br	H	CO₂Et		35:65	(60)

324

BPO, CCl₄, 77°

(93) 3:1 ratio

136

TsBr, MeCN, hv, 18°

I, II +   III, IV   219

I + II (66)   III + IV (34)
I:II = 58:42   III:IV = 45:55

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

TsBr, MeCN, hv

I + II   219

I + II (67)   I:II = 52:48

Bu₃SnH, AIBN, C₆H₆, heat

(60) *cis:trans* = 3:1   320

Bu₃SnH, AIBN, C₆H₆, 80°, 3 h

I +   II   79

I + II (98)

(PhS)₂, AIBN
C₆H₆, 80°
or
(BuS)₂, hv

I,II   324a

R¹	R²
i-Bu	H
CH₂OH	H
PhS	H
n-Bu	H
OTMS	Me

I,II	*cis:trans*
(81)	56:54
(57)	81:19
(88)	80:20
(47)	76:24
(64)	33:67

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(83) two isomers 2.5:1	325
R¹ R¹ CO₂Et H CO₂Et Me Ph H Me H	Bu₃SnH, AIBN, C₆H₆, 80°	*cis:trans* (94) 2.1:1 (80) 1.4:1 (83) 1.3:1 (67) 1.3:1	199
	Bu₃SnH, AIBN, C₆H₆, 80°	(85)	118
TMSO SePh	Bu₃SnH, AIBN, C₆H₆, 80°	OTMS (65) *trans:cis* = 7:1	80
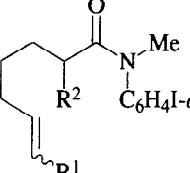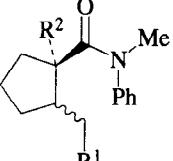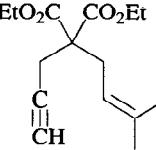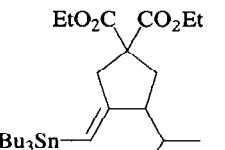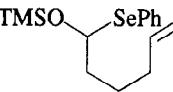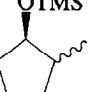
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
PhS Cl CO₂Et Z E	Bu₃SnH, AIBN, C₆H₆, 80°	SPh CO₂Et (67) *trans:cis* = 45:55 (67) *trans:cis* = 35:65	326
	Bu₃SnH, AIBN, C₆H₆, 80°	(45)	79
X Cl F F C≡CTMS X OTBDMS NHBn	Bu₃SnH, AIBN, C₆H₆, 80°, 10 h	(81) (60)	288
HO C≡CH OTHP	Ph₃SnH, Et₃B, C₆H₆	HO SnPh₃ (84) OTHP	27
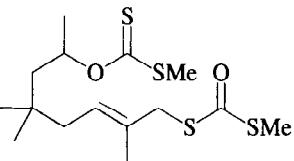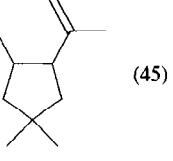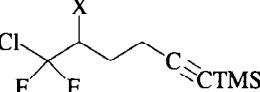
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{16}$

	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, t-BuOH, 80°	(53)	197
	BPO, CCl$_4$, 77°	(51) 3:1 ratio	135
	BPO, CCl$_4$ TsNa, AcOH, H$_2$O	(80) (53)	316, 316a
	BPO, CCl$_4$ TsNa, AcOH, H$_2$O	(90) (95)	316, 316a
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(72)	38
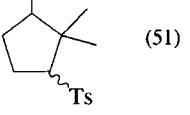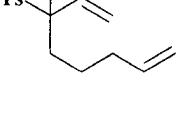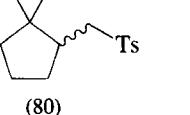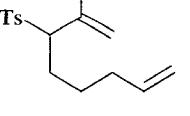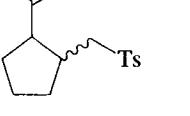
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

R^1	R^2	Y		I : II : III : IV	
H	H	OBu-n	A	6.1 : 1.4 : 1.3 : 1	(94)
			B	14.2 : 2.0 : 2.2 : 1	(75)
H	H	O$_2$CBu-t	A	4.0 : 2.2 : — : 1	(55)
			B	12.8 : 10.9 : 1 : 4.4	(52)
H	H	CO$_2$Bu-t	A	4.2 : 1.2 : 1 : 1.9	(53)
			B	10.3 : 4.0 : 1 : 1.3	(52)
Me	H	OBu-n	A	4.2 : 1.4 : 1 : 1.1	(96)
			B	7.0 : 2.6 : 1 : 1.2	(70)
H	Me	OBu-n	A	1.0 : 1.0 : — : —	(66)
			B	1.8 : 1.0 : — : —	(69)

A: (PhS)$_2$, AIBN, C$_6$H$_6$, 80°
B: (PhS)$_2$, AIBN, AlMe$_3$, C$_6$H$_6$, 80°

| | Cp$_2$TiCl, H$^+$ | X = OAc , 4 isomers (74)
X = OBn, 45:30:15:19 (44) | 172 |

I, II, III, IV

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(BuS)₂, hv, 25°		328

Y
OBu-*i* (81)
Bu-*n* (47)
SPh (47)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnCl, AIBN, *t*-BuOH, Na(CN)BH₃		197
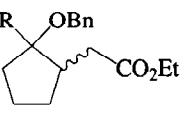
cis : trans
(56) 1 : 2.5
(46) 1 : 2.5
(45) 1 : 4

R X
H I
H Br
Me I

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°		329

R
CN (56) 89 : 11
CO₂Me (56) 98 : 2
COMe (53) 97 : 3
SO₂Ph (57) 97 : 3

E : Z

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	R cis : trans H 1.2 : 1 (81) Me 1 : 1 (84)	199
	Me₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 80°	**I, II** I + II (92) I : II = 2 : 1	330
	Bu₃SnH, AIBN, C₆H₆, 80°	(12) + (61)	331
	Mn(OAc)₃, Cu(OAc)₂, AcOH	(86)	211
	Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 80°	(66) *cis : trans* = 40 : 60	197

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(78)	332
C$_{17}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(70) 1 : 1 mixture	333, 334
	TsNa, AcOH, 100°	(68) 3 : 1 *ratio*	135
			316, 316a
	BPO, CCl$_4$	(50)	
	TsNa, AcOH, H$_2$O	(60)	

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_{14}$, 60°	(22) + (35)	335
			316, 316a
	BPO, CCl$_4$	(60)	
	TsNa, AcOH, H$_2$O	(90)	
	Bu$_3$SnH, AIBN, Na(CN)BH$_3$, *t*-BuOH, 80°	(61) *cis : trans* = 1.1 : 1	197
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		336

R	
n-C$_6$H$_{13}$	(66)
n-C$_9$H$_{19}$	(83)
CH$_2$OCOPh	(81)
Ph	(69)

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R^1 R^2 H C_6H_{13} Me $(CH_2)_2OC_6H_{13}$ H CH_2Ts	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH	(81) 2.5:1 (60) 1:1 (56)	210
C$_{18}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(81)	337
	C$_6$H$_6$, *h*v, 25°	(63)	168
	SnBu$_3$ AIBN, C$_6$H$_6$, 80°	(61)	338
+ CO$_2$Me	(PhS)$_2$, AIBN, C$_6$H$_6$, *h*v, 80°	(58)	327
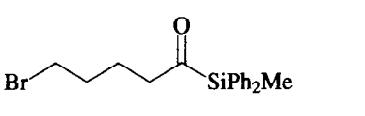
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
SO$_2$Ph + R_1 R_2	(BuS)$_2$, AIBN		339
R^1 R^2 H OBu-*i* H CH$_2$OH Me OTMS H Bu-*n*		*cis:trans* (81) 56:44 (57) 83:17 (57) 61:39 (42) 77:23	
Br SO$_2$Ph EtO$_2$C CO$_2$Et	Ph$_3$SnH, AIBN	SO$_2$Ph (35) EtO$_2$C CO$_2$Et	340
CO$_2$R^1 CO$_2$R^1 + R^2 R^3	Mn(OAc)$_3$, Cu(OAc)$_2$,	R^2 R^3 R^{1}O$_2$C CO$_2$R^1	210
R^1 R^2 R^3 Et H C_6H_{13} Et Me $(CH_2)_2OC_6H_{13}$ Me Me CH_2Ts		(80) (60) (55)	
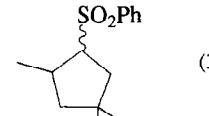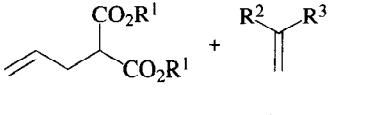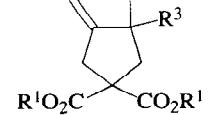
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{19}$			
	1. Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° 2. AcOH, MeOH	(56)	341
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(76) *cis:trans* = 55:45	342
	Bu$_3$SnH, AIBN, PhMe, 110°	(85)	343
	Me$_3$SnCl, AIBN, Na(CN)BH$_3$, *t*-BuOH, 80°	(95) *cis:trans* < 4:1	330
C$_{20}$			
	(Bu$_3$Sn)$_2$, *hv*	(82)	85

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II + III	344

R^1	R^2	X
H	H	I
Me	H	I
TMS	H	I
CO$_2$Me	Ac	Br

I	II + III	II:III
(8)	(80)	78:22
(16)	(80)	62:38
(3)	(74)	86:14
(—)	(44)	30:70

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (52) I:II 1:1.3	199
	Bu$_3$SnH, AIBN, PhMe, 110°	R = H (84) R = Me (96)	343

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		345

R
_____
C$_6$H$_{11}$ ... (27)
Bu ... (43)
Bu ... (38)
(CH$_2$)$_4$CH=CHCO$_2$Et ... (82)

| | Bu$_3$SnH, AIBN, PhMe, 110° | | 343 |

		I + II	**I:II**
R			
H		(67)	87:13
Me		(92)	94:6

C$_{21}$

| | Cp$_2$TiCl, THF, rt | (83) | 346 |
| | Cp$_2$TiCl, THF, rt | (83) | 346 |

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, PhMe, 110°	(89)	343
	1. C$_6$H$_6$, hv, 80° 2. Bu$_3$SnH	I + II	347

I + II (48)   I: 99:1 mixture of diastereomers
I:II = 71:29   (major isomer is shown)
II: one diastereomer

C$_{22}$

| | Ce(NH$_4$)$_2$(NO$_2$)$_6$ | (42) | 348 |

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{23}

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(81)	38

| | | Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80° | (81) | 38 |

R^1	R^2			
H	CO$_2$Et	A	(64)	
H	CO$_2$Et	B	(51)	
CO$_2$Et	CO$_2$Et	A	(53) 1.1:1	
H	Me	B	(65)	
H	Cl	B	(86)	
H	H	B	(49)	

A. TsCl, BPO, PhMe
B. (Bu$_3$Sn)$_2$, C$_6$H$_6$, *hv*

349

C_{24}

THF, *hv*, 25° (92) 350

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° (61) 209

cis:trans = 2.4:1

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° 37

R = Bn I:II = 62:38 I + II (93)
R = Me I:II = 60:31 I + II (82)

PhMe, 110° 351, 210, 349

R^1	R^2		
H	CO$_2$Et	(64)	
H	COMe	(60) 9.6:1	
CO$_2$Et	CO$_2$Et	(53) 1.1:1	

Bu$_3$SnH, AIBN, 80° 37

R^1	R^2	R^3	X		I + II	I:II
C$_6$H$_{11}$	H	H	PhOC(=S)O	C$_6$H$_6$	(84)	52:48
C$_6$H$_{11}$	H	Me	PhOC(=S)O	PhMe	(74)	69:31
C$_6$H$_{11}$	Me	H	Br	C$_6$H$_6$	(63)	78:22
p-MeOC$_6$H$_4$	H	H	PhOC(=S)O	C$_6$H$_6$	(42)	>98:2
BnOMe	H	H	PhOC(=S)O	PhMe	(59)	50:50

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{25}$

Ph₃SnH, AIBN — (64) — 352

C$_{26}$

+ PhMe, heat — 11

R^1	R^2	
Bn	H	(50)
Bn	Me	(52)
n-C$_{10}$H$_{21}$	H	(63)

Ph₃SnH, AIBN, C₆H₆, 80° — (79) — 353, 354, 354a

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu₃SnH, AIBN, PhMe, 110° — (92) — 343

C$_{27}$

Bu₃SnH, AIBN, PhMe, 110° — R = H (62), R = Me (82) — 343

C$_{29}$

Bu₃SnH, AIBN, C₆H₆, 80°, 6 h — **I** + **II** — 84

I + II (90), I:II = 4:1
R* = 8-phenylmenthyl

I: *cis:trans* = 64:36
II: *cis:trans* = 35:65

Heat, sunlamp — (25) + (28) — 355

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₃₀			
SePh OTMS + Bu₃Sn	AIBN, C₆H₆, 80°	I + II (67) I:II = 7:1	80
CO₂Me BzO OBz OBz	Me₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 80°	Me₃Sn CO₂Me BzO OBz OBz (52)	330
BnO CHBr₂ HO BnO OBn CO₂Me	Bu₃SnH, AIBN, C₆H₆, 80°	BnO HO BnO OBn CO₂Me (80)	356, 357
BnO CHBr₂ CO₂Me HO BnO OBn	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (66), I:II = 1:4.5	356, 357

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₃₁			
AcO AcO O Im S AcO NOBn NHCbz	Bu₃SnH, AIBN, C₆H₆, 80°	I + II	358
C₃₂			
Ph Co(salophen)py O	Heat, sunlamp	Ph (42)	355
C₃₃			
Br CO₂Et TBDPSO OBn HCO₂	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (77) I:II = 8:1	359

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{39}$	Bu$_3$SnH, AIBN, PhMe, 110°	I + II + III	82, 360
Y = H		I + II + III (61) I:II:III = 74:14:12	
Y = OMe		I + II + III (63) I:II:III = 78:20:2	

D. 6-Membered Rings

C$_6$	(Me$_3$Sn)$_2$, C$_6$H$_6$, *h*ν	I + II	18
		R **I + II** **I:II**	
		H (56) >97:3	
		Me (73) 75:25	

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_7$	PhSH, AIBN, TMTHF, reflux	PhS= (70)	361
C$_8$			
HC≡CCO$_2$Et + =R	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	CO$_2$Et 1:1 mixture	362
R			
CO$_2$Me		(43)	
CN		(48)	
	Carbon rod cathode, MeOH, dioxane, Et$_4$NOTs	HO (75)	246
		HO I + HO II	178
		I + II (91) I:II = 36:1	
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH	OH O	363, 321
R			
OMe		(94)	
Me		(96)	

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	A. (PhS)$_2$, AIBN, $h\nu$ B. Bu$_3$SnH, AIBN		314

R			
H	A	(82)	
H	B	(81)	
Me	A	(85) 46:37	
Me	B	(87)	

C$_9$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(82)	200
	(Bu$_3$Sn)$_2$, C$_6$H$_6$, $h\nu$	 **I** + **II** + **III** (91) I:(II + III) = 55:45	364
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH	(71)	363
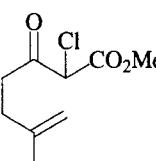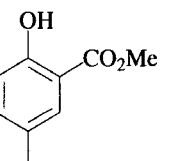
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)
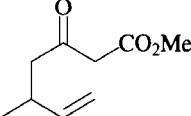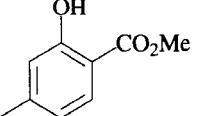
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH	(38)	363
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH	(78)	363
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH	(70)	363
	SmI$_2$, THF, HMPA	(86) diastereomeric ratio = 4:1	178
	SmI$_2$, THF, HMPA	(89) diastereomeric ratio = 6:1	178
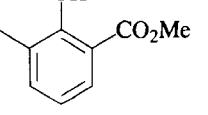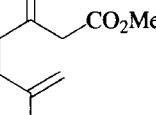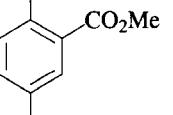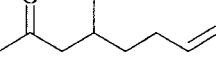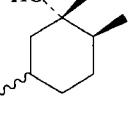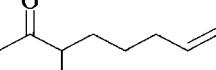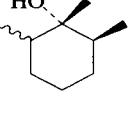
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
OHC—…—CO₂Me	Hg cathode, Et₄NOTs, H₂O, CH₂(CO₂Et)₂	(72) *trans:cis* 1.8:1	365
C₁₀ (iodo dinitrile)	AIBN, C₆H₆, 80°, 10 h	(95) 52:48 *ratio*	251
HC≡CCO₂Et + ⟩=⟨CO₂Me	Bu₃SnH, AIBN, C₆H₆, 80°	(46)	362
CO₂Et / Br	Bu₃SnH, AIBN, C₆H₆, *hv*	(100)	366
O / CO₂Me	Mn(OAc)₃, Cu(OAc)₂, AcOH	(91)	363
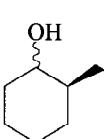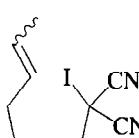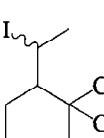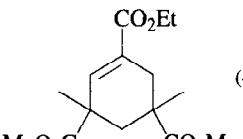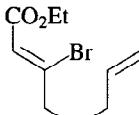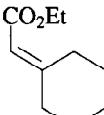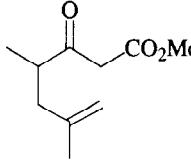
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
O / CO₂Me	Mn(OAc)₃, Cu(OAc)₂, AcOH	(40)	363
X (SePh / SPh / Cl)	Bu₃SnH, AIBN, C₆H₆, 80°, 2.5 h	(84) / no reaction / (59)	35, 367
R¹ / R² (Bn, H) / (H, TMS)	Bu₃SnH, AIBN, PhMe, 110°	(71) / (41)	368
Br	(Bu₃Sn)₂–resin, Mc₂CO, *i*-PrOH, *hv* (300 nm), 40°	(89)	369
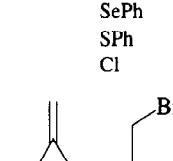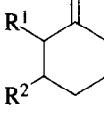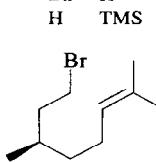
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, PhMe, 110°		370

R¹	R²	R³		I + II	I : II
Ac	OBn	OMe		(100)	34 : 68
TBDMS	OBn	OMe		(90)	68 : 34
Ac	H	OBn		(80)	37 : 63
TBDMS	H	OBn		(91)	55 : 45
Ac	OBn	H		(72)	50 : 50
TBDMS	OBn	H		(70)	74 : 26
Ms	H	H		(81)	35 : 65

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}	(Me₃Sn)₂, Bu₃SnH, *hv*	(84)	18
	Mn(OAc)₃, Cu(OAc)₂, AcOH, 60°, 1 h	α-OH (41) β-OH (8)	271

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	BPO, *c*-C₆H₁₂, 85°	(75)	22
	Bu₃SnH, C₆H₆, *hv*, heat	(72)	24
	BPO, Ph₂CO, *hv*		371

	I + II	I:II
−25°	(45)	1:1.4
4°	(57)	1:1.3
25°	(41)	1:1.2
78°	(43)	1:1.2

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Mn(OAc)₃, Cu(OAc)₂, AcOH, 60°	(41)	271, 192

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(O, CO$_2$Me ketone with alkene)	1. Mn(OAc)$_3$, Cu(OAc)$_2$, 2. AcOH, LiCl, 100°	OH, CO$_2$Me aromatic (50)	363
(O, CO$_2$Me with alkene chain) Z / E	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 50°	I (O, CO$_2$Me) + II (OH, CO$_2$Me); I + II (71); I + II (64)	192
MeSe, ketone with prenyl	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	cyclohexanone I, II; I + II (85) I:II = 2:1	34
R^1–C(=CH...)–O–Si(Me)(Me)R^2 — R^1/R^2: Ph/Me; Ph/*t*-Bu; C$_6$H$_{11}$/Me; Me/Me	DCA, MeCN, *h*v, 65°	R^1–C(=O)–cyclohexyl — (38); (31); (27); (4)	372

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{12}$			
(thiolactone with prenyl chain)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	HO-cyclohexane I + HO-cyclohexane II; I + II (80) I:II = 1:1	117
TBDMS–C(=O)–(CH$_2$)$_n$–Br	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	cyclohexyl-OTBDMS (64)	337
MeO$_2$C, MeO$_2$C, I, with alkene	1. (Me$_3$Sn)$_2$, C$_6$H$_6$, *h*v 2. Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	MeO$_2$C, MeO$_2$C ethyl-cyclohexane (62)	18
R^1 (alkene), I, F, F, OMOM — R^1: Ph; CO$_2$Et; BnOCH$_2$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	R^1, F, F, OMOM cyclohexane — (53); (79); (64)	317

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Hg cathode, Et$_4$NOTs	(70) *trans:cis* 1:2.9	365
C$_{13}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(76)	19
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		287
Z ⎯⎯⎯⎯ S(O)Ph SO$_2$Ph POPh$_2$		(72) (81) (85)	
Z E	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 50°	(73) (62)	192

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 60°, 1 h	(75)	271
t-Bu	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(85) *t*-Bu	17
	1. Ph$_3$SnH, AIBN, C$_6$H$_6$ 2. H$_2$O$_2$	(95) (5)	373
	CrCl$_2$, DMF, 25°	(85)	274
C$_{14}$ OBz	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II** I + II (94) I:II = 11:1	313

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(EtO₂C, CO₂Et dienyl bromide structure with Br)	Bu₃SnH, AIBN, C₆H₆, 80°	(cyclohexene with EtO₂C, CO₂Et and two methyls) (75)	24
(keto ester with SePh, O O, OMe, pentenyl)	hv	(cyclohexanone OMe ester, SePh) (60) + (cyclopentanone OMe ester, CH₂SePh) (20)	88
(aldehyde O=CH, Ph, iodide chain)	Bu₃SnH, AIBN, C₆H₆, 80°	(cyclohexanol OH, vinyl, Ph) (85)	41, 40
(p-MeC₆H₄–S(O) sulfoxide, CCl₂F, OH, pentenyl)	Bu₃SnH, AIBN, C₆H₆, 80°	(fused ring O, OH, Cl, F, p-MeC₆H₄) (60)	374
(p-MeC₆H₄–S(O) sulfoxide, CClF₂, OH, pentenyl)	Bu₃SnH, AIBN, C₆H₆, 80°	(fused ring O, OH, F, F, p-MeC₆H₄) (52)	375

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R¹O, R, X with SPh, exocyclic methylene	A. (Bu₃Sn)₂, C₆H₆, hv, 10° B. (Me₃Sn)₂, Ph₂CO, C₆H₆, hv, 10° C. (Me₃SnOCPh₂)₂, C₆H₆, 80°	R¹O, R cyclohexane with exocyclic =CH₂, –Cl	376

R	R¹	X			*cis:trans*
H	Me	Br	A	(35)	—
H	(CH₂)₂OH	Br	A	(75)	—
Ph	Me	Cl	A	(60)	1.2:1
n-C₅H₁₁	Me	Br	A	(44)	1.3:1
Me	Me	Br	A	(55)	1.1:1
Me	Bz	Br	B	(61)	1.3:1
Me	Bz	OC(S)Im	C	(61)	1.2:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(OTMS, n-Bu, Br, diene structure)	Bu₃SnH, AIBN, C₆H₆, 80°	(cyclohexanol OH, n-Bu, exocyclic methylene) (72)	30
C₁₅ (X, C₆H₄Me-p, gem-dimethyl, exocyclic methylene)		(cyclohexane with C₆H₄Me-p, gem-dimethyl)	
X = Br	Bu₃SnCl, AIBN, Na(CN)BH₄	(70)	333
X = I	Bu₃SnH, AIBN, C₆H₆, 80°	(90)	377

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, PhMe, 110°	(48)	233
 E *Z*	Bu₃SnH, AIBN, C₆H₆, 80°	 **I + II** (100) **I:II** = 1:1 **I + II** (98) **I:II** = 94:6	378
	 hv, rt, 15 min		379

X	R	
4-MeOC₆H₄	SO₂Ph	(77)
4-MeOC₆H₄	P(O)(OEt)₂	(53)
Ph	CO₂Me	(70)
4-MeOC₆H₄	CO₂Me	(74)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, heat	(93)	313

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, heat	(90)	313
	Bu₃SnH, AIBN, C₆H₆, 80°		378

R		**I** diastereomeric ratio		**II** diastereomeric ratio	
OH	*E:Z* = 46:54	(68)	(54:46)	(7)	(1:1)
OAc	*E:Z* = 67:33	(85)	(78:22)	(6)	(100:0)
OMe	*E*	(81)	(73:27)	(—)	
OMe	*Z*	(82)	(74:26)	(—)	
OPr-*i*	*Z*	(78)	(71:29)	(—)	
Me	*E:Z* = 60:40	(70)	(61:39)	(—)	

C₁₆

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. MgI₂ 2. Bu₃SnH, AIBN, C₆H₆, 80°	(50)	238
	Me₂SnCl, Na(CN)BH₃, AIBN, *t*-BuOH	**I, II I + II** (97) **I:II** = 1:1	330

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
PhSe—(ketone, isopropenyl chain)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(ketone with isopropyl) (84)	34
(gem-dimethyl, CHO, diene chain)	(*t*-BuO)$_2$, *c*-C$_6$H$_{12}$, 85°	(cyclohexanone with dimethylbutenyl chain) (40)	380
Br—(chain)—CO$_2$Bu-*t*, *t*-Bu	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	*t*-Bu—(cyclohexyl)—CO$_2$Bu-*t* **I** + ; *t*-Bu—(cyclohexyl)—CO$_2$Bu-*t* **II** ; **I + II** (75) **I:II** = 1:9 ; **I + II** (85) **I:II** = 1:3	17
Z E ; Br CN —NMePh ; R ; R / Ph *E* / Ph *Z* / Me *E*	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	CN —NMePh (cyclohexane) R **I, II** ; **I** **II** ; (87) (5) ; (83) (4) ; (70) (15)	325

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{17}$; Ph—C(=O), CO$_2$Et (diene)	1. Hg(OAc)$_2$, AcOH ; 2. NaBH(OMe)$_3$	CO$_2$Et ; AcO—(cyclohexane)—Ph, O (77)	299
MOMO—(chain)—I, OBn	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	MOMO—(cyclohexane)—OBn (62)	317
R^1, R^2, Br, R^1, =N—OBn, R^2 ; R^1 R^2 / OAc OAc / OBz OBz / OBn OH / OBn OAc	Bu$_3$SnH, AIBN, PhMe, 110°	R^1, R^2, R^1—NHOBn, R^2 **I** + R^1, R^2, R^1—NHOBn, R^2 **II** ; **I + II** **I:II** ; (52) 83:17 ; (55) 75:25 ; (40) 80:20 ; (42) 78:22	217, 381
C$_{19}$; SePh ; TMSO—(chain, isopropenyl)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	TMSO—(cyclohexane, isopropyl) (61)	80

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	AIBN, C₆H₆, 87°	(60)	338

C₂₀

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, reflux	I + II	37

R^1	R^2	X		$I + II$	$I:II$
C_6H_{11}	H	PhOC(S)O	PhMe	(71)	33:67
C_6H_{11}	Me	Br	C_6H_6	(68)	33:67
p-MeOC₆H₄	H	PhOC(S)O	C_6H_6	(18)	<2:98

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, PhMe, 110°	(85)	343

C₂₁

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	$I + II$ (71) $I:II = 1.1:1$	209

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	C₆H₆, $h\nu$, 25°	(51)	168

C₂₂

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
Z / E	Bu₃SnH, AIBN, C₆H₆, 80°	(35) Z:E = 14:1 (48) Z:E = 1:77	382
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II (91) I:II = 55:45	383

C₂₃

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	C₆H₆, $h\nu$, 25°	(94)	168

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
EtO$_2$C (TBDMSO, OTBDMS, Br)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	EtO$_2$C ... (TBDMSO, OTBDMS) (94)	384
I ... =N—N ... Ph, EtO$_2$C CO$_2$Et + =Y; Y = CN; Y = CO$_2$Me	Bu$_3$SnH, AIBN, PhMe, 110°	...Y, EtO$_2$C CO$_2$Et (86) (87)	343
C$_{24}$ Ph Ph, O—C(=S)Im	Bu$_3$SnH, AIBN, xylene, 140°	Ph ... CH$_2$Ph (30-40) + ...Ph (6)	385
...Ts, CO$_2$Me, MeO$_2$C + =R^1; R^1: C$_6$H$_{13}$, CH$_2$Ts	Mn(OAc)$_3$, Cu(OAc)$_2$,	...R^1, MeO$_2$C CO$_2$Me (35) (28)	210

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{25}$ Ph$_3$Ge—C(=O)...	THF, *hv*, 25°	...CH$_2$GePh$_3$ (86)	350
C$_{28}$ Ph ... =N—N ... N—N= ... Ph, EtO$_2$C CO$_2$Et	Bu$_3$SnH, AIBN, PhMe, 110°	EtO$_2$C CO$_2$Et (65)	34 3
py(dmgH)$_2$Co, HO, HO	C$_6$H$_6$, *hv*, 25°	HO, HO (87)	168
C$_{29}$ PhSe—C(=O)..., TBDPSO	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	TBDPSO I, II + TBDPSO III; I, II (41) III (11) I:II = 1:1	386, 387
C$_{31}$ PhS ... RO RO O ...SePh; R = TBDMS	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	...SPh, TBDMSO OTBDMS; I, II (90) I:II = 1:1	388, 389

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{35} R = TBDMS	Bu₃SnH, AIBN, C₆H₆, 80°	(67)	384, 390

E. 7-Membered Rings

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + **II** **I + II** (90) **I:II** = 45:51	391
C_9	SmI₂, THF, HMPA	(52)	178
	Bu₃SnH, AIBN, C₆H₆, 80°	(73)	74, 75, 200
C_{10}	Mn(OAc)₃, Cu(OAc)₂, AcOH	**I** + **II** **I + II** (68) **I:II** = 2.8:1	193

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}	Mn(OAc)₃, Cu(OAc)₂, AcOH	(35)	194
	Mn(OAc)₃, Cu(OAc)₂, AcOH	**I** + **II**	194
C_{15}	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + **II** **I + II** (86) **I:II** = 93:7	313
	Bu₃SnH, AIBN, C₆H₆, 80°	+	392, 387

R¹	R²	R³	R⁴		**I**	**II**
H	H	O(CH₂)₂O			(32)	(55)
O(CH₂)₂O		H	H		(72)	(12)
OTBDPS	H	H	H		(17)	(54)
O(CH₂)₂O		OTBDPS	H		(24)	(—)
H	H	H	OEt		(27)	(1)

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	F. 8-Membered Rings		

C_{10}
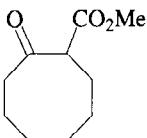
| | Bu₃SnH, AIBN, C₆H₆, 80° | (90) | 200 |
| | Bu₃SnH, AIBN, C₆H₆, 80° | (55) | 200 |
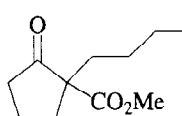
C_{11}
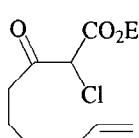
| | Mn(OAc)₃, Cu(OAc)₂, AcOH | (47) | 193 |
| | Mn(OAc)₃, Cu(OAc)₂, AcOH | **I** + **II** | 194 |

I + **II** (69) **I:II** = 2.5:1

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{12}

| | Mn(OAc)₃, Cu(OAc)₂, AcOH | (35) | 194 |
| | Mn(OAc)₃, Cu(OAc)₂, AcOH | (38) | 193 |

G. Macrocycles

C_{10}

| | Bu₃SnH, AIBN, C₆H₆, 80° | n = 7   (15)
n = 11 (55-65)
n = 15 (55-65) | 78, 393 |

C_{14}
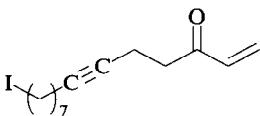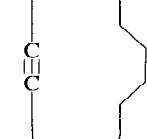
| | Bu₃SnH, AIBN, C₆H₆, 80° | (70-80) | 78, 393 |

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)
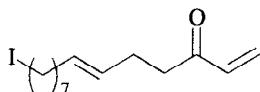
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(70-80)	78, 393
	Bu₃SnH, AIBN, C₆H₆, 80°	(75)	78, 393
C₁₇	Bu₃SnH, AIBN, C₆H₆, 80°	I + II **I** **II** I + II (52) I:II = 3:1	394, 395
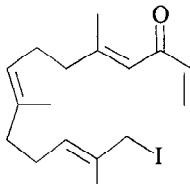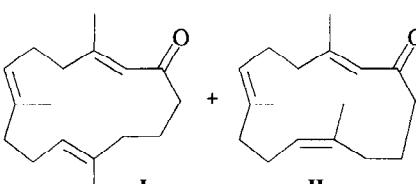
TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₂₀	Bu₃SnH, AIBN, C₆H₆, 80°	(54)	208
	Bu₃SnH, AIBN, C₆H₆, 80°	I + I + II (40) I:II = 4:1 II	394, 395

TABLE I. MONOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23}	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(50)	78
C_{26}	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(40)	396
C_{29}	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(89)	76

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

A. 3-Membered Rings

C_9

$(t\text{-BuO})_2$, ZH,

 N•BH₃

C_6H_6, $h\nu$, 30°

Z	R = H	R = Me
HC(CO$_2$Me)$_2$	(75)	(80)
C(CO$_2$Et)$_3$	(50)	(58)
HC(CN)CO$_2$Et	(50)	(56)
CH$_2$(CO$_2$Me)	(54)	(60)

397

C_{10}

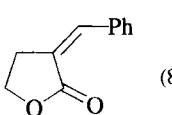Bu$_3$SnH, $h\nu$

  (45)

398

B. 4-Membered Rings

C_{19}

Bu$_3$SnH, AIBN,
C_6H_6, 80°

  (71)

399

R¹	R²
Et	Me
Et	Bu-t
Et	C$_6$H$_{11}$
Me	C$_6$H$_{11}$

Bu$_3$SnH, AIBN,
C_6H_6, 80°

(40)
(58)
(70)
(69)

400

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(R^1 = Et, R^2 = H) (45) (R^1 = H, R^2 = SPh) (45) + (R^1 = H, R^2 = H) (24) (R^1 = Et, R^2 = SPh) (45) + (R^1 = Et, R^2 = H) (3)	401
C_{22}	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II (69) I:II = 1:1 I + II (64) I:II = 2:1	401
	1. Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° 2. NaOH, Py	(50)	401
	CH$_2$Cl$_2$, hv	(45)	402
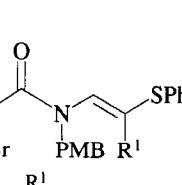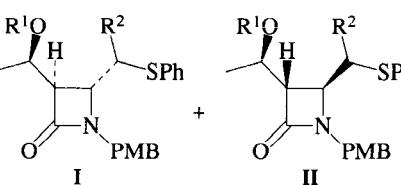
R^1 — R^2 table (reactant C_{20}):

R^1	R^2
Et	H
H	SPh
Et	SPh

R^1 (reactant C_{22}):

R^1
H
SPh

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	hv		403

solvent	
C$_6$H$_6$	(92)
MeCN	(69)
MeOH	(84)
CHCl$_3$	(16)

C. 5-Membered Rings

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	Et$_3$GeH, MeOH	(80)	404
C_5	HgO, I$_2$, hv	(50)	61
	C$_6$H$_6$, hv	(68)	405

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_6$			

| | C$_6$H$_{12}$, hv, 80° | | 406, 407 |

R^1	R^2
H	Me
Et	Me
Bz	H

I + II + III	**I:(II + III)**
(46)	66:34
(70)	30:70
(87)	60:40

| | Ph$_3$SnH, AIBN, C$_6$H$_6$, 80° | | 408 |

R
H
Me
Ph

I + II
(40)
(42)
(62)
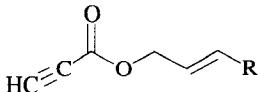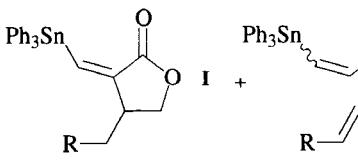
| | TsSePh, AIBN, PhMe, 110° | (97) *cis:trans* = 3.2:1 | 281 |

| | TsBr, AIBN, MeCN, hv, 25° | (58) *cis:trans* = 4.2:1 | 409 |

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

| | γ-Irradiation, *i*-PrOH | | 410 |

Y
O
CH$_2$
C(CO$_2$H)$_2$
NH
NMe
NCH$_2$CH=CH$_2$
NMe$_2^+$Cl$^-$

I + II	**I:II**
(97)	4:1
(93)	3.2:1
(83)	5.7:1
(80)	4.6:1
(44)	4.9:1
(49)	4.3:1
(80)	4:1
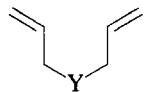
| | A. (PPh$_3$)$_2$ReCl$_3$, CCl$_4$, reflux B. (PPh$_3$)$_2$RuCl$_2$, CCl$_4$, reflux | | 282 |

Y	
O	A
NC(O)Me	A
	B

I + II	**I:II**
(87)	4.3:1
(64)	6:1
(77)	6:1

| | TsBr, CH$_2$Cl$_2$, hv | (40) *cis:trans* = 1.2:1 | 411 |

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(*t*-BuO)$_2$, 135°	(72) + (13)	412
	MeOH, hv, H$^+$	I + II I + II (83) I:II = 4:1	413
  R —— Me Et *i*-Pr	CuCl, MeCN, 110°, 3 h, sealed tube	I + II I + II I:II (60) 89:11 (50) 92:8 (80) 98:2	90
	(Bu$_3$Sn)$_2$, C$_6$H$_6$, hv, 80°	(87)	51

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_7$ R —— Bn Bn Me Ts Ms Cbz Boc	 CuCl, MeCN, 80° CuCl, CH$_2$Cl$_2$, bipyridine, -15°	I + II I + II I:II (72) 86:14 (93) 95:5 (98) 90:10 (90) 15:85 (98) 20:80 (76) 20:80 (80) 14:86	91, 414
	CuCl, MeCN, 140°	(54)	415
	NIS	(54)	166

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu₃SnH, AIBN, C₆H₆, 80°

89

		trans:cis
Me	(68)	71:29
Bn	(80)	72:28
Ph	(90)	83:17

R¹	R²	Conditions	I + II	I:II
Me	H	CuCl, CuCl₂, HOAc, H₂O	(79)	9:91
Me	H	FeSO₄, HOAc, H₂O	(93)	0:100
H	Me	CuCl, CuCl₂, HOAc, H₂O	(81)	100:0
H	Me	FeSO₄, HOAc, H₂O	(74)	100:0

416

Cu(bpy)Cl, reflux

R	Conditions	I + II	I:II
H	CH₂Cl₂	(84)	71:29
Et *E*	THF	(85)	60:40
Et *Z*	MeOAc	(76)	67:33

417

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

(*t*-BuO)₂, PhCl, 135°

(57)

255
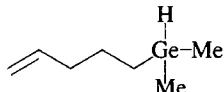
AIBN, heat

(70)

418

Bu₃SnH, AIBN, C₆H₆, 80°, 2 h

R	I + II	I:II
Me	(>84)	4.6:1
i-Pr	(>82)	100:0
t-Bu	(>71)	100:0
CH₂=CH	(>72)	5.5:1
Ph	(>59)	11:1

56

Ph₃SnH, AIBN, C₆H₆

R	I + II	I:II
H	(74)	81:19
Me	(86)	78:22

419

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$(Bu_3Sn)_2$, C_6H_6, $h\nu$, heat	(68)	420
	Bu_3SnH, AIBN, C_6H_6, 80°		421

R¹	R²	R³	
H	Me	Me	
H	H	H	(88–92)
Me	H	H	
Me	H	Me	

| C lCo(dmgH)₂py, NaBH₄, MeOH, NaOH, 50° | | | 223 |

R¹	R²	R³	
H	H	Ph	(78)
H	Me	Ph	(73)
H	Ph	Ph	(85)
–(CH₂)₃–		H	(48)
–(CH₂)₄–		H	(64)

C₈

| | Bu_3SnH, AIBN, C_6H_6, 65–70° | | 241 |

R	
Ph	(82)
p-ClC₆H₄	(85)
Et	(76)
Ph(CH₂)₂	(88)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu_3SnH, AIBN, C_6H_6, 80°	(74)	89
	1. Hg(OAc)₂ 2. NaBr 3. NaOH 4. NaBH₄	(82)	422
	1. PhSh, O₂ 2. Ph₃P		423

R¹	R²	
H	Me	(59)
Me	H	(49)

| | Bu_3SnH, AIBN, C_6H_6, 80° | | 424 |

R	
H	(95)
Me	(95)

| | Bu_3SnH, AIBN, PhMe, 110° | | 425 |

Y	R¹	R²	
NH	Me	Me	(95)
O	Me	Me	(—)
O	Me	Ph	(—)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°		426

R

	I + II	I:II
Me	(52)	96:4
Et	(71)	96:4
i-Pr	(66)	98:2

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnCl, AIBN, Na(CN)BH₃, *t*-BuOH, 80°	(70)	427
	Bu₃SnH, AIBN, PhMe, 80°	I + II	428

R^1	R^2	R^3		I + II	I:II
H	Et	H		(50)	—
Et	H	H		(72)	—
Me	H	Et		(80)	4:96
Et	H	Et		(77)	4:96
m-MeOC₄H₆	H	*m*-MeOC₆H₄		(75)	10:90
H	-(CH₂)₃-			(71)	99:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	C₇H₁₆, *h*ν, reflux	(84)	264

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cu(bipy)Cl, AcOMe, reflux	I + II	417

I + II (89) **I:II** = 5.8:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph₃SnH, AIBN, C₆H₆, 80°		429

R^1	R^2	R^3	
H	*n*-C₅H₁₁	H	(>77)
n-C₈H₁₇	H	H	(>62)
H	Me	Me	(>69)
n-C₄H₉	*n*-C₄H₉	H	(>65)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH, H₂SO₄, Fe²⁺	(66)	430
	Bu₃Sn⌒⌿ AIBN, C₆H₆		431

R^1	R^2	R^3	
Ph	H	H	(35)
Ph	H	Me	(25)
Me₂	CH₂OH	H	(37)

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_9$

TsX

  I +   **II**   219

R	X		**I + II**	**I:II**
Bn	Br	MeCN, *hv*, 18°	(65)	24:76
Bn	Cl	MeCN, *hv*, 18°	(60)	10:90
Bn	Cl	PhMe, 110°	(65)	26:74
CH$_2$CH=CH$_2$	Br	MeCN, *hv*, 18°	(66)	20:80
t-Bu	Br	MeCN, *hv*, 18°	(53)	5:95

Bu$_3$SnH, AIBN

    432

R^1	R^2	
CN	CO$_2$Et	(74)
COMe	CO$_2$Me	(75)
COMe	COPh	(54)
CO$_2$Et	CO$_2$Et	(81)

Mn(OAc)$_3$

  (40)   433

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

(Ph$_2$Se)$_2$, O$_2$, AIBN, MeCN, *hv*, 0°

  I +   **II**   434, 435

R	**I + II**	**I:II**
CO$_2$Bu-*t*	(41)	1:1.8
CH=CHCO$_2$Me	(88)	> 95:5
Ph	(88)	> 95:5
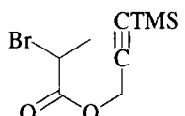
Bu$_3$SnH, AIBN, PhMe, 110°
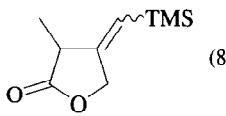
  (80)   425
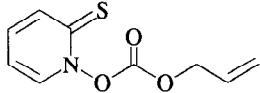
	Y	
THF, *hv*, 25°	*S*-(2-pyridyl)	(85)
THF, (PhSe)$_2$, *hv*, 25°	SePh	(70)
THF, *t*-BuSH, *hv*, 25°	H	(100)

    436

Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°

  (96)   27

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu₃SnH, Et₃B, THF, -78° — 437

$$\frac{R}{\text{TMS} \quad (66)}$$
$$\text{Ph} \quad (53)$$

Bu₃SnH, AIBN, C₆H₆, 80° — I + II — 111, 438

I + II (85) I:II = 70:30

Bu₃SnH, AIBN, C₆H₆, 80° — I + II — 111, 438

I + II (90) I:II = 65:35

1. MeOH, *hv*
2. MeC≡CMe — 439

(41) + (39)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

ClCo(dmgH)₂py, NaBH₄, MeOH, NaOH, 0° — (60) — 439a

AcOH, H₂SO₄, Fe²⁺ — (55) — 430

(PhS)₂, *hv* — 440
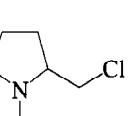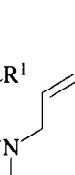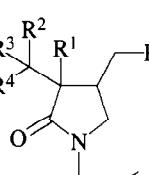
Substrate Product (%) *cis:trans*
A I (57) 0:100 II (22) 1:1
B III (89) 1:1 IV (2)
C V (37) 2:1
D VI (63) 2:1

Substrate	R¹	R²	R³
A	H	H	H
B	Me	H	H
C	H	Me	H
D	H	Me	Me

Product	R¹	R²	R³	R⁴	R⁵
I	H	H	H	SPh	H
II	H	H	H	H	SPh
III	Me	H	H	SPh	H
IV	Me	H	H	H	SPh
V	H	Me	H	H	SPh
VI	H	Me	Me	H	SPh

C₁₀

Bu₃SnH, AIBN, C₆H₆, heat — (48) — 441

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 + R²SH	AIBN, *hv*		442

R¹	R²		
H	Et	C_6H_6, 40°	(98)
H	$MeO_2C(CH_2)_2$	PhMe, 110°	(93)
Ph	$MeO_2C(CH_2)_2$	C_6H_6, 40°	(86)

| H | $HO(CH_2)_2$ | 1. C_6H_6, 40°
2. H_2O | (98) | |
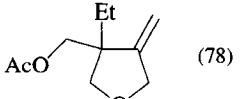
	Bu_3SnH, AIBN, C_6H_6, 80°	(78)	111, 438
	Bu_3SnH, AIBN, C_6H_6, 80°	(81)	52, 53
	Bu_3SnH, AIBN, C_6H_6, 80°		443

R		
H		(62)
Me		(65)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 + $R^3CO_2^-$	Pt electrode, MeOH, 40-45°		167

R¹	R²	R³	
H	Me	Me	(58)
H	Me	C_5H_{11}	(46)
H	H	Me	(58)
H	H	C_5H_{11}	(45)
Me	Me	Me	(56)
Me	H	Me	(67)
Me	H	C_5H_{11}	(63)

| | Bu_3SnH, AIBN,
PhMe, 110°
or
Bu_3SnCl, AIBN,
$Na(CN)BH_3$,
t-BuOH, 80° | | 444 |

R¹	R²	R³	
H	H	H	(60)
H	H	Me	(55)
H	Me	H	(54)
Me	Me	H	(50)

| | Bu_3SnH, 85° | **I, II** | 445 |

I + II (70-80)   **I:II** = 1:1

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(bromo enol ether with CR substituent; EtO)	Bu₃SnCl, AIBN, Na(CN)BH₃, *t*-BuOH	(tetrahydrofuran with =CHR, EtO)	446

R	
n-C₆H₁₃	(89)
n-Bu	(67)
CO₂Et	(65)
(trisubstituted alkene)	(67)
(diene)	(75)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(vinyl cyclopropane with R^1, R)	(Ph₂Se)₂, O₂, AIBN, MeCN, *hv*, 0°	I + II (dioxolane products)	435

R	R^1	I + II	I:II
CH=CHCO₂Me	H	(55)	6.4:1
CH=CHCO₂Me	Me	(73)	> 95:5
Ph	Me	(63)	> 95:5

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(RO, Br, O–CH=CH–CO₂Et)	Bu₃SnH, (slow addition), AIBN, C₆H₆, 80°, 6 h	I + II (tetrahydrofurans with CH₂CO₂Et, RO)	424

R	I + II	I:II
TBDMS	(89)	1:1.6
MOM	(95)	1:0.7

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(vinyl cyclopropane with R)	(Ph₂Se)₂, O₂, AIBN, MeCN, *hv*, 0°	I + II (dioxolane products)	447

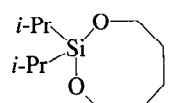| R	I + II	I:II
Ph	(63)	> 10:1
CO₂Bu-*t*	(66)	1:1.8
CO₂Ph	(63)	1:3
CO₂C₆F₆	(60)	1:5.4
CO₂CH(CF₃)₂	(70)	1:6
CO₂CH(CF₃)₂	(65)	> 1:10

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(EtO₂C, Br, EtO, O, R^1, R^2)	Cr(OAc)₂, THF, 25°	I + II (tetrahydrofurans EtO₂C, R^2, EtO, O, R^1)	448, 449

R^1	R^2	I + II	I:II
H	H	(79)	1:3.9
Me	H	(83)	1:0.9
H	*E/Z*-Me	(83)	1:1.7
n-C₅H₁₁	H	(73)	1:1
i-C₃H₇	H	(57)	1:1.1
H	*E/Z*-Ph	(76)	1:0.6
Ph	H	(99)	1:0.9
Me	Me	(85)	1:0.3

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
EtO$_2$C, I, allyl ether; R = H, Me	Cr(OAc)$_2$, THF, 25°	I + II **I + II** **I:II** (93) 4:1 (93) 1:1	262
EtO$_2$C, I, propargyl ether	Cr(OAc)$_2$, THF, 25°	I + II + III **I + II + III** (92) **I:II:III** = 2:1:1.1	262
I—CH$_2$CH$_2$—O—allyl + R—C(=O)—R R Et Pr –(CH$_2$)$_4$– –(CH$_2$)$_5$– –CH(Me)(CH$_2$)$_4$– –(CH$_2$)$_2$CH(Bu-*t*)(CH$_2$)$_2$–	SmI$_2$, HMPA, THF	tetrahydrofuran, R$_2$C(OH) Diastereomeric ratio (57) (38) (53) (52) (74) 1.3:1 (55) 5:1	176

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

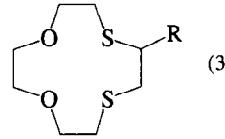| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{11}$, structure with CMe, I, O–C(=O)	BPO, C$_6$H$_6$, 80°	lactone product (75)	160
Ph–C(=CH$_2$)–N(Me)–C(=O)–CH(R^1)(R^2) R^1 R^2 Cl H Cl Cl I H SPh SPh	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	Ph–pyrrolidinone, R^2, N–Me (17) (—) (47) (75)	450
Y, Z, X, Ph, O–allyl X Y Z Br H H Cl Cl Cl Cl Cl H	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II **I + II** **I:II** (83) 34:66 (92) 90:10 (78) 5:95	451

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, O₂, PhMe, 0°, 5-24 h		260
R		*trans:cis*	
H		(84) 100:0	
Ph		(74) 87:13	
	Bu₃SnH, AIBN, C₆H₆, heat	R	452
		H (87)	
		Me (85)	
	CH₂Cl₂, *hv*		453
Y			
NAc		(77)	
O		(—)	
	Mn(OAc)₃, AcOH	(40)	433

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
+ ArN₂⁺Cl⁻	TiCl₃, MeOH, 0°		454
Ar			
p-ClC₆H₄		(40)	
p-MeOC₆H₄		(30)	
Ph		(45)	
	Bu₃SnH, AIBN, *t*-BuPh, 80°	(73)	455
	Cl(CH₂)₂Cl, 85°	I + II (78) I:II = 80:20	456,
	Me₂CO, reflux	I + II (83) I:II = 11:89	417
	t-BuO₂H, AIBN, O₂, 2,2,4-trimethyl-pentane, 60°	(73) +	457
		(19)	

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(PhSe)$_2$, AIBN, O$_2$, MeCN, *hv*, 0°	**I** + **II**	447, 435

$$\begin{array}{ccc} \underline{R} & \underline{I+II} & \underline{I:II} \\ Me & (70) & 1:1.7 \\ t\text{-Bu} & (84) & 1:1 \end{array}$$

| | Ph$_3$SnH, AIBN, C$_6$H$_6$, 80° | | 458, 215, 459, 460 |

R^1	R^2	R^3	I + II	E:Z
Me	Me	CH$_2$CH=CH$_2$	(67)	70:30
Me	Me	(CH$_2$)$_2$CH=CH$_2$	(75)	75:25
Me	Me	(CH$_2$)$_2$CH=CH$_2$	(70)	95:5
Me	Me	(CH$_2$)$_3$OTHP	(60)	0:100
H	*n*-Bu	*n*-Bu	(65)	100:0
Me	Me	Ph	(84)	25:75
Me	Me	TMS	(85)	35:65

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaCo(dmgH)$_2$py, MeOH, NaOH, 0-25°		461

$$\begin{array}{cc} \underline{R} & \\ H & (60) \\ Me & (80) \end{array}$$
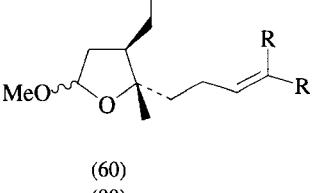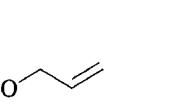
| | Bu$_2$SnH$_2$, THF, ultrasound | (60-70) | 86 |

$$\begin{array}{cc} & \textit{trans:cis} \\ 6° & 87:13 \\ -55° & 94:6 \end{array}$$

C$_{12}$
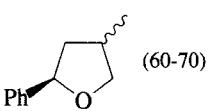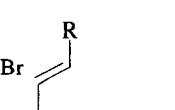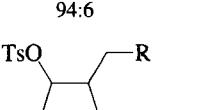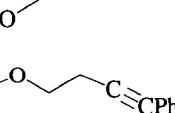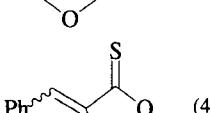
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 70°	$\begin{array}{cc} \underline{R} & \\ H & (67) \\ Me & (56) \\ \textit{n}\text{-Pr} & (63) \end{array}$	462
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(49)	463
	(Ph$_3$Sn)$_2$, *t*-BuNC, C$_6$H$_6$, *hv*, 50°	(61)	206

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn, NH$_4$Cl B$_{12}$ (2 mol%), DMF, 20°	(77)	464
	BPO, C$_6$H$_6$, 80°	(63)	160
	Me$_3$SnCl, Na(CN)BH$_3$ AIBN, *t*-BuOH	I, II I + II (84) I:II = 2:1	218
	MeC(O)SH, AIBN	(67)	452
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(99)	36, 465
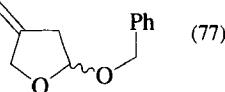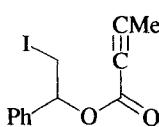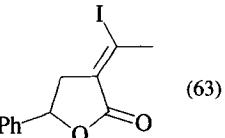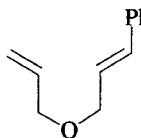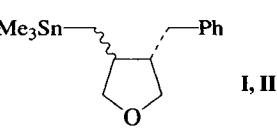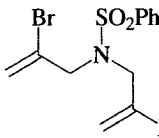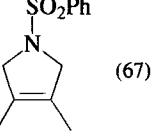
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R^1 / R^2 H / H H / Me Me / H	MeC(O)SH, AIBN	I + II I II (—) (—) I:II = 3:1 (67) (—) (—) (80)	452
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (92) I:II = 2.5:1	36, 465
n-Pr	C$_6$H$_6$, *h*v *t*-BuSH, reflux	I + II R = (*S*)-2-pyridyl; I + II (70), I:II = 3:1 R = H; I + II (65)	466

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
Ph, Br / MeO, O (allyl)	Bu$_3$SnCl, AIBN, NaBH$_4$, C$_6$H$_6$, EtOH, *hv*	Ph / MeO—O **I** + Ph / MeO—O **II** **I + II** (60) **I:II** = 86:14	426
Ph / O–C(=S)–SMe	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	Ph—CH$_2$ (lactone thione) O (77)	467, 463
R PhSO$_2$ R / N	MeC(O)SH, AIBN, C$_6$H$_6$, 80°	AcS—R...R / N—SO$_2$Ph R: H (100) *cis:trans* = 2:1 ; Me (64)	452
R—CH(NHMe)—CH$_2$CH$_2$CH=CH$_2$	BuLi	R—(pyrrolidine)—Me / N—Me R: Ph (52); *p*-MeC$_6$H$_4$ (48); *p*-MeOC$_6$H$_4$ (46)	468, 469
(prenyl) S N—CO$_2$Et / O	(TMS)$_3$SiH, PhMe, AIBN, 88–90°, 2 h	CO$_2$Et / iPr, N—CH$_2$CH$_2$—S—Si(TMS)$_3$ / O **I, II** **I + II** (82) **I:II** = 2.5:1	470

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
XTs (X = O, S)	BPO, 80–90°	Ts—CH$_2$—(ring)—X (100)	471
Ph (cyclopropane) vinyl	(Ph$_2$Se)$_2$, AIBN, MeOH, *hv*, 50°	vinyl—O–O—Ph **I** + vinyl—O–O—Ph **II** **I + II** (73) **I:II** = 2.8:1	434, 435
Br, CH≡C / Ph—O—C(Me)$_2$	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH, 80°	Ph—(ring)=CH$_2$ / O—C(Me)$_2$ (90)	472
O=C–O / SePh–C(=O)R (allyl)	C$_6$H$_6$, *hv*	(lactone) C(=O)R / CH$_2$—SePh R: OEt (41); Me (47)	88
Ph (epoxide) vinyl + R^1, R^2 (alkene)	PhSH, C$_6$H$_6$, 80°	R^1, R^2 / Ph—O—vinyl **I** + R^1, R^2 / Ph—O—vinyl **II** see table below	473

R^1	R^2
CN	H
CO$_2$Me	H
Ph	H
CO$_2$Me	Me

I + II	**I:II**
(53)	2.1:1
(56)	1.8:1
(57)	4:1
(55)	1:1

C$_{13}$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(N-tosyl diallylamine)	TsSePh, AIBN, CHCl$_3$, 65°	(Ts—…—SePh pyrrolidine) (96) *cis:trans* = 60:40	281
	TsBr, AIBN, MeCN, 25°	(Ts—…—Br pyrrolidine) (74) *cis:trans* = 77:23	409
(Br—CH$_2$CH$_2$—N(SO$_2$Ph)—CH$_2$CH=CMe$_2$)	Bu$_3$SnH, AIBN	(3-isopropyl-1-(SO$_2$Ph)pyrrolidine) (84)	452
(BuO, CF$_3$ diene ether) diastereomeric ratio = 5:1 ; diastereomeric ratio = 1:2	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II** (62) (12) ; (21) (42)	313
(*n*-Bu—CHBr—…—imidazole ester)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(*n*-Bu lactone with N-Me imidazolylmethyl) (40)	474

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(Tol—Y—CH$_2$—O—… CF$_2$Cl, R^1, R^2, R^3 alkene)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(tetrahydrofuran with F, F, R^1, R^2, R^3)	475

Y	R^1	R^2	R^3		*cis:trans*
SO	H	H	H	(70)	9:1
S	H	H	H	(55)	9:1
SO$_2$	H	H	H	(51)	9:1
SO	H	H	Ph	(80)	4:1
S	H	H	Ph	(59)	4:1
SO$_2$	H	H	Ph	(66)	4:1
S	H	Me	Me	(67)	3:1
SO	H	H	Cl	(84)	3:1
SO	H	H	Cl	(62)	3:1
SO	Cl	H	H	(25)	1:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(R^1, R^2 alkene with O—SiMe$_2$—CH$_2$Br)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 2 h	(oxasilolane with Ph—CH$_2$) **I** + **II**	56

R^1	R^2		**I + II**	**I : II**
H	Ph		<(85)	84 : 16
Ph	H		<(94)	100 : 0

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{14}

Ph$_3$SnH, AIBN, C$_6$H$_6$, 80° — (66) — 49

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — (70) + (11) — 465

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — 476

R^1	R^2		*trans:cis*
H	H	(87)	9:1
H	H	(70)	9:1
CO$_2$Et	H	(92)	4:1
Me	Me	(85)	2:1

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — 198

R	
H	(14)
Me	(53)
n-Bu	(63)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

(PhSe)$_2$, AIBN, O$_2$, MeCN, 0° — I + II (48) I:II = 1:1.4 — 434, 435

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — (70) — 463

Bu$_3$SnH, AIBN, C$_6$H$_6$, heat — (82) — 477

Bu$_3$SnH, AIBN, C$_6$H$_6$, heat — R: Me (69), H (71) — 478

Bu$_3$SnH, AIBN, C$_6$H$_6$, heat — (53) *cis:trans* = 57:43 — 479

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(90) *cis:trans* = 3:1	465
	t-BuSH, CH₂(CO₂H)₂, MeCN, *h*ν, 25°	(70)	68
	C₆H₆, *h*ν C₆H₆, *t*-BuSH, *h*ν C₆H₆, (PhSe)₂, *h*ν	Y (S)-2-pyridyl (95) SePh (70) Me (73)	480
	CH₂Cl₂, *h*ν	(68)	453
	ClCo(dmgH)₂py, MeOH, NaOH, NaBH₄, 0°	(60)	439a

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₅			
	Bu₃SnH, AIBN, C₆H₆, 80°	(68)	478
	Ph₃SnH, AIBN, C₆H₆, heat	I + II (74) I:II = 8:92	419
	Ph₃SnH, AIBN, C₆H₆, heat	I + II (77) I:II = 96:4	419
			481
	AIBN, CCl₄ *t*-BuOH, *h*ν	(80) (60)	

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, heat	(70)	195
	Bu₃SnH, AIBN, C₆H₆, 80°	(78)	482
	Bu₃SnH, AIBN, C₆H₆, 80°	(88) E:Z = 50:50	479
			68, 483
	t-BuSH, CH₂(CO₂H)₂, MeCN, hv, 25°	Y: Me (92)	
	THF, BF₃•OEt₂, 22°, hv	(S)-2-pyridyl (98)	
	THF, BF₃•OEt₂, (Ph₂Se)₂, −78°, hv	SePh (80)	
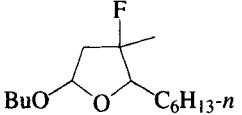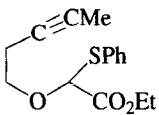
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 65°	(77)	484
	Me₃SnCl, Na(CN)BH₃, AIBN, t-BuOH, 80°	(92) cis:trans = 2:1	218
	CH₂Cl₂, hv, 25°	(—)	485
	Bu₃SnH, AIBN, C₆H₆	(46) syn:anti = 1:1	478
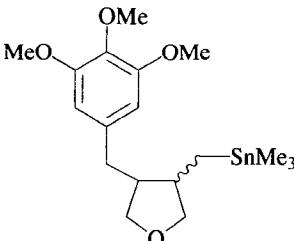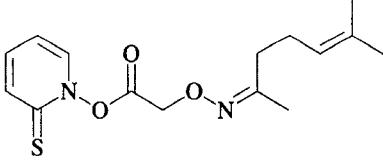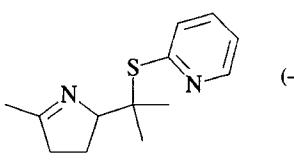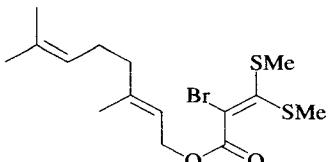
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{16}

	Pt electrode, MeCN, Et$_4$NClO$_4$	(81)	486

	THF, BF$_3$•Et$_2$O, *hv*, -78°	(63-74)	483

	1. Bu$_3$SnCl, Na(CN)BH$_3$, AIBN 2. TsH		487

R^1	R^2	
n-C$_6$H$_{13}$	Ph	(50)
n-C$_6$H$_{13}$	*p*-MeC$_6$H$_4$	(60)
n-C$_6$H$_{13}$	*i*-Pr	(55)
n-Bu	Ph	(52)
n-Bu	*p*-MeC$_6$H$_4$	(53)

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

	H$^+$, *hv*	I, II	488

R				
		I + II	**I:II**	**X**
n-Pr	*t*-BuSH	(38)	—	Spy
n-C$_7$H$_{15}$	*t*-BuSH	(56)	1:1.4	H
n-Bu		(48)	2:1	H

	Bu$_3$SnH, AIBN, PhMe, heat	(75) *E:Z* = 59:41	489, 113

	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat		479

E		(77) *cis:trans* = 35:65
Z		(65) *cis:trans* = 54:46

	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(80-82)	490

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 75°	**I** + **II** (82) **I**:**II** = 3.1:1	491

C$_{17}$
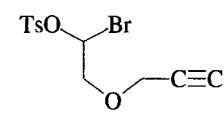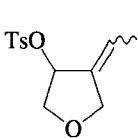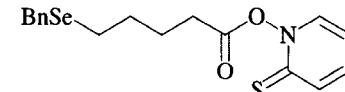
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 $\underline{R}$ *cis : trans* Ph (85) 54 : 46 n-C$_5$H$_{11}$ (93) 0 : 100	462
	C$_6$H$_6$, $h\nu$, 80°	(79)	492, 493
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(92)	494

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	ClCo(dmgH)$_2$py, MeOH, NaOH, Py, NaBH$_4$, 0°	**I** + **II** **I** + **II** (50) **I**:**II** = 9:1	495
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(87)	465, 496
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II** $\underline{R}$ H **I + II** **I:II** Me (95) 2.6:1 (83) 2.2:1	497, 48
	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	(36)	452
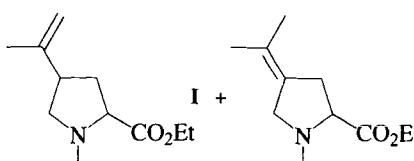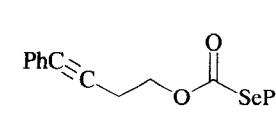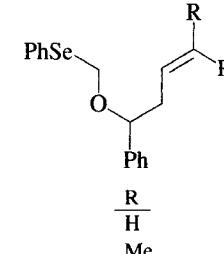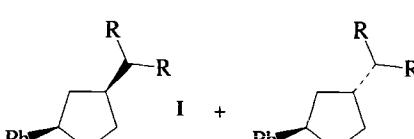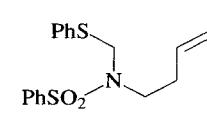
TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
Ph⌒⌒O–C(=O)–SePh	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(80) [lactone with CH$_2$Ph]	36, 465
Ph⌒⌒O–C(=S)–OPh	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(47) [lactone with CHPh$_2$] + (9) [thionolactone with CH$_2$Ph] + (12) [thiolactone with CH$_2$Ph]	463
MeO$_2$C–CH(SPh)–N(CO$_2$Me)–CH$_2$CH$_2$CH=CR^{1}R^2	Bu$_3$SnH, AIBN, PhMe, 80°	[pyrrolidine: R^{1}CH–R^2 at 3-position, CO$_2$Me at 2, CO$_2$Me on N]	489, 113, 456

	R^1	R^2		cis:trans
	Et	H	(93)	35:65
	H	Et	(91)	30:70

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
PhS–CH(CO$_2$Et)–O–CH$_2$C(Me)$_2$CH=CHMe	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	(72) cis:trans = 44:56 [tetrahydrofuran, dimethyl, ethyl, CO$_2$Et]	479

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
[N-SPh imine of citronellal derivative] + CH$_2$=CR^{1}R^2	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	[dihydropyrrole with C(Me)$_2$CH$_2$CHR^{1}R^2 side chain]	69

	R^1	R^2	
	CO$_2$Me	H	(83)
	CO$_2$Bu-*t*	CO$_2$Bu-*t*	(68)
	CN	H	(60)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO$_2$C–CH(SePh)–CO$_2$Me + CH$_2$=CHCH$_2$OCH$_2$CH=CH$_2$	C$_6$H$_6$, *h*ν, 12 h	(86) cis:trans = 1.8:1 [tetrahydrofuran with CH(CO$_2$Me)$_2$ and CH$_2$SePh]	498

C$_{18}$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
[R^{2}CH=C(R^1)CH$_2$–N(Boc)–CH(CH$_2$SePh)–CO$_2$Me]	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°, 8 h	[pyrrolidine: R^1, R^{2}CH$_2$ at 4-position, CO$_2$Me at 2, Boc on N]	87

	R^1	R^2		cis:trans
	H	H	(90)	62:38
	H	Me	(85)	60:40
	H	Pr	(75)	60:40
	H	Ph	(85)	55:45
	Me	H	(83)	—

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
PhSe— ... CMe ... O ... Ph	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	Ph—O ring (83) 1.5:1 isomer mixture	497, 48
R^1 ... Co(dmgH)$_2$py ... R^2	Cl$_3$CSO$_2$Cl, CH$_2$Cl$_2$, *hv*, 15°	Cl$_3$C— ring **I** + ring **II**	499

R^1	R^2		I	II
H	H		(82)	(—)
Me	H		(22)	(—)
Me	Me		(48)	(19)
H	Me		(60)	(17)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
PhSe—...O...Ph	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	Ph—O ring **I** + Ph—O ring **II** I + II (>98) I:II = 3.2:1	497, 48
TsO—...X...R	Bu$_3$SnH, AIBN, NaI, DME, 80°, 1-2 h	ring—R, X	500

R	X		
H	NTs		(80)
Ph	NTs		(82)
Ph	O		(76)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{19}$ TMS—N(CO$_2$Bn)—...—C(O)—Y	DCA, MeOH, MeCN, *hv*	Y—C(O)— pyrrolidine ring, N–BnO$_2$C Y: Me (83), OMe (88)	188
Br—...—BnO$_2$C—N(CH≡C)—SO$_2$Ph	Bu$_3$SnH, AIBN, PhMe, heat	BnO$_2$C— pyrrolidine ring, N–SO$_2$Ph (58)	501
C$_{20}$ Im—C(S)—O—...epoxide...—OTBDMS	Bu$_3$SnH, AIBN, THF, heat	O ring —OTBDMS (45)	204
Ph...cyclopropane...cyclopropane...Ph	(Ph$_2$Se)$_2$, AIBN, O$_2$, MeCN, 0°, *hv*	Ph—O–O ring structure **I** + Ph—O–O ring structure **II**	434, 435

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{22}$ PhS SPh (pyridin-3-yl) N-Me O	Bu$_3$SnH, AIBN, PhMe, 110°	(pyridin-3-yl pyrrolidinone N-Me) (77)	450
I TBDMSO N CO$_2$Ph (with prenyl)	ClCo(dmgH)$_2$py, NaBH$_4$, MeOH, NaOH, 0°	TBDMSO N CO$_2$Ph (60) *cis:trans* = 58:42	502
C$_{23}$ (pyridinethione carbamate) N O n-Bu S + SO$_2$Ph	H$^+$, *hv*	(pyridyl-S pyrrolidine) N—Bu-n PhO$_2$S (56)	503
Br n-BuO O (allyl) + SO$_2$Ph CO$_2$Bu-*t*	I$_2$CoL, Zn, DMF, *hv*, 20°	n-BuO O CO$_2$Bu-*t* **I** + n-BuO O CO$_2$Bu-*t* **II** I + II (66) I:II = 81:19	184

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
Ph (biscyclopropyl) Ph	(Ph$_2$Se)$_2$, AIBN, O$_2$, MeCN, *hv*, 0°	O—O Ph O—O O—O Ph (38)	434, 435
C$_{24}$ Ph$_3$Ge O (allyl O Me)	C$_7$H$_{16}$, *hv*, 25°	O GePh$_3$ (furanone Me) (75)	350
Ph$_3$Ge O N Me (allyl)	C$_7$H$_{16}$, *hv*, 25°	O GePh$_3$ N Me (82)	350
CO$_2$Me R X O O OTBDPS	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	R CO$_2$Me O O OTBDPS **I** + R CO$_2$Me O O OTBDPS **II**	419

R	X
H	Cl, I
Me	Cl
i-Pr	Br

I + II	I:II
(81)	88:12
(81)	80:20
(91)	91:9

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{26}

TsCl, BPO,
PhMe, 110°

351

	R¹	X	R²	R³
	H	O	Bn	OEt
	H	O	Bn	NHBn
	Me	O	Bn	OEt
	H	H₂	C(O)Bu-*t*	NHBn
	H	H₂	C(O)Ph	OEt

	ratio
(51)	3.6:1
(46)	3.5:1
(51)	1.5:1
(53)	1.8:1
(58)	1.6:1

C_{28}

A. TsCl, BPO, PhMe
B. (Bu₃Sn)₃, C₆H₆, *hv*, 4 h

   I, II

504

	R	X	R¹
	Bn	O	CO₂Et
	Bn	O	CONHBn
	Ts	H₂	CO₂Et
	Bn	O	CO₂Et

I + II	I:II
(51)	3.6:1
(46)	3.5:1
(68)	1.8:1
(54)	2:1

ClCo(dmgH)₂py,
NaBH₄, MeOH,
NaOH, 0°

   (80) *cis:trans* = 62:38

502

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{29}

PhMe, 110°

I + II (62)

402

C_{32}

Bu₃SnH, AIBN,
C₆H₆, 80°

   (86)

505

D. 6-Membered Rings

C_5

506

	I + II + III	I:II:III
CuCl₂, AIBN, 170°	(17)	0:100:0
Bu₃SnH, AIBN, 80°	(—)	7:93:0
Bu₃SnH, ultrasound	(—)	100:0:0
Ph₃SiH, *hv*	(—)	14:78:8

$HC\equiv C$——SH

C_5H_{12}, *hv*, 36°

   I +   II   I + II (61)   I:II = 70:30

507

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_6$	1. BPO, O$_2$, C$_6$H$_6$, rt 2. PPh$_3$	(30)	508
	Cyclohexane, *h*v, 80° C$_6$H$_{14}$, *h*v, -65°	**I + II** (46) **I:II** = 97:3 **I + II** (61) **I:II** = 23:77	509
C$_9$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	R = H (96) R = Me (96)	424
C$_{10}$	Bu$_3$SnH, AIBN,		510

X	Y	
CO$_2$Me	H	(61)
H	Me	(35)
F	F	(39)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	**I** + **II** **I + II** (85) **I:II** = 4.7:1	511
	Bu$_3$SnH, AIBN, Na(CN)BH$_3$, C$_6$H$_6$, benzo-15-crown-5, 80°	**I** + **II**	512

R	I + II	I:II
MeO	(40)	75:25
EtO	(53)	80:20
	(53)	75:25
	(35)	85:15
	(33)	90:10

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{11}

AIBN, C_6H_6, *hv*, 80°

R^1	R^2		*cis:trans*
Cl	Cl	(54)	1:1
Br	Br	(50)	1.1:1
Ph	H	(51)	1:1
OBn	H	(65)	2:1

Bu_3SnH, AIBN, C_6H_6, 80°

I + II (29) I:II = 20:80

1. Bu_3SnH, AIBN, C_6H_6, 80°
2. TsOH, 80°

515

R^1	R^2	I + II	I:II
H	H	(80)	
Me	H	(74)	3:1
H	Me	(74)	1:3
Me	Me (*anti*)	(64)	1:2
Me	Me (*syn*)	(80)	1:3

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{12}

(*t*-BuON=)$_2$, O_2, C_6H_6, 30°   (70)   516

Bu_3SnH, AIBN, C_6H_6, 80°   (55)   465

Bu_3SnH, AIBN, PhMe   517

75°	(17)
30°, sunlight	(33)
10°, Hg lamp	(64)

DCA, *hv*   I + II   518, 188

R^1	R^2	I	II
Me	Me	(90)	—
Me	Bn	(90)	—
OMe	Me	(55)	(48)
OMe	Bn	(40)	(41)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{13}$ (bromo/CO$_2$R/EtO alkene structure)	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	(tetrahydropyran CO$_2$R structure) $\quad$ R: Me (88), Et (97)	519, 93
TMS—N(Bu)—pentenyl structure	DCN, *i*-PrOH, *h*ν	(N-Bu methylpiperidine) (70–78)	520
O$_2$S—O—butynyl / naphthalene X structure	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(cyclic sultone naphthalene X structure) $\quad$ X: N (57), CH (53)	510
Ph / N—Me—Cl pentenyl structure	TiCl$_3$, AcOH, H$_2$O, 0°	(4-Ph-2-chloromethyl-N-Me-piperidine) (92)	521
hexenyl O—C(=O)—SePh structure	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(3-Et-δ-valerolactone) (74)	465

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R^1 / SCN / R^2 alkene structure	Bu$_3$SnH, AIBN, PhMe, 75°	(thiolactam piperidine-2-thione structure)	517

R^1	R^2	E:Z
SPh	CO$_2$Me	1.8:1
CO$_2$Bu-*t*	CO$_2$Me	1.3:1
SPh	Ph	12:1

(90)
(93)
(69)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{14}$ EtO$_2$C / Et / Br / OEt structure	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(tetrahydropyran CO$_2$Et structure) I + (tetrahydropyran CO$_2$Et structure) II	522, 93
acryloyl N(Bn)—butenyl structure	(PhS)$_2$, *h*ν	(PhS-methyl piperidinone N-Bn structure) (87) *cis:trans* = 6:1	440
Me—Si(Me)—O—CH$_2$Br / cyclohexyl / alkene R structure	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH, 80°	(cyclic siloxane cyclohexyl R structure) $\quad$ R: H (90), Me (89)	72

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₅	Bu₃SnH, AIBN, C₆H₆, 80°	(86)	465
(Br—R ... Ts ... O ... SMe) R: Me *E*, Ph *Z*	Bu₃SnH, AIBN, C₆H₆, 80°	**I, II** I + II diastereomeric ratio (97) (60:40) (82) (74:26)	378
C₁₇ (MeO₂C ... I ... CO₂Me ... O ... OTBDMS)	Bu₃SnH, AIBN, C₆H₆, heat	**I** + **II** I + II (85) I:II = 80:20	511

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(R ... CO₂Bu-*t* ... O ... SPh) R: H, *cis*-TMS, *trans*-TBDPS, *cis*-TBDPS	Bu₃SnH, AIBN, C₆H₆, 80°, 3.5–27 h	**I** + **II** I + II *trans:cis* I:II (85) 1.6:1 (91) 5:1 (66) 1.3:1 (82) 1:0	94
C₁₈ (SPh ... O ... CO₂Et)	Bu₃SnH, AIBN, C₆H₆, heat	(62)	479
(SePh ... O ... Ph)	Bu₃SnH, AIBN, C₆H₆, 80°	**I, II** + **III** I, II + III (97), I, II:III = 14.3:1	48, 497
(Br ... CO₂Et ... N–Bz) *Z*, *E*	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + **II** I + II (90), I:II = 1:1 I + II (90), I:II = 1:1	523

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C₁₉

R¹	R²	R³	
Me	OMe	H	(90)
Me	OPr	H	(83)
Me	OBu	H	(81)
Me	OBu-*t*	H	(65)
Ph	OEt	H	(68)
Me	OCH₂CH₂O		(85)

Mn(OAc)₃, Cu(OAc)₂, AcOH, O₂, 23°   524

Bu₃SnH, AIBN, C₆H₆, 80°, 3.5-27 h

I + **II**   94

I + II (74) **I:II** = 1:1

DCA, MeOH, MeCN, *hv*   188

Y	
Me	(75)
OMe	(78)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C₂₁

Bu₃SnH, AIBN, C₆H₆, 80°, 3.5-27 h

(74)   94

C₂₅

Ph₃SnH, AIBN

I +   419

II

R	X
H	I
Me	Cl

I + II	I:II
(51)	23:77
(63)	78:22

C₂₉

Bu₃SnH, AIBN, C₆H₆, 80°, 3-27 h

(61)   94

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₃₀	Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 1 h	(78)	92
C₃₁	PhMe, 110°	I + II + III (65), I:II:III = 78:11:11	402
	1. Bu₃SnH, AIBN, C₆H₆, 80° 2. TsOH, 80°	I + I + II (58) I:II = 4:1	515

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 80°	(95)	72
	Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 80°	(98)	72

E. 7-Membered Rings

C₅ HC≡C—S—SH	C₅H₁₂, *hv*, 36°	I + II + III (51) I:II:III = 77:3:2	507

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_7$	(t-BuO)$_2$, PhCl, 132°	R^1: H (60), Me (58)	525
C$_{12}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(25) + (12)	392
C$_{13}$	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, t-BuOH, 80°	(92)	72
C$_{14}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II (51) I:II = 93:7	526

TABLE II. MONOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{16}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II (63) I:II = 91:9	526
C$_{19}$	Bu$_3$SnH, AIBN, PhMe, 60°	(60-70)	527
C$_{28}$	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, t-BuOH, 80°	(95)	72

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH, 80°	(95)	72

F. 8-Membered Rings

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{14}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(59)	526
	C$_6$H$_6$, *hv*	(49)	528
C$_{15}$	(PhS)$_2$, *hv*	(15)	440

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

G. Macrocycles

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_6$	Bu$_3$Sn$_2$, C$_6$H$_6$, *hv*	(66)	420
C$_9$ R = Me, Bu, CH$_2$OAc	Pr$_3$B, O$_2$	(30)	529
C$_{18}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		95

X	Z	n
CH$_2$	CO$_2$Et	10
CH$_2$	CONEt$_2$	9
CH$_2$		9
CH$_2$	"	10
O	CO$_2$Et	11

I + II	I:II
(57)	>98:<2
(40-45)	10:1
(40-45)	14:1:1:1
(40-45)	13:1:1:1
(40-45)	2.5:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{19}$

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

$$\begin{array}{c} \underline{n} \\ 16 \ (63\text{-}67) \\ 20 \ (68\text{-}76) \end{array}$$

77

C$_{21}$

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

(68)

530

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

$$\begin{array}{cc} \underline{R} & \\ H & (30) \\ Me & (74) \end{array}$$

530

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

(74)

530

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{28}$

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

531

$$\begin{array}{ccc} \underline{n} & & \text{Ring size} \\ 5 & (54) & 10 \\ 6 & (46) & 11 \\ 7 & (61) & 12 \\ 8 & (50) & 13 \\ 9 & (80) & 14 \\ 10 & (72) & 15 \end{array}$$

C$_{32}$

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

(54)

532

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{42}$

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°
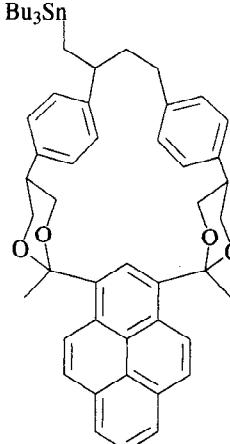
(74) 532

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
		A. (3+ n) -Membered Rings	

C_7

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

I + II (63) **I:II** = 5:1

533

C_{19}

TsI, CH$_2$Cl$_2$, 40°

 (80) *ratio* = 1:1

139

C_{20}

TsI, CH$_2$Cl$_2$, 40°
Me$_2$NSO$_2$Cl, CH$_2$Cl$_2$, 50-60°

R = Ts (76)
R = Me$_2$NSO$_2$ (72)

139

TsI, CH$_2$Cl$_2$, 40°

 (77) *ratio* = 1:1

139

C_{21}

TsI, CH$_2$Cl$_2$, 40°
Me$_2$NSO$_2$Cl, CH$_2$Cl$_2$, 50-60°

R = Ts (78)
R = Me$_2$NSO$_2$ (68)

139

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

B. (4 + 5)-Membered Rings

C_7

R^1	R^2	R^3
Me	Me	H
H	H	Me

p-Xylene, *h*v, heat

(100)
(43)

534

C_8

Bu₃SnH, AIBN,
C_6H_6, 80°

(85)

535

C. (5 + 5)-Membered Rings

C_8

Sn cathode, *i*-PrOH,
Et₄NOTs, 25°

(68)

536

A. Carbon cathode,
   MeOH, dioxane,
   Et₄NOTs
B. HMPA, *h*v

A. (69)

B. (67)

246

180

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_9

Hg cathode,
DMF, rt

(41)

225

NaC₁₀H₈

(53)

225

Bu₃SnH, AIBN,
C_6H_6, 80°

(60)

537

Carbon cathode, MeOH,
dioxane, Et₄NOTs

(87)

246

HMPA, *h*v

(81)

180

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI$_2$, THF, HMPA		178

n	m		ratio
1	1	(90)	>150:1
2	1	(92)	93:5:2
1	2	(89)	>150:1
2	2	(85)	2:1:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_5$H$_{12}$, reflux	**I** + **II** **I + II** (50) **I:II** = 8.1:1	538
	(Bu$_3$Sn)$_2$ (cat.), C$_6$H$_6$, sunlamp	(40) 1.5:1 ratio of isomers	213

C$_{10}$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	R H (47) TMS (78)	537

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° 2. NaOH, EtOH	**I** + **II** **I + II** (95) **I:II** = 7:3	117, 116
			225
	Hg cathode, DMF, rt NaC$_{10}$H$_8$	(37) (23)	
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II**	539

R	I + II
H	(45)
MOM	(64)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Cp$_2$TiCl 2. I$_2$	(63)	172

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn, TMSCl, 2,6-lutidine, THF, reflux	(82)	540
C$_{11}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II** **I + II** (61) **I:II** = 81:19 (R = H) **I + II** (64) **I:II** = 20:1 (R = Me)	208
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	$\dfrac{R}{H}$ (83) Me (63)	291
	Zn, TMSCl, THF, 2,6-lutidine, reflux	(77)	540
	HMPA, *hv*	(80)	180
	Et$_3$N, MeCN, *hv*	(86)	180

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(PhS)$_2$, AIBN, C$_6$H$_6$, *hv*, 80°	(70) 3:2	541
	Zn, TMSCl, THF, 2,6-lutidine, reflux	**I + II** (82) **I:II** = 83:17	540
	HMPA, *hv*	**I + II** (90) **I:II** = 97:3	180
	Hg cathode, Et$_4$NOTs, MeCN, H$_2$O, 25°	**I** + **II** **I + II** (79) **I:II** = 92:8	365
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **III** **I + III** (69) **I:III** = 75:24	115
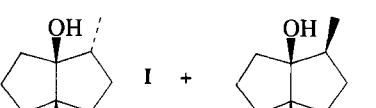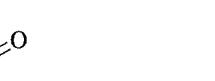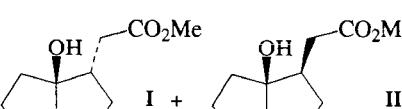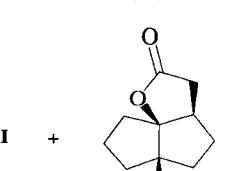
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
$\dfrac{X}{\begin{array}{c}H_2\\O\end{array}}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	$\begin{array}{l}R\\\hline (CH_2)_2SH \quad (66)\\ H \text{ (after ester cleavage)} (93)\end{array}$	117
	Mn(OAc)$_3$, EtOH	$\begin{array}{cc}R^1 & R^2\\\hline Me & H \quad (35)\\ H & Me \quad (32)\end{array}$	296
	SmI$_2$, Me$_2$CO, THF, -30° to rt	(66)	179
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(90)	17

C$_{12}$

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° 2. TBAF, THF	(81)	342
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	$\mathbf{I}$ + $\mathbf{II}$ $\mathbf{I} + \mathbf{II}$ (44) $\mathbf{I:II} = 3:1$	542
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(52) ratio = 1.3:1	96
	Mn(OAc)$_3$, EtOH, H$^+$	(54)	543

C$_{13}$

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
trans/cis 6:1	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + **II** **I + II** (56)	544
	Bu₃SnH, AIBN, C₆H₆, 80°	(75) Z:E = 4:1	537
	Bu₃SnH, AIBN, C₆H₆, 80°	R: H (71), Me (73)	545
	Zn, TMSCl, THF, 2,6-lutidine, reflux	(76)	540
C₁₄	Ph₃SnH, AIBN, C₆H₆, 80°	(64)	19
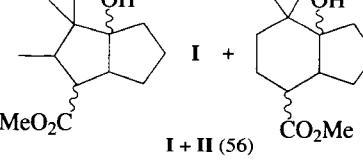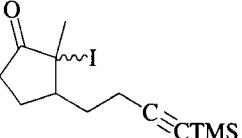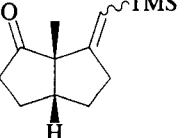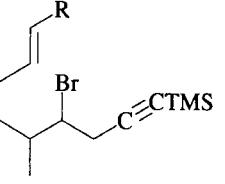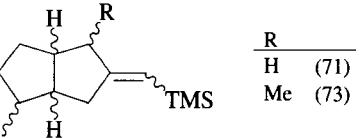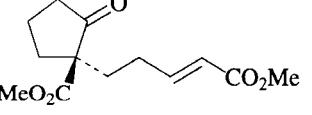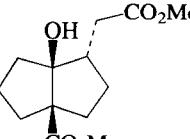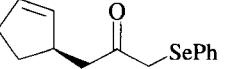
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Mn(OAc)₃, Cu(OAc)₂, AcOH	R: OMe (75), OEt (100)	211
	Bu₃SnH, AIBN, C₆H₆, 80°	(90)	546
	(Bu₃Sn)₂, C₆H₆, hv, 25°	(81)	323
	PhMe, 110°	(52)	547
C₁₅	Bu₃SnH, Et₃B, air, C₆H₁₄, rt, 3 h	(76)	548
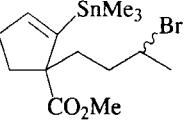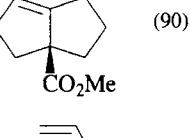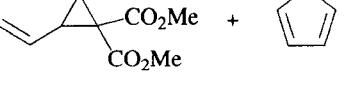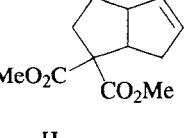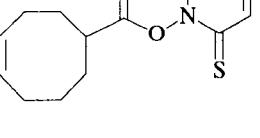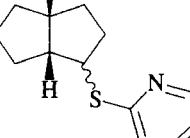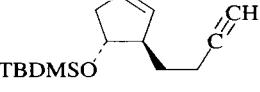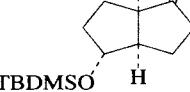
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C. (5 + 5)-Membered Rings

C_15

| | Me₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH | (54) 6:1 *ratio* | 330 |

C_16

| | Ph₃SnH, AIBN, C₆H₆, 80° | (89) | 549 |

| | Ph₃SnH, AIBN, C₆H₆, 80° | | 102 |

Ring fusion	Isomer ratio	
cis	80:20	(93)
cis	90:10	(83)
cis and *trans*	72:14:11:2	(71)

n = 1, 2, 3

| | Bu₃SnH, AIBN, C₆H₆, 80° | (75) | 544 |

four isomers 5.3:3:2.5:1

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°		340

X	Y	
SO₂Ph	Br	(61)
SO₂Bu-*t*	Br	(74)
CO₂Me	PhSe	(80)

| | 1. (Bu₃Sn)₂, C₆H₆, *hv* 2. Bu₃SnH, AIBN | I + II I + II (73) I:II = 89:11 | 256 |

| | Bu₃SnH, AIBN, C₆H₆, 80° | (60) *cis:trans* = 1:1.2 | 549a |

| | Bu₃SnH, AIBN, C₆H₆, 80° | I + II + III   I + II + III (75) I:II:III = 45:20:35 | 539 |

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	Bu₃SnH, AIBN, C_6H_6, 80°	(49)	80
	Mn(OAc)₃, Cu(OAc)₂, AcOH	I + II **I** **II** I + II (49) I:II = 8:1	211
C_{18}			
	1. Ph₃SnH, AIBN, C_6H_6, 80° 2. H₂O₂	(51)	215 550
	Bu₃SnH, AIBN	(85)	551
	1. Bu₃SnH, AIBN, C_6H_6, 80° 2. AcOH, MeOH	(90)	341

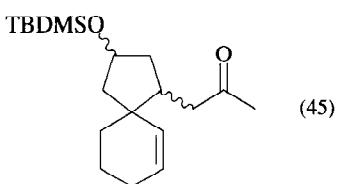TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C_6H_6, 80°	(80)	552
C_{19}			
	Bu₃SnH, AIBN, C_6H_6, 80°	(95) 1:1 *ratio*	553
	Bu₃SnH, AIBN, C_6H_6, 80°	(80)	553
C_{20}			
	*h*ν	(74)	554

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}	TsCl, BPO, PhMe	(49)	351
C_{22} $\dfrac{R}{\text{CN}}$ SO_2Ph	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(89) (30)	353, 354, 354a
	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(68)	352
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	$\dfrac{R}{\text{H} \ (62)}$ Me (71)	199
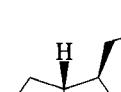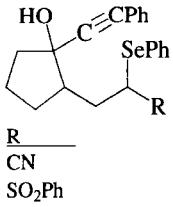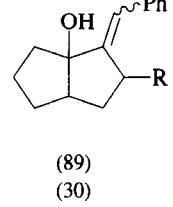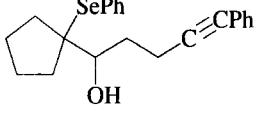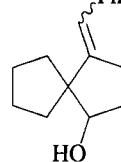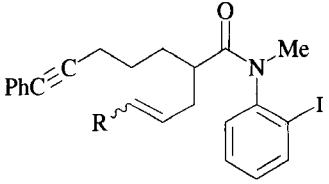
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(82)	555
C_{29}	VCl$_3$(THF)$_3$, Zn, CH$_2$Cl$_2$, 0°	(71) α:β = 4.2:1	252
C_{44}	Bu$_3$SnH, (*t*-BuO)$_2$, C$_6$H$_6$, 65°, 4 h	(86) Z:E = 1:1	556
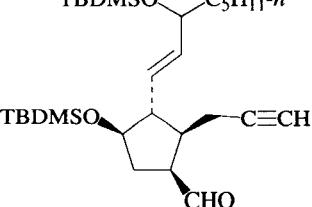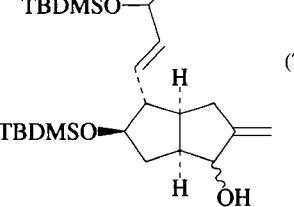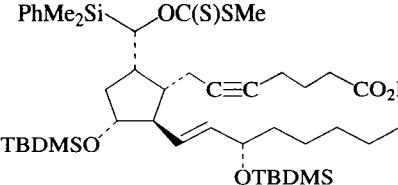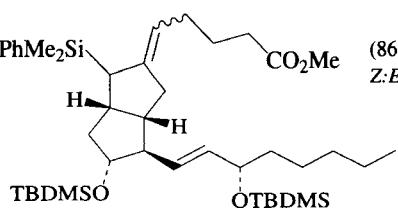
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

D. (5 + 6)-Membered Rings

C₈

	Bu₃SnH, AIBN, C₆H₆, 80°	(80)	557, 558

C₉

	Mn(OAc)₃, Cu(OAc)₂	(38)	192
	SmI₂, THF, HMPA	(88) diastereomeric ratio = 17:1	178
	Zn, TMSCl, THF, 2,6-lutidine, reflux	(78)	540
	Sn cathode, *i*-PrOH, Et₄NOTs, 25°	(63)	536

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

	Sn cathode, *i*-PrOH, Et₄NOTs, 25°	(60)	536

C₁₀

	HMPA, *h*v	(76)	180
	Carbon cathode, MeOH, dioxane, Et₄NOTs	(65) one isomer; stereochemistry not determined	246
	1. Hg(OAc)₂, THF, H₂O, CaO, rt, 1 h 2. NaBH₄, MeOH, 0°	R¹ R² : Me OH (35) OH Me (35)	559

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(69)	560, 561
	Bu₃SnH, AIBN, C₆H₆, 80°	—SnBu₃ (76)	118
	1. Bu₃SnH, AIBN, C₆H₆, 80° 2. Ester cleavage	**I** + **II** **I** + **II** (81) **I:II** = 2:1	117
	Mn(OAc)₃, Cu(OAc)₂	(48)	192

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. MgI₂ 2. Bu₃SnH, AIBN, C₆H₆, 80°	(40) + (40)	238
	Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 110°, 3 d	(63)	332
	Bu₃SnH, AIBN, C₆H₆, 80°	R = H (83) R = Me (85)	562
	Bu₃SnH, AIBN, C₆H₆, 80°	(>88)	563
	Bu₃SnH, AIBN, C₆H₆, 80°	(56) + (16)	97

$$\text{NHOMe}$$

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R Me Ph	(Bu₃Sn)₂, C₆H₆, *hν*	(66) 2.5:1 (75) 6.2:1	213
C₁₁	Hg cathode, DMF, rt	(43)	225
	Bu₃SnH, AIBN, PhMe, 80°	(76)	564
R¹ R² CO₂Me H Me H H CO₂Me H Me	Bu₃SnH, AIBN, C₆H₆, 80°	(90-98) *cis:trans* 1.4:1 2.1:1 0.14:1 0.27:1	565

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 70°	(82) 1 : 1 mixture of isomers	566
	Bu₃SnH, AIBN, C₆H₆, 65°	(50)	567
	1. DTBP, Cl₃SiH, C₆H₆, 140°, sealed tube 2. H₃O⁺	(68)	568
R Cl OPO(OEt)₂ Me	Mn(OAc)₃, Cu(OAc)₂, AcOH, 25°	(—) (72) (77)	569
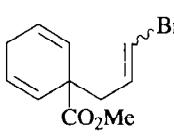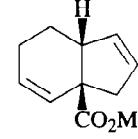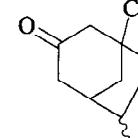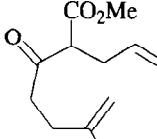
where the formulas are CO_2Me, CO_2Et, $(Bu_3Sn)_2$, Bu_3SnH, $Mn(OAc)_3$, $Cu(OAc)_2$, Cl_3SiH, H_3O^+.

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R X H I Me Br	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II I:II (81) 100:0 (65) 42:58	570
	Bu₃SnH, AIBN, C₆H₆, 80°	(90) α:β = 45:55	570
	Bu₃SnH, AIBN, C₆H₆, 80°	R H (96) Me (85) OMe (92)	570, 567
	Mn(OAc)₃, EtOH, H⁺	(51)	543
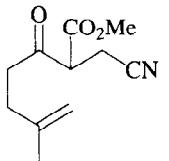
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
X = Br X = I	Bu₃SnH, AIBN, C₆H₆, 80°	(91) (93)	562
	Bu₃SnH, AIBN, C₆H₆, 80°	R H (93) Me (59)	293
	Bu₃SnH, AIBN, C₆H₆, 80°	(70) + (10)	571
R H Me	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I II (31) (9) (26) (15)	572

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + **II** **I + II** (71) **I:II** = 2:1	24
	HMPA, *hv* Et₃N, MeCN, *hv*	**I** + **II** **I + II** (65) **I:II** = 90:10 **I + II** (74) **I:II** = 77:23	573
	DTBP, Et₃SiH, C₆H₆, 140°	(71)	568
	(Bu₃Sn)₂, C₆H₆, *hv*	(40)	213

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
  R Me OPO(OEt)₂ OCH₂O(CH₂)₂OMe H	Mn(OAc)₃, Cu(OAc)₂, AcOH	**I** + **II** **I** **II** (86) (—) (77) (—) (52) (—) (48) (18)	574, 296, 196
C₁₂ 	Bu₃SnH, AIBN, C₆H₆, 80°	 R H (79) Me (45)	291, 208
 cis:trans = 1.5:1	Bu₃SnH, AIBN, C₆H₆, 80°	+ 4 isomers 14:2:2:1 (55)	

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

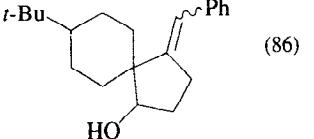| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI$_2$, THF, DMPU	$\dfrac{R}{CO_2Me}$ (77) H (36)	203
R: Me, OMe	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I : II α–R : II β-R Me (80) 32 : 14 : 54 OMe (89) 48 : 13 : 39	570, 567
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°, hv	(70)	24
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (80) I:II = 1:1	575
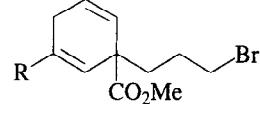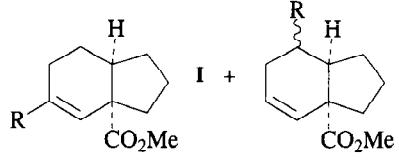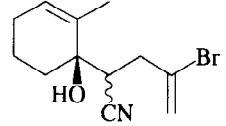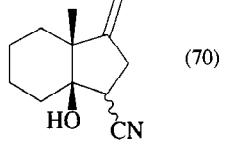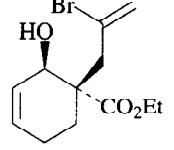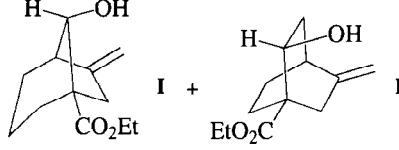
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et$_3$SiH, C$_6$H$_6$, 140°, sealed tube	(68)	568
	(Me$_3$Sn)$_2$, AIBN, C$_6$H$_6$, 80°	(65)	18
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (88) I:II 58:42	115
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(70)	118
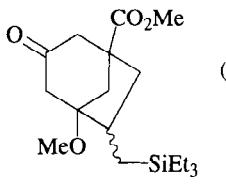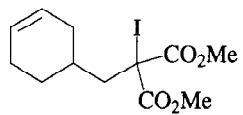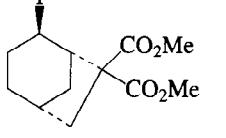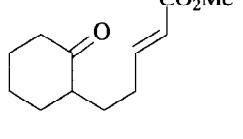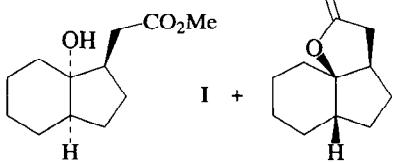
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
		I + II	364
X = H X = Br	Mn(OAc)$_3$, LiCl (Bu$_3$Sn)$_2$, (10%), $h\nu$	Y = Cl I + II (50) I:II = 2:1 Y = Br I + II (74) I:II = 2:1	
X = H	Mn(OAc)$_3$, Cu(OAc)$_2$	(86)	
	(Bu$_3$Sn)$_2$, C$_6$H$_6$, $h\nu$	(52)	213
	Hg cathode, Et$_4$NOTs	(73) *trans:cis* = 1.7:1	365

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Hg cathode, Et$_4$NOTs	I + II I + II (74) I:II = 2.5:1	365
  R Me CH$_2$=CH Ph	(Ph$_2$S)$_2$, AIBN, C$_6$H$_6$, 80°, $h\nu$	I + II I + II I:II (73) 3:2 (82) 13:1 (60) 4:1	541
C$_{13}$ E:Z = 1:1 R COPh TBDMS Ms	Bu$_3$SnH, AIBN, PhMe, 110°	I + II I + II I:II (70) 90:10 (83) 90:10 (64) 100:0	370

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R² / R¹ / Br structure R¹ R² R³ H H CO₂Me Me H CO₂Me H OAc H	Bu₃SnH, AIBN, C₆H₆, 80°	bicyclic product with R¹, R², R³ (86) (92) (58)	293
thiocarbonylimidazolide cyclohexane with CN chain	Bu₃SnH, AIBN, C₆H₆, 80°	hydrindanone (67)	38
cyclopropane ketone with C≡CR chain	SmI₂, THF, DMPU	spirocyclic ketone R TMS (79) H (57)	203
cyclopentene with CO₂Et, CN chain	BPO, c-C₆H₁₂, heat	bicyclic product (37) NC CO₂Et	576

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
ketone with CN, CO₂Me chain	Mn(OAc)₃, EtOH, H⁺	bicyclic diketone CO₂Me (57) H ethyl	543
cyclohexene with I, CO₂Me, CO₂Me	Bu₃SnH, AIBN, C₆H₆, 80°	bicyclic CO₂Me, CO₂Me (>76)	18
OMe / MeO dimethoxy cyclohexadiene with Br, CO₂Me	Bu₃SnH, AIBN, C₆H₆, 80°	MeO bicyclic product CO₂Me (60) α:β 26:74	570
ketone with CO₂Me and diene chain	Mn(OAc)₃, Cu(OAc)₂, AcOH	bicyclic ketone CO₂Me (65) + bicyclic ketone CO₂Me (5) 2:1 mixture	574

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. TsNHNH$_2$, THF, 2. ZnCl$_2$, NaCNBH$_3$	 **I + II** (66) **I:II** = 1:3.5	577
	SmI$_2$, THF, DMPU	(36)	203
 $\dfrac{X}{\text{H}}$ Br	Mn(OAc)$_3$, Cu(OAc)$_2$ 1. (Bu$_3$Sn)$_2$, C$_6$H$_6$, *hv* 2. DBU, 120°	 (67) 11:1 mixture (40) single isomer	364
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	X = Br (82) X = I (86)	562

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 Z E	Mn(OAc)$_3$, Cu(OAc)$_2$	**I + II** **I + II** (67) **I:II** = 25:1 **I + II** (46) **I:II** = 2:1	574, 569, 196
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(43)	537
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(73) *Z:E* = 6:1	537
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(90)	578

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₄	Mn(OAc)₃, EtOH, AcOH	(41)	543
	Mn(OAc)₃, Cu(OAc)₂	(41)	579
	Bu₃SnH, AIBN, C₆H₆, 80°	(65) *Z:E* = 5:1	537
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II	96

R
Me
CO₂Me
Ph

I + II	I:II
(68)	2.7:1
(69)	2.7:1
(47)	2.7:1

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(Ph₃P)₃RuCl₂, CCl₄, reflux	(48)	282
	Bu₃SnH, AIBN, C₆H₆, 80°	(58)	33
	Bu₃SnH, AIBN, C₆H₆, 80°	(69)	33
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II	580

R	Y
Ph	CH₂
t-Bu	CH₂
H	CH₂
Ph	O

I + II	*cis:trans*
(29)	87:13
(37)	86:14
(—)	78:22
(55)	70:30

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH		192
C$_{15}$	Li, THF, ultrasound	(84)	581
	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH	R = NEt$_2$ (45) R = (90) 86% de R = (89) 60% de	582

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(Me$_3$Sn)$_2$, AIBN C$_6$H$_6$, *h*v, 6 h Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II** **I** (56) **I + II** (72) **I:II** = 22:1	571
R^1 R^2 —————— Ph H Ph Me *p*-MeC$_6$H$_4$ Me	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 25°	(40) (44) (44)	583, 584
	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(34)	549
+	(Bu$_3$Sn)$_2$, C$_6$H$_6$, *h*v	(80) *E:Z* = 3:1	256

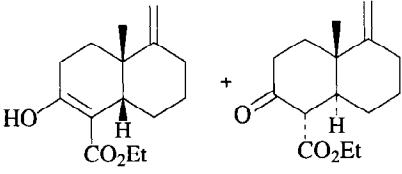TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(cyclohexenyl CH2COCH2SePh)	Ph₃SnH, AIBN, C₆H₆, 80°	(bicyclic ketone) (64)	585, 19
	Bu₃SnH, AIBN, C₆H₆, 80°	(72)	
n-BuC≡C–CH=CH–C≡C–...–CH=CH–CH₂OH	1,4-CHD, C₆H₄Cl₂, 170–230°	(indane CH₂CH₂OH, *n*-Bu) (54)	586
(cyclohexenyl CH2C(R¹)(R²)C(O)SePh)	Bu₃SnH, AIBN, C₆H₆, 80°	(bicyclic R¹, R², ketone)	33

R¹ R²
H   H   (86)
Me H   (68)
Me Me (49)

| (cyclohexenyl CH2CH2C(O)SePh) | Bu₃SnH, AIBN, C₆H₆, 80° | (bicyclic ketone) (86) | 35 |

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO₂C, MeO₂C, I, (allyl) + (methylenecyclohexane)	(Bu₃Sn)₂, C₆H₆, *h*v	(spiro product, I, MeO₂C, CO₂Me) (72)	256
EtO₂C–CH=... (cyclohexane with dithiolane)	Bu₃SnH, AIBN, C₆H₆, 80°	EtO₂C... HS I + EtO₂C... HS II I + II (70) I:II = 2:1	117
(cyclohexenyl CH2CH(OTBDMS)CF2Cl)	Bu₃SnH, AIBN, C₆H₆, 80°	(bicyclic F, F, OTBDMS) I, II I + II (82) I:II = 1:1	288
(aryl C(O)SePh, CH2CH=CH–R)	Bu₃SnH, AIBN, C₆H₆, 80°	(indanone, R)	33, 35

R
H   (81)
CO₂Me (88)

| (cyclohexanone, H, OH, CH2SePh, vinyl, H) | Ph₃SnH, AIBN, C₆H₆, 80° | (bicyclic ketone, H, OH) (58) | 549 |

C₁₆

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

First entry:

R		1 + II	I:II
H	C$_6$H$_6$-d_6	(100)	20:1
H	MeOH-d_6	(100)	2:1
Et	C$_6$H$_6$-d_6	(100)	30:1
Et	MeOH-d_6	(100)	4.3:1

Conditions: $h\nu$ — Ref. 587

Second entry:

Conditions: 1. Hg(OAc)$_2$, MeOH 2. NaBH$_4$ — Product (70) — Ref. 131

Third entry:

Conditions: (PhS)$_2$, AIBN, $h\nu$ — Product (60), diastereomeric ratio = 5:1 — Ref. 314

Fourth entry:

Conditions: Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — Product (75) — Ref. 195

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yiel d(s) (%)	Refs.

First entry (OTBDMS):

Conditions: Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — Ref. 588

R	I + II	I : II
Ph	(68)	100 : 0
OBn	(80)	88 : 12
CH=CH$_2$	(61)	95 : 5
Me	(67)	—

Second entry (SePh):

Conditions: Ph$_3$SnH, AIBN, C$_6$H$_6$, 80° — Ref. 102

n		ring fusion	isomer ratio
1	(93)	cis	80:20
2	(83)	cis	90:10
3	(71)	cis and trans	72:14:11:2

Third entry (C$_{17}$):

Conditions: Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — Product (71) — Ref. 313

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(86) *cis:trans* > 97:3	589
+ (15 equiv.)	Ph₃SnH, AIBN, C₆H₆, 80°	(64)	354
	Ph₃SnH, AIBN, C₆H₆, 80°	(53)	340
	Bu₃SnH, AIBN, PhMe, 110°	(47) + (25)	590

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph₃SnH, AIBN, C₆H₆, 80°	I + II	549
	Ph₃SnH, AIBN, C₆H₆, 80°	(51)	549
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II	80
	DCA, MeCN, *hv*	(59)	372

For the first product (I + II) of the fifth table row:

	I + II	I:II
β-OH	(69)	1.4:1
α-OH	(81)	1:1.6

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Bu₃SnH, PhCl, -40° 2. O₂, -40 to 0° 3. Ph₃P, *i*-PrOH, 0° 4. PyTs, MeOH, 23°	**I** + **II** (60-90) **I:II** = 2:1	591, 592
	1. (Bu₃Sn)₂, C₆H₆, *hv* 2. Bu₃SnH, AIBN, 80°	**I** + **II**	256
C₁₈	Ph₃SnH, Et₃B, air	(92)	593
	1. Ph₃SnH, Et₃B, air 2. PCC	(58)	594

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, Et₃B, -30°	(97)	595
R Ph *t*-Bu	Bu₃SnH, AIBN	**I** + **II** **I + II** **I:II** (21) 31:63 (—) 22:60	580
R Y H CO₂Me H CN H Ph Me CO₂Me	Bu₃SnH, AIBN, C₆H₆, 80°	(63) (68) (52) (60)	209

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
TBDMSO, I, CO_2Me	Bu_3SnH, AIBN, C_6H_6, 80°	CO_2Me / OTBDMS (61-78)	332
TBDMSO, Br, CO_2Me	Bu_3SnH, Et_3B, -30°	H, CO_2Me / TBDMSO (87) *trans:cis* 95:5	595
EtO_2C, EtO_2C +	(BuS)$_2$, *hv*, 25°	EtO_2C, EtO_2C (77)	328
Ts, Br	Bu_3SnH, AIBN, C_6H_6, 80°	Ts (61)	112
NOBn, C≡CH, CO_2Me	1. Bu_3SnH, AIBN, C_6H_6, 80° 2. AcOH, MeOH	BnO, NH, CO_2Me (82)	341

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
OTMS, SePh	Bu_3SnH, AIBN, C_6H_6, 80°	OH (51) + OH (16) *trans:cis* = 2:1	80
TBDMSO, I, O	Bu_3SnH, AIBN, C_6H_6, heat	TBDMSO, O (45)	332
$PhSO_2$ +	(BuS)$_2$, *hv*	$PhSO_2$ (59)	34
CO_2Me, PhSe, CO_2Me	Ph_3SnH, AIBN, C_6H_6, 80°	CO_2Me, H, H, CO_2Me (80)	112

C_{19}

C_{20}

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{21}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(71)	202, 596
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(81)	202, 596
(EtO$_2$C, CO$_2$Et; R/Y: H SO$_2$Ph, Me SO$_2$Bu-*t*)	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(93) (98)	340
CO$_2$Me ... SePh	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	R: Ph (96), Pr (82)	597
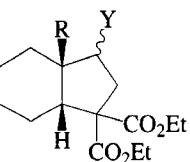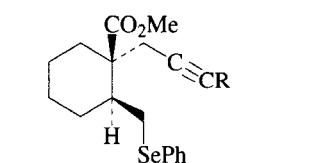
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{22}$ (R = D-Camphorsultam)	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 25°	(49) + (17)	598
C$_{23}$ PhSe ... CPh	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(77)	209
PhSe ... CPh	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(72)	209
PhSe OH ... CPh	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(75)	585, 352
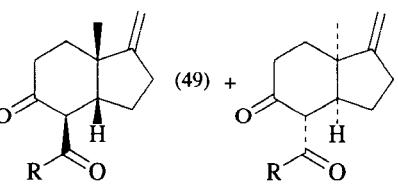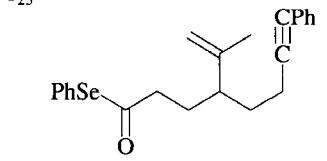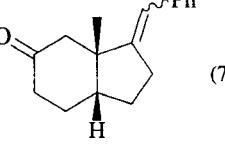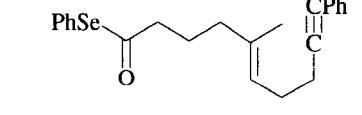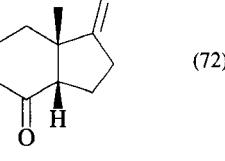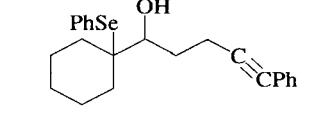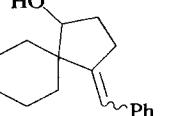
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Mn(OAc)_3$, $Cu(OAc)_2$,		584
		R = (90) 86% de	
		R = (89) 60% de	
		R = (87) 23% de	
	Ph_3SnH, AIBN, C_6H_6, 80°	CN (94)	354, 354a
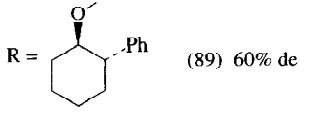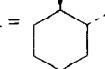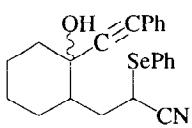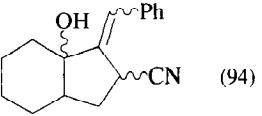
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24}	**A.** TsCl, BPO, PhMe **B.** $(Bu_3Sn)_2$, C_6H_6, $h\nu$, 4 h		504, 351
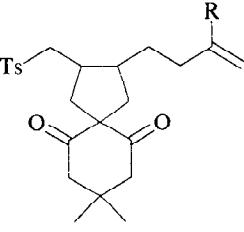
R		Yield	Ratio
CO_2Et	**A**	(63)	6.7:1
Cl	**B**	(81)	7.5:1
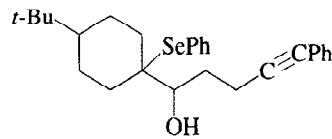
C_{27}	Ph_3SnH, AIBN, C_6H_6, 80°	(86)	352
C_{28}	C_7H_{16}, $h\nu$, 25°	(73)	350
	Ph_3SnH, AIBN, C_6H_6, 80°	SO_2Ph (55)	353
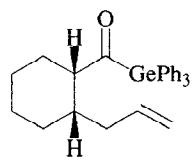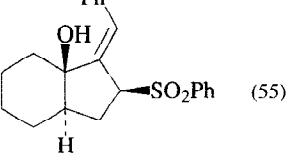
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	C_7H_{16}, $h\nu$, 25°	(75)	350
C_{30}	Hg cathode, MeCN, n-Bu$_4$NBr, CH$_2$(CO$_2$Me)$_2$	(90)	310
	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(78)	597
C_{32}	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(65)	353

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	E. (5 +7)-Membered Rings		
C_9	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(10) + (70)	557, 558
C_{10}		**I**	599
	SmI$_2$, MeOH	(68)	
	Bu$_3$SnH, AIBN	(60)	
	SmI$_2$, t-BuOH, HMPA	**I** (40)	599
	Bu$_3$SnH, AIBN	**I** (56)	
	Sn cathode, i-PrOH, Et$_4$NOTs, 25°	(76) 2:1 mixture of isomers	536
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** **II** **III**	600, 601

I + II + III (84) **I:II:III** = 16:4:1

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + **II** + **III** **I** + **II** + **III** (—) **I:II:III** = 6.2:1:2	600, 601
	Hg(OAc)₂, CaO, NaBH₄, MeOH	MeO⌇ (70) 1:1 ratio	602
	Mn(OAc)₃, Cu(OAc)₂	(33) Δ3:Δ4 = 1:1	192
C₁₁	IBDA, I₂, *h*ν	$\dfrac{R}{\text{Me (78)}}$ H (40)	603

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Mn(pic)₃[a], Bu₃SnH DMF, 0°	(75)	103
C₁₃	Mn(OAc)₃, Cu(OAc)₂	(68)	196, 194
C₁₄	Bu₃SnH, AIBN, C₆H₆, 80°	(65)	38
	Mn(pic)₃[a], Bu₃SnH DMF, 0°	(66)	103

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{15}

	Na, MeOH	**I + II** (71) **I:II** = 1:1	604
	HMPA, *hv*	**I + II** (—) **I:II** = 100:0	
	TiCl$_4$, Mg/Hg	**I + II** (—) **I:II** = 0:100	

C_{16}

| | Ph$_3$SnH, AIBN | (72) | 585, 19 |

| | Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° | (52) | 605 |

C_{18}

| | Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° | (80) ring fusion *cis:trans* 44:56 | 589 |

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

| | Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° | (58) ratio = 1:1 | 96 |

C_{22}

| | | **I** + **II** | 606 |

		I	**II**	
	SnCl$_4$, THF, -70°, 2 h	(57)	(6)	
	Na, C$_{10}$H$_8$, THF, 25°, 3 min	(56)	(0)	
	SmI$_2$, MeOH, THF, 25°, 5 min	(51)	(13)	

| | Ph$_3$SnH, AIBN, C$_6$H$_6$, 80° | (79) | 597 |

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{24}$	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(91)	354, 354a, 353
C$_{25}$	Mn(pic)$_3$^{a}, DMF, 0°	(81)	103

F. (5 + (n+7))-Membered Rings

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{11}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(54) + (19)	600, 601
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		607

R	
H	(18)
CO$_2$Et	(22)
OSiEt$_3$	(51)

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 X *cis*-OH (70) O (79)	105
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II	105

X	
H$_2$	
cis-OH	
trans-OH	
O	

		I	II
	I + II	*trans:cis:trans:cis*	
H$_2$	(—)	73:11:11:5	
cis-OH	(65)	>99:<1:0:0	
trans-OH	(70)	50:10:20:20	
O	(65)	95:5:0:0	

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II	104

I + II (51) **I:II** = 73:27

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	R efs.
C_12	Bu_3SnH, AIBN, C_6H_6, 80°	$\dfrac{R}{}$ Me (20); H (50)	603
C_14	Hg cathode, DMF, Bu_4N^+BF_4^-, DMP^+BF_4^-	(29) + (20)	608
A + B	Bu_3SnH, AIBN, C_6H_6, 80°	I + II I + II cis:trans A (55) 6.4:1 B (81) 0.63:1	78
C_17	Bu_3SnH, AIBN, C_6H_6, 80°	(79)	33

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_19	Bu_3SnH, AIBN, C_6H_6, 80°	(85)	589
C_22	Ph_3SnH, AIBN, C_6H_6, 80°	(77)	597
C_26	Mn(pic)_3^a, DMF, 0°	(63)	103

G. *(6 + 6)-Membered Rings*
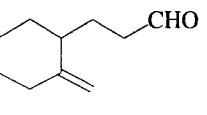
| C_10 | Mg, TMSCl, THF, I_2, rt, 60 h | (36) + (24) | 609 |
| | SmI_2, THF, HMPA | (66)   diastereomeric ratio 17:1 | 178 |
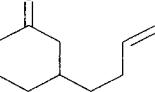
TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}	Sn cathode, *i*-PrOH, Et$_4$NOTs, 25°	I + II I + II (60) I:II = 2:1	536
	SmI$_2$, THF, HMPA	(85) diastereomeric ratio 2:1:1	178
	A. Hg cathode, DMF, Bu$_4$N$^+$BF$_4^-$, DMP$^+$BF$_4^-$ B. Sn cathode, *i*-PrOH, Et$_4$NOTs, rt	A R = Me (80) B R = Me (70) B R = Et (55)	244 610 610
	Sn cathode, *i*-PrOH, Et$_4$NOTs, rt	R 7-Me (56) 6-Me (19) 5-Me (29) 7-OMe (73) 8-OMe (17) 7-Cl (63)	610

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} R CN CO$_2$Pr-*i*	Sn cathode, *i*-PrOH, Et$_4$NOTs, rt	I + II I II (32) (24) (13) (34)	610
R^1 R^2 R^3 Me H H H Me H H H Me	Sn cathode, *i*-PrOH, Et$_4$NOTs, rt	(60) (68) (60)	610
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(76)	570
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (79) I:II = 85:15	570

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			573
	HMPA, *hv* Et₃N, MeCN, *hv*	(55) (68)	
	Mn(OAc)₃, Cu(OAc)₂	(46)	363
	Mn(OAc)₃, Cu(OAc)₂, AcOH, LiCl	(37)	363
C₁₃ $\dfrac{R}{\text{H}}$ *n*-Bu	1. Bu₃SnH, AIBN, C₆H₆, 80° 2. HCl, MeOH	 (72) (74) 1:1 mixture	30

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(93)	578
	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + **II**	611
C₁₄	Pb(OAc)₄, MeCN	(80)	612
	Bu₃SnH, AIBN, C₆H₆, 80°	(84)	613
	Bu₃SnH, AIBN, C₆H₆, 80°	(40) *Z:E* = 9:1	537

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{15}$

TsNa, Cu(OAc)$_2$,
AcOH, 90°
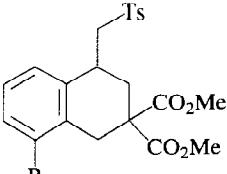
R	
H	(72)
CN	(82)

280
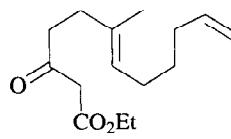
Mn(OAc)$_3$,
Cu(OAc)$_2$,
AcOH

(12)   (43)

614

C$_{16}$
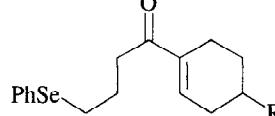
Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°
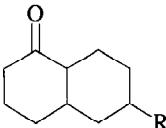
R	
H	(82)
t-Bu	(83)

605
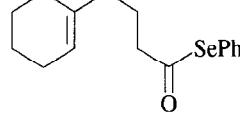
Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°

(82)   *cis:trans* = 38:62

35,
33

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{17}$

Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°

MeO$_2$C   (48)

202

Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°

R	
H	(76)
CO$_2$Me	(84)

35,
33
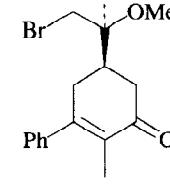
Bu$_3$SnH, AIBN,
PhMe

I + II
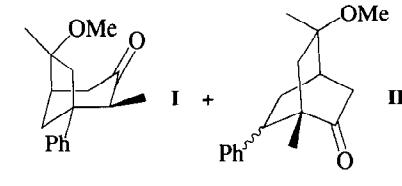
I + II (80) I:II = 1:1.5

590

C$_{18}$
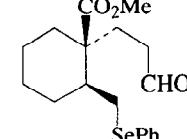
1. Ph$_3$SnH, Et$_3$B, air
2. PCC

(73)

594

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(PhSe–CO– ... triene structure)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(bicyclic ketone isomers I, II and III, IV with substituents R^1, R^2) I: R^1 = H, R^2 = Me II: R^1 = Me, R^2 = H III: R^1 = Me, R^2 = H IV: R^1 = H, R^2 = Me I + II + III + IV (71) I:II:III:IV = 57:11:11:21	209
C$_{19}$ (aryl–CH$_2$CH$_2$CO–SePh, CH=CH–CO$_2$Me)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(tetralone with CH$_2$CO$_2$Me) (83)	35, 33
(O SePh aryl structure, CO$_2$Me)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(tetralone, CO$_2$Me) (37) + (indane, CO$_2$Me) (42)	35
C$_{20}$ (cyclohexanone, CO$_2$Me, CO$_2$Me, SPh)	Bu$_3$SnH, AIBN	(decalin, CO$_2$Me, CO$_2$Me) (85)	615

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{21}$ (S=C(Im)O cyclohexyl, C≡CPh)	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	(=CHPh decalin) (79)	38
C$_{22}$ (aryl–CH$_2$CH$_2$CO–SePh, CO$_2$Et, N–OMe)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(tetralone, CH$_2$–C(=N–OMe)CO$_2$Et) (62)	33
C$_{23}$ (PhCH$_2$CH$_2$–C(Me)(CO–SR)–CH$_2$–Co(dmgH)$_2$py)	C$_6$H$_6$, $h\nu$	(tetralin, CO–SR) R = Et (81) R = t-Bu (86)	403
C$_{24}$ (PhSe–CO– ... C≡CPh)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(=CHPh decalone) (82)	209
C$_{28}$ (methylenecyclohexane, CO$_2$Me, TBDPSO, Br)	Bu$_3$SnH, AIBN, PhMe, heat, 2 h	(decalin, CO$_2$Me, OTBDPS) (86) *cis:trans* = 1:7	613

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

H. ((n+6) + (n+6))-Membered Rings

C_{11}

	AIBN	**I** + **II**	616

		I + II	**I:II**
cis	Bu₃SnH, 80°	(99)	2.4:1
cis	(TMS)₃SiH, 80°	(100)	4.0:1
cis	Bu₃SnH, 145°	(100)	4.1:1
trans	Bu₃SnH, 80°	(82)	0.2:1
trans	Bu₃SnH, 145°	(94)	0.4:1
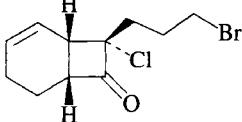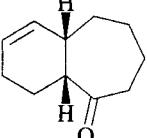
	Bu₃SnH, AIBN, C₆H₆, 80°	(39)	600, 601
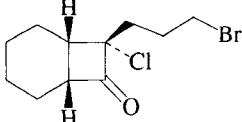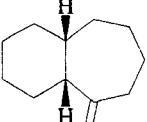
	Bu₃SnH, AIBN, C₆H₆, 80°	(63)	600, 601

C_{12}
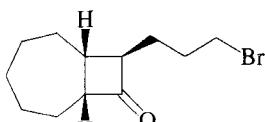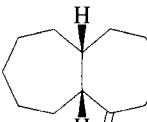
	Bu₃SnH, AIBN, C₆H₆, 80°	(6 4)	600, 601

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{13}

	Mn(OAc)₃, Cu(OAc)₂	**I** + **II**	192

I + II (35) **I:II** = 1:1.1

	NaC₁₀H₈	(28)	225
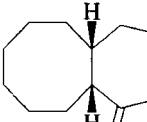
	Bu₃SnH, AIBN, C₆H₆, 80°	(43)	600, 601

C_{15}
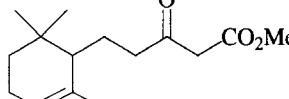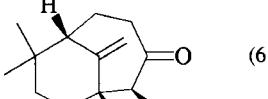
	Mn(OAc)₃, Cu(OAc)₂, AcOH, 25°	(61)	617, 618

C_{17}
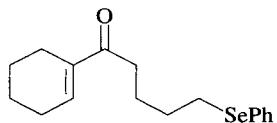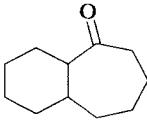
	Bu₃SnH, AIBN, C₆H₆, 80°	(76)	605

TABLE III. BICYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(82)	605
C$_{18}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	$\begin{array}{ll} \text{R} \\ \hline \text{H} & (74) \\ \text{CO}_2\text{Me} & (92) \end{array}$	35, 33
C$_{19}$	1. Ph$_3$SnH, Et$_3$B, air 2. PCC	$\begin{array}{ll} \text{n} \\ \hline 1 & (80) \\ 2 & (77) \end{array}$	617, 618
C$_{20}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(71)	35, 33
C$_{21}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(80)	615

[a] Mn(pic)$_3$ = Manganese(III) tris(2-pyridinecarboxylate).

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

A. (3+n)-Membered Rings

C_8

Mn(OAc)₃,
Cu(OAc)₂,
AcOH, 25°

I + II (62) I:II = 9.3:1

491

C_5H_{12}, *hv*

I + II + III

-70°   I + II + III (65) I:II:III = 98:2:0
80°   I + II + III (85) I:II:III = 36:3:61

619

C_9

620

TiCl₃, AcOH, H₂O, -5°   (55)
MeOH, *hv*   (18)

C_{14}

hv   (51)   528

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{17}

R^2Me_2Si ... Br, R^1, O, allyl

R^1	R^2
Me	Ph
Ph	Mc
C_6H_{13}	Me

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

R^2Me_2Si ... R^1 ... O (cyclopropane-fused tetrahydrofuran)

(58)
(54)
(48)

621

B. (4+5)-Membered Rings

C_8

(β-lactam with vinyl and 2-bromoallyl, H)

Bu$_3$SnH, AIBN

I + **II**

C$_6$H$_6$, 80°   **II** (50)
C$_6$H$_6$, *h*v, 25°   **I** (58)

622, 623

C_9

(β-lactam with methyl, vinyl and 2-bromoallyl)

Bu$_3$SnH, AIBN

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

I	**II**	**III**
(59)	(3)	(30)
(58)	(10)	(10)

C$_6$H$_6$, 80°
C$_6$H$_6$, *h*v, 25°

622, 623

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

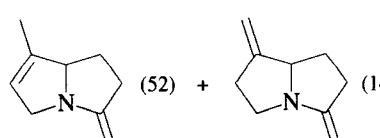| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{18}

(β-lactam with C≡CPh and CHCl, *t*-BuO$_2$C)

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

I + **II**   (CO_2Bu-*t*), (=CHPh)

I + **II** (66) **I:II** = 2:1

624

(β-lactam with CH=CHPh and CHCl, *t*-BuO$_2$C)

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

I + **II**   (CO_2Bu-*t*), (CH$_2$Ph)

I + **II** (62) **I:II** = 1.1:1

625

C_{19}

(β-lactam with SePh and CH$_2$CH=CHPh)

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

I + **II**

I + **II** (80) **I:II** = 1.8:1

625

C_{27}

MeO, Ph (CH=CHPh), dithiane, dioxolane

Bu$_3$SnH, AIBN, PhMe, 90°

MeO, H, Ph (CH$_2$Ph), S-propyl

(68)

626

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{33}$	Bu$_3$SnH, AIBN, PhMe, 90°	(70)	626

C. (4+6)-Membered Rings

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_8$	C$_6$H$_6$, *h*v	(44)	164
C$_{12}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(50)	625
	Na$_2$S$_2$O$_8$, CuCl$_2$•2 H$_2$O, H$_2$O, 90°, 5 h	(60)	627

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

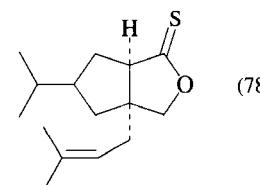| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{15}$ R SPh SePh	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 (43) (59)	628, 629
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(55)	630
C$_{17}$ R^1 R^2 Et Me CH$_2$CH(OTBDMS)Me Me CH$_2$CH(OTBDMS)Me Bn	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(50-60) ca. 2:1	629, 631
C$_{18}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 I + II (64) I:II = 1:1.3	632

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = COCH₂COPh	Fe(ClO₄)₃, Ac₂O, MeCN, 0-5°	 **I + II** (42) **I:II** = 80:20	633
	Fe(NO₃)₃•9H₂O, Ac₂O, MeCN, 0°, 3 h	**I + II** (49)	634
C₂₅ 	Bu₃SnH, AIBN, PhMe, 90°	 **I, II** (—) α:β = 4:1	635

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

D. (4+7)-Membered Rings

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₇ R Cl SePh SPh	Bu₃SnH, AIBN, C₆H₆, 80°	 (57) (38) (56)	636, 637
C₉ 	Bu₃SnH, AIBN, C₆H₆, 80°	(77)	623
C₁₂ 	Bu₃SnH, AIBN, C₆H₆, 80°	(49)	636
 R H CO₂Me Ph	Bu₃SnH, AIBN, C₆H₆, 80°	 **I** **II** (47) (—) (4) (68) (—) (68)	638

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

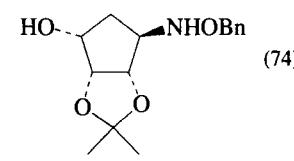| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

E. (5+5)-Membered Rings

C₆

A. (TMS)₃SiH, Et₃B, 25°
B. (TMS)₃SiH, AIBN, PhMe, 80°

I + II + III

X		I	cis:trans	II	cis:trans	III	cis:trans	
C(CO₂Me)₂	A	(11)		(87)		(—)		639
C(CO₂Me)₂	B	(71)	15:1	(17)	1:2	(8)	5:1	639
CH₂	B	(62)	6:1	(27)	1:5	(4)	3:1	639
O	B	(53)	100:0	(26)	1:8	(3)	3:1	639
O	B	(55)		(15)		(15)		142
CH₂	B	(35)		(19)		(21)		142

C₇

| Bu₃SnH, AIBN, C₆H₆, 80° | (>90) | 640 |

| Bu₃SnH, AIBN, C₆H₆, 80° | (>90) | 640 |

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

R			641
H	CuCl, MeCN, 110–140°	(71)	
Bn	110–140°	(89)	
H	RuCl₂(PPh₃)₃,	(71)	
Bn	C₆H₆, 110–140°	(88)	

C₈

| CuCl, MeCN, 150° | (93) | 222 |

| Bu₃SnH, AIBN, C₆H₆, 80° | (84) | 642 |

| Bu₃SnH, AIBN, C₆H₆, 80° | (88–92) | 421 |

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 R^1 R^2 H H H SPh H SMe CO$_2$Et SPh	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 (56) (49) (60) (77)	643
	BrCCl$_3$, hv	(89)	164
 R^1 R^2 R^3 H H H H H Ph Me H H (CH$_2$)$_3$ H H H Me H Me H	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 (70) (72) (54) 65:35 (58) (72) (52)	644, 645
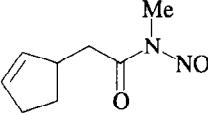
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(Bu$_3$Sn)$_2$, EtI, hv	 I + II (58) I:II = 30:1	646, 51
	AcOH, H$_2$O, TiCl$_3$ (15%), –10°	(66)	647
	HgO, I$_2$, hv	(68)	61
C$_9$	2,4,6-Collidine, Ph$_2$CO (cat.), MeOH, i-PrOH, hv, 350 nm	(88)	648
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(88)	300, 298
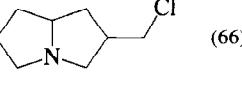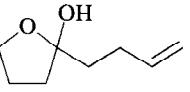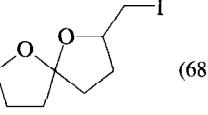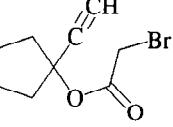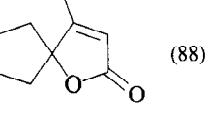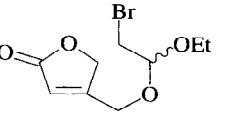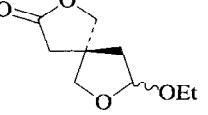
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$ClCo(dmgH)_2py$, Pt cathode, Et_4NOTs, NaOH, MeOH	R: Et (87), C_5H_{11} (84)	649
	BPO, C_6H_6, 80°	R: Me (88), TMS (85)	160
	Bu_3SnH, AIBN, C_6H_6, 80°	(70)	228
	Bu_3SnH, AIBN, C_6H_6, 80°	SMe (60)	650
	$(Ph_3Sn)_2$, C_6H_6, t-BuNC, $h\nu$, 50°	R: H (62), Me (65) 6:1	206

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Mn_2(OAc)_7$, AcOH, 64°	(64)	191
C_{10}	Pt anode, AcOH, MeOH, 45°	I + II I + II (60) I:II = 2:1	167
	$Mn(OAc)_3$, EtOH, rt, 1 h	R: H (60), Me (55)	433
	Bu_3SnH, AIBN, C_6H_6, 80°	R: H (30), Et (70)	651
	SmI_2, t-BuOH, THF, −78 to 0°	(87)	286

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI$_2$, Me$_2$CO, THF, -30° to rt	(85) + diastereomer 11:1	286
	(PhS)$_2$, AIBN, rt, 4 h	**I** + **II** **I + II** (61) **I:II** = 15:1	227
  $\dfrac{R}{H}$ Me Ph	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 α:β (76) 76:24 (67) 86:14 (53) 58:42	652
	1. Bu$_3$SnCl, AIBN, Na(CN)BH$_3$, *t*-BuOH, sealed tube, 110° 2. Jones reagent	(79)	653
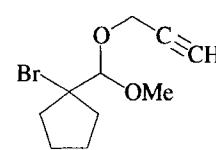
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{11}$ $\dfrac{R}{CO_2Me}$ Me	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II** I + II : I:II (80) 100:0 (—) 50:50	298

	(TMS)$_3$SiH, AIBN, C$_6$H$_6$, reflux	(48) +
		  (6) +
		  (39)
			639

	Me$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH	(42)	330

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph₂CO, C₆H₆, *h*ν	X Y S S (78) S O (15)	654
	1,4-Dicyanonaphthalene, *i*-PrOH, *h*ν	I + II **I + II** (90) **I:II = 97:3**	655
	Bu₃SnH, AIBN, C₆H₆, 80° or Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 80°	(>80)	656
	MeCOSH, AIBN	N—SO₂Ph (55)	452
	Bu₃SnH, AIBN, C₆H₆, 80°	(44)	652

C₁₂

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, reflux	(38)	197
+ RCO₂H R: Me, (CH₂)₂CO₂Me	Pt anode, MeOH, 40-45°	R: (35), (33)	187
	Ph₂CO, C₆H₆, *h*ν	(58)	654
R: H, Me	Mn(OAc)₃, EtOH, rt, 1 h	I + II I II (47) (3) (47) (3)	433

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II	657, 658

R		I + II	I:II
H	Z	(80)	6:1
H	E	(80)	2:1
COMe	Z	(80)	5:1
COMe	E	(82)	1:1
COPh	Z	(89)	10:1
COPh	E	(87)	1:1.2
COBu-*t*	Z	(87)	11:1

C$_{13}$

	1. Cp$_2$TiCl 2. I$_2$	(52)	172

	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		243

X	
NPh	(60)
NBu-*t*	(63)
O	(61)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	AIBN, *c*-C$_6$H$_{12}$, heat 24 h	Ph (47)	659
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (89) I:II = 4.8:1	660
	(Bu$_3$Sn)$_2$, C$_6$H$_6$, *hv*, 25°	(80)	323
	Bu$_3$SnH, AIBN	I + II	661
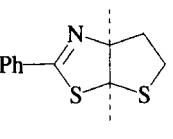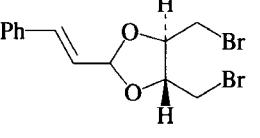
R		I + II	I:II
CN		(71)	4.8:1
CO$_2$Et		(92)	10.5:1
COPh		(57)	4.2:1
n-C$_5$H$_{11}$		(76)	2.6:1

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeCN, H⁺, 25°	(82)	152
C₁₄	CuCl, bipyridine, 25°	(61)	91
	AIBN, C₆H₁₄, 2 h	(92)	659
	Bu₃SnH, AIBN, C₆H₆, 80°		662, 663
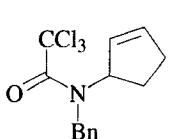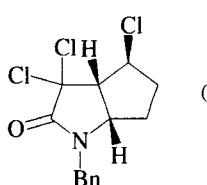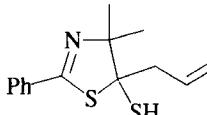
R	R¹	
H	H	(55)
H	H	(60)
Me	Me	(80)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI₂, CSA, MeCN	I + II	664
	Bu₃SnH, AIBN, C₆H₆, 80°	(52) + (14)	665
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II	665

R¹	R²	R³	I	II
H	H	H	(45)	(24)
Me	H	H	(42)	(22)
H	Me	H	(45)	(4)
Me	Me	H	(60)	(0)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II	666

I + II (84) I:II = 10:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 65°	**I** + **II** I + II (58) I:II = 88:12	484
	Bu₃SnH, AIBN, C₆H₆, 65°	(95)	484
	AIBN, c-C₆H₁₂, 2 h	(29)	659
	Bu₃SnH, AIBN, C₆H₆, 80°	(67)	197
			483, 152, 67
	MeCN, t-BuSH, H⁺, 25°	R = H (56)	
	MeCN, H⁺, 25°	R = S-pyr (90)	
	CH₂Cl₂, BF₃·OEt₂, hv, -78°	" (70)	

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			152
	MeCN, t-BuSH, H⁺, 25°	R = H (68)	
	MeCN, H⁺, 25°	R = S-pyr (96)	
	Bu₃SnH, AIBN, C₆H₆, 80°	(75)	667

C₁₅

| | Bu₃SnH, AIBN, C₆H₆, 80° | **I** + **II** + reduced product **III** | 668 |

R	I	II	III
Me	(—)	(27)	(61)
TMS	(48)	(22)	(—)
t-Bu	(49)	(—)	(—)
C(Me)₂OMe	(20)	(4)	(65)
i-Pr	(49)	(24)	(—)
n-Pr	(53)	(40)	(—)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R¹ R² / Me H / H Me	Bu₃SnH, AIBN, C₆H₆, 80°	I + II + III (I:II:III) — (69) 7:61:33 / (56) 12:81:7	666
R / CO₂Bu-*t* / CN	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (I:II) — (72) 9:1 / (85) 9:1	669
		(85) 9:1 (no significant induction)	
	Bu₃SnH, AIBN, C₆H₆, 80°	(78)	652

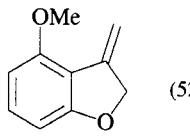TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(94)	670
	Bu₃SnH, AIBN, C₆H₆, 80°	(74)	671
C₁₆	ClCo(dmgH)₂py, NaBH₄, NaOH, 1 MeOH, 0°	(67)	672
	Bu₃SnH, AIBN, C₆H₆, heat	(79)	673
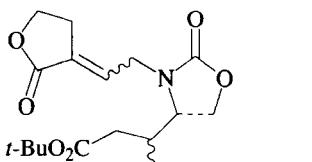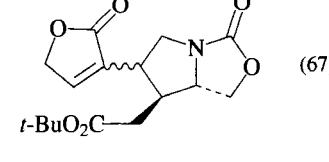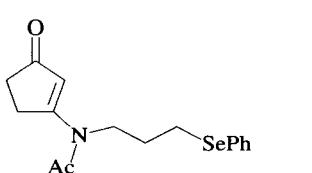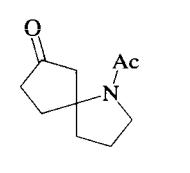
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph$_3$SnH, AIBN	(73)	352
			674
	Co(OAc)$_2$, rt	**I + II** (60) **I:II** = 95:5	
	Ag(OAc)$_2$, rt	**I + II** (51) **I:II** = 94:6	
C$_{17}$	Bu$_3$SnH, AIBN. C$_6$H$_6$, 80°	(88)	675
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		329

R		E:Z
H	(59)	—
TBDMS	(57)	80:20

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		676

R		
	I	II
H	(65)	(9)
Me	(49)	(—)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		676

R		
	I	II
H	(41)	(9)
Me	(50)	(—)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$. 80°		669

R	
H	(64)
Me	(86)

mixture of isomers

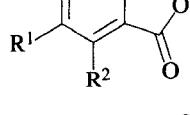TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(89) α:β = 13:87	113
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(72)	677
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		678

R^1	R^2	R^3	
Me	H	H	(75)
Et	H	H	(70)
Ph	H	H	(32)
Me	Me	H	(74)
H	H	Me	(72)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeCN or MeOH, hv	X: H (47), F (47), OMe (46-65)	679
	Bu$_3$SnH, AIBN, PhMe, 110°, 5 h	I + II I + II (76) I:II = 88:12	680
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(70)	681
C$_{18}$	ClCo(dmgH)$_2$py, NaBH$_4$, NaOH, MeOH, 0°	(69) cis:trans = 1:1	672

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Bu$_3$SnH, AIBN, CO$_2$Me C$_6$H$_6$, heat 2. F$^-$	(64)	682
	Bu$_3$SnH, AIBN, PhMe, 110°	(80) 4 isomers in ratio 11.3:2.3:2:1 main isomer 7-β	680
C$_{19}$		I + II	683
		+ III	
		I + II + III **I:II:III**	
	(Bu$_3$Sn)$_2$, C$_6$H$_6$, *hv*, 3 d	(50) 33:28:39	
	AgOAc, SnCl$_2$, MeOH, *hv*, rt	(68) 35:31:34	

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(76)	684
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(61)	652
	1. Mn(OAc)$_3$, EtOH 2. AcOH, H$_2$O	+ I II I + II (72) I:II = 1:1	685
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(60-71)	678, 668

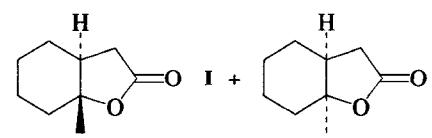TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R / H / Me	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	$\qquad$ α:β (71) $\quad$ > 99:1 (58) $\quad$ 90:10	652
C$_{20}$ 	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(49) + (8)	686
	Et$_3$B, O$_2$, C$_6$H$_6$ Mn(OAc)$_3$, AcOH, NaOAc, 80°	(75) (95)	687
+	$h\nu$, H$^+$	(52)	488

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
+	1. (Bu$_3$Sn)$_2$, C$_6$H$_6$, $h\nu$ 2. Et$_3$N	(50)	688
C$_{21}$ 	ClCo(dmgH)$_2$py, NaBH$_4$, NaOH, MeOH	(64)	689
	Bu$_3$SnH, AIBN, PhMe, 110°	 I + II (87) $\quad$ I:II = 2:1	690
C$_{22}$ 	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(63) *endo:exo* = 6.4:1	691

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23}	Bu₃SnH, AIBN, C₆H₆, 80°	(72)	692
	Bu₃SnH, AIBN, C₆H₆, 80°	(58) + (13)	669
R = I + Bu₃Sn⟋⟍C₅H₁₁	Bu₃SnH, ACN, PhMe, 110°	(72)	205
R = Br + H—C≡C—C₅H₁₁	Vitamin B₁₂, C-felt cathode, LiClO₄, DMF, *hv*	(>55)	224

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
TBDPSO … R/H = Me	Ph₃SnH, AIBN, C₆H₆, 80°	(54) + (37)	419
C_{24} R = PhMe₂Si	Bu₃SnH, AIBN, C₆H₆, 80°	I + II + III	693

	I	II	III
	(63)	(10)	(18)
	(64)	(11)	(12)

cis:trans = 18:1
cis:trans = 1.3:1

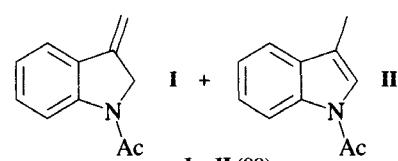TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II** **I + II** (74) **I:II** = 6.4:1	497
	Bu$_3$SnH, AIBN, PhMe, 110°	(85) *E:Z* = 1.3:1	690
C$_{25}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(50)	694
C$_{26}$	Bu$_3$SnCl, THF, Na(CN)BH$_3$, *h*ν	(58)	100

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{27}$	*h*ν	**I** + **II** **I + II** (45) **I:II** = 11.3:1	132, 695
C$_{29}$	Bu$_3$SnH, ACN, PhMe, 110°	(74)	205
C$_{33}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(<95)	696
C$_{34}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(<75)	696

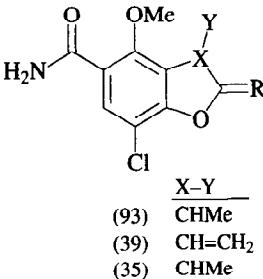TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	F. (5+6)-Membered Rings		

C_7

R^1	R^2			
			I + II	**I:II**
H	H		(82)	100:0
H	Me		(80)	100:0
H	Et		(72)	100:0
H	Bn		(70)	100:0
Me	Me		(35)	100:0
Me	Me	MeOH, *hv*	(45)	60:40
Me	Me	MeOH, H⁺, *hv*	(43)	55:45

PhCl, *t*-(BuO)₂, heat or *c*-C₆H₁₂, *hv*, heat — 697

C_8

	RuCl₂(PPh₃)₃ (1-5%), xylene, 140°	(71)	698
	CuCl, CH₂Cl₂, bipyridine, 25°	(98)	91

| | Bu₃SnH, AIBN, C₆H₆, 80° | (63) | 642 |

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

R			
H		(65)	699, 700
Me		(65)	

Bu₃SnH, AIBN, C₆H₆, 80°

| | (Bu₃Sn)₂, C₆H₆, *hv*, 80° | (83) | 156, 51 |

R^1	R^2		
H	H	(35)	
C₅H₁₁	H	(70)	649
C₅H₁₁	Me	(82)	

ClCo(dmgH)₂py, Et₄NOTs, NaOH, MeOH, Pt cathode

| | Et₃B, C₆H₁₄, 25° | R = H (75) R = TMS (90) | 275 |

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	ClCo(dmgH)$_2$py, Et$_4$NOTs, NaOH, MeOH, Pt cathode	(44)	649
	Polymer-SnCl, AIBN, NaBH$_4$, C$_6$H$_6$, EtOH, *h*v	" (73)	426
			426
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	" (50)	

R^1 R^2

	PhSiH$_2$, BPO, C$_8$H$_{18}$, 110°		272
		isomer ratio	

R^1	R^2		
H	H	(65) 3.5:1	
H	Me	(65) 2.5:1	
Me	Me	(63) 1.3:1	

C$_9$

RC≡CPh

	(PhS)$_2$, 100°		701

R	
Me	(35)
t-Bu	(42)
Ph	(40)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$		29

X	
CH$_2$	(50)
O	(99)
NMe	(78)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CoI(salen) or CoI(salophen)py, *h*v	L (salen) (65) (salophen)py (55)	186
	CoI(salophen)py, NaHg, dark	(70)	169
	Ni(II)complex, DMF, NH$_4$ClO$_4$, Et$_4$ClO$_4$, Hg cathode	(75)	702
	10-Me-9,10-dihydro-acridine (cat.), DMF, NaBH$_4$, *h*v	X = Br (65) X = I (82) X = Cl (48) X = F (21)	703

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

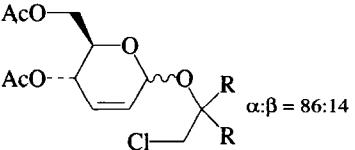| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI$_2$, E$^+$		174

E$^+$	E	
H$_2$O	H	(—)
D$_2$O	D	(80)
I$_2$	I	(70)
(PhS)$_2$	SPh	(65)
(PhSe)$_2$	SePh	(72)
Bu$_3$SnI	Bu$_3$Sn	(82)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
BF$_4^-$	N-Oxide **A** or **B**, Me$_2$CO, 60°		704

N-Oxide	X	R^1	R^2	
A	O	H	DBA	(76)
B	O	H	TMP	(84)
A	O	Me	DBA	(68)
B	O	Me	TMP	(82)
A	NAc	H	DBA	(75)
B	NAc	H	TMP	(80)
A	NAc	Me	DBA	(35)
B	NAc	Me	TMP	(51)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
BF$_4^-$			705, 706

R		X	
H	CuBr$_2$	Br	(82)
Me	CuBr$_2$	Br	(89)
Me	CuCl$_2$	Cl	(63)
Me	Cu(CN)$_2$	CN	(40)
Me	NaSPh	SPh	(60)
H	NaSPh	SPh	(53)
Me	Cu, NaSBu-n	SBu-n	(64)
Me	NaSC(S)OEt	SC(S)OEt	(75)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
BF$_4^-$	NaI, Me$_2$CO, 25°		707

R^1	R^2	
H	H	(86)
Me	H	(89)
H	Me	(73)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(72)	708

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

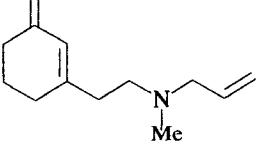| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

SmI$_2$, HMPA, THF, MeCN — 175

X	R^1	R^2	
H	H	H	(70)
H	H	Ph	(59)
Ac	H	H	(88)
Ac	Me	Me	(99)

Ph$_2$PH, AIBN, C$_6$H$_6$, 80° — X = O (66) 1.7:1 ; X = NCO$_2$Me (66) 6.1:1 — 301

Ph$_3$SnH, Et$_3$B — (60) — 709, 27

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — (94) — 710

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

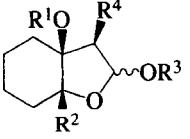| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu$_3$SnH, AIBN, PhMe, *hv* — 607

X		R	
O	-20°	SnBu$_3$	(72)
O	-20°	H	(28)
NTs	17°	H	(22)

Bu$_3$SnH, AIBN, PhMe, heat

R	
H	(92)
Me	(47)

711, 712

Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH — (96) — 713

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

R	
H	(63)
Me	(73)
Ph	(75)

714, 715

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(71)	228
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II + III I + II + III (69) I:II:III = 19:39:42	115
	TsSePh, AIBN, C₆H₆, 80°	(53) 1.5:1	302
	Bu₃SnH, AIBN, C₆H₆, 80°	(88-92)	421

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	I + reduced II product I + II (80) I:II = 1:2	646
	(Bu₃Sn)₂, EtI, C₆H₆, hν	Ia, Ib + reduced II product I + II (88) Ia R¹=I R²=H (57) Ib R¹=H R²=I (11) II (20)	646
	(Bu₃Sn)₂, C₆H₆, hν, 80°	I (60-70)	51
C₁₀	Me₂CO,	R¹ = H, R² = Me (72) R¹ = R² = Me (quant., NMR)	716
	Bu₃SnH, AIBN, C₆H₆, 80°	(50)	52

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE H ETEROATOMS (*Continued*)

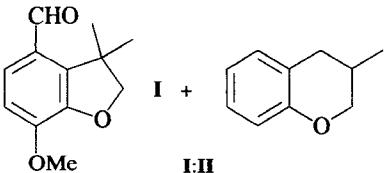| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(75)	717
	Bu₃SnH, AIBN, C₆H₆, 80°	(52)	718
	Bu₃SnH, AIBN, C₆H₆, 80°		719
	Bu₃SnH, AIBN, C₆H₆, 80°		718

R^1 R^2 R^3
H H H
H Me H
H Me Me
Me H H
(CH₂)₄ H

I **II**
(79) (—)
(72) (—)
(80) (—)
(72) (18)
(69) (22)

R
H (80)
Ph (88)
CO₂Et (75)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	R^1 R^2 Me Me (88) H CO₂Et (75)	718
	1. HgO, I₂, C₆H₆ 2. *hv*	R^1 R^2 H H (41) H Cl (56) H OMe (54) OMe OMe (67)	720
	Bu₃SnH, AIBN, C₆H₆, 80°	R C₆H₁₁ (92) *t*-Bu (80) *n*-Bu (70) *i*-Pr (49) Me (39) Ph (<5)	721
	2,4,6-Collidine, Ph₂CO (cat.) MeOH, *i*-PrOH, *hv*	(69)	648
	Bu₃SnH, AIBN, C₆H₆, 80°	(85)	722
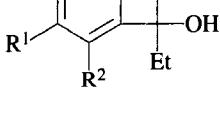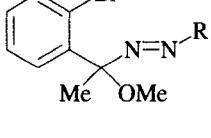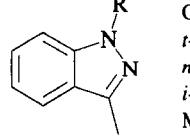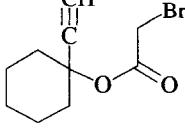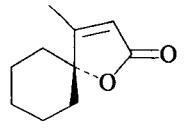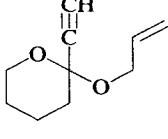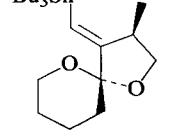
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et$_3$N, MeCN, *hv*	$\dfrac{X}{O\quad(50)}$ CH$_2$ (40)	181
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(50) + (16)	723
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(43) + (5)	723
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(72)	723
	BPO, C$_6$H$_6$, 80°	$\dfrac{R}{\text{Me}\quad(59)}$ TMS (93)	160

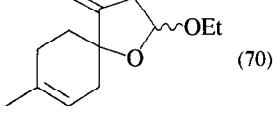TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH 2. TsOH, C$_6$H$_6$	$\begin{array}{ccc} R^1 & R^2 & R^3 \\ H & H & Me\ (38) \\ H & H & Et\ (42) \\ H & Me & Me\ (45) \\ Me & H & Me\ (45) \end{array}$	724
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(63)	725
	Cu(bipy)Cl, MeOAc, reflux	I + II I + II (63) I:II = 2.5:1	417
X = Br	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I R = H (50)	52
X = Br	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH, *t*-BuNC	I R = CN (60)	122
X = Br	(Ph$_3$Sn)$_2$, *t*-BuNC, C$_6$H$_6$, *hv*, 50°	I R = CN (58)	122

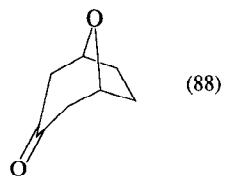TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
X = I + Bu$_3$Sn—CH=CH—CO—C$_5$H$_{11}$	Bu$_3$SnH, ACN, PhMe, 110°	(60)	205
(R, Br, N-Tf cyclohexene)	1. Ph$_3$GeH, AIBN 2. H$^+$	R: Me (82); Ph (60)	54
(ketone, CO$_2$Me enoate)	SmI$_2$, THF, reflux	**I** + **II** **I + II** (56) **I:II** = 3:7	726
(OEt, O, Br methylcyclohexene)	Vitamin B$_{12}$, Zn, NH$_4$Cl, MeOH, H$_2$O	(80)	186
(thiolactone allyl) + MeC≡CMe	MeOH, *hv*	MeO$_2$C (45) + CO$_2$Me (15)	727
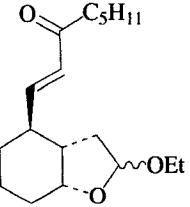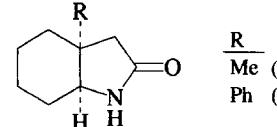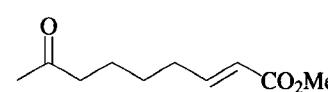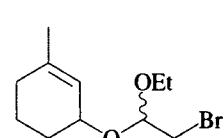
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(MeO, Br, N-Me acrylamide)	Bu$_3$SnH, AIBN, PhMe, 110°	(63) MeO oxindole N-Me	728
(Br, allene, N-Ac)	Bu$_3$SnH, AIBN	**I** + **II** **I + II** (99)	729
	SmI$_2$, HMPA, THF	(47) 3-methylindole	175
(Br, N-Ac, R^1, R^2, R^3 alkene)	Bu$_3$SnH, AIBN	R^1, R^2, R^3 indoline N-Ac	729

R^1	R^2	R^3	
H	H	H	(91)
H	Me	H	(93)
Me	H	H	(93)
H	Ph	H	(92)
H	Me	Me	(93)
OMe	H	CO$_2$Et	(81)

C$_{11}$

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaI, Mc$_2$CO, 25°	(84)	707
R X–Y H$_2$ CH=CH$_2$ H$_2$ C≡CH O CH=CH$_2$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	X–Y (93) CHMe (39) CH=CH$_2$ (35) CHMe	730
	ClCo(dmgH)$_2$py, NaBH$_4$, EtOH, NaOH (0.1 M), 40°	**I** (18) + **II** (29)	731
	ClCo(dmgH)$_2$py, NaBH$_4$, EtOH, NaOH (0.01 M), 40°	**II** (47)	731

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(53)	478
	(Me$_3$Sn)$_2$, *hv*	**I** + **II** (66) **I:II** = 60:40	18
	TsSePh, AIBN, C$_6$H$_6$, heat	(78) 6:1 ratio	301
	TsSePh, AIBN, C$_6$H$_6$, heat	(94) 1.3:1 ratio	301

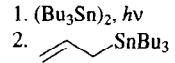TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Bu₃SnH, AIBN, C₆H₆, 80° 2. TsOH (cat.), C₆H₆	$\dfrac{R}{H}$ (45) Me (46)	732
	Bu₃SnH, AIBN, C₆H₆, 80°	$\dfrac{R}{H}$ (88-92) Me	421
	1. Bu₃SnCl, Na(CN)BH₃, AIBN, t-BuOH 2. Jones reagent	(96)	653
	Bu₃SnH, AIBN, C₆H₆, 80°	(13) + (25)	733
	Bu₃SnH, AIBN, PhMe, 110°	(85)	425

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₂ + $\dfrac{R}{\begin{array}{l}CO_2Et\\CN\\Ph\\SO_2Ph\end{array}}$	Bu₃SnH, AIBN, PhMe, 110°	 (60) (57) (58) (60)	207, 734
+	Bu₃SnCl, Na(CN)BH₃, AIBN, t-BuOH, heat, 18 h	(—)	735
	MeCN or MeOH, hv		736

R¹	R²		R¹	R²	
Ph	CH=CH₂	MeOH	CH=CH₂	Ph	(66)
Ph	CO₂Me	MeOH	Ph	CO₂Me	(44)
Ph	TMS	MeCN	Ph	TMS	(65)
Ph	TMS	MeOH	H	Ph	(71)
H	TMS	MeCN	TMS	H	(76)
H	CH=CH₂	MeOH	CH=CH₂	H	(79)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II (90) I:II = 85:15	52
	RuCl₂(PPh₃)₃, xylene, 140°, 8 h	(64)	154
	1,4-Dicyanonaphthalene, *i*-PrOH, *h*ν	I + II I + II (85) I:II = 2:98	655
	1,4-Dicyanonaphthalene, *i*-PrOH, *h*ν	I + II I + II (87) I:II = 95:5	655

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI₂, HMPA, THF, MeCN	(61)	175
	SmI₂, HMPA, THF,	(55)	175
	MeCN, Et₄NClO₄, Pt electrode	(60)	486
 R CHO CH₂OH CN	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I — II (—) (50) (47) (—) (60) (40)	31

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

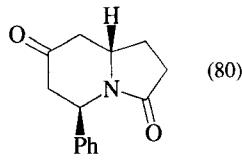| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, PhMe, heat	(77)	737
		I	
	Bu₃SnH, AIBN, C₆H₆, 80°	**I** R = H (76)	738
	Bu₃SnCl, NaCNBH₃, AIBN, *t*-BuOH	**I** R = H (88)	738
	AIBN, C₆H₆, 80° + ⟍⟍SnBu₃	**I** R = CH₂CH=CH₂ (56)	739
α:β = 86:14	Bu₃SnH, AIBN, C₆H₆, 80°		740

$$\begin{array}{c|cc} & \textbf{I + II} & \textbf{I:II} \\ \hline \text{H} & (96) & 86{:}14 \\ \text{Me} & (96) & 86{:}14 \end{array}$$

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	A. Co(I)(salen) B. Bu₃SnH	**I** + **II** + **III**	741, 742
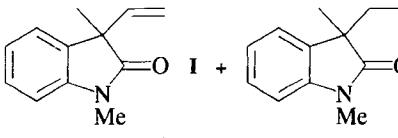
$$\begin{array}{ccc} \underline{X} & & \\ \text{I} & \text{A} & \\ \text{Br} & \text{A} & \\ \text{Br} & \text{B} & \end{array} \quad \begin{array}{cc} \textbf{I + II + III} & \textbf{I:II:III} \\ (66) & 72{:}2{:}26 \\ (40) & 72{:}2{:}26 \\ (65) & 0{:}72{:}28 \end{array}$$
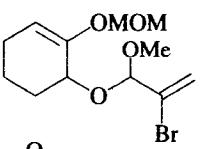
	Bu₃SnH, AIBN	(50)	743
	MeOH, *hv*	(79) 1:1 ratio	226
	Bu₃SnH, AIBN, C₆H₆, 80°	 R: *t*-Bu (77), PhCMe₂ (73), Ts (80)	54
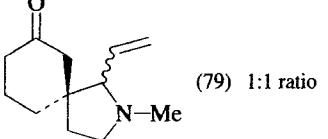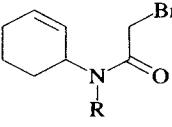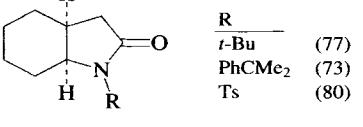
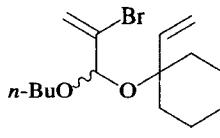TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph$_2$CO, C$_6$H$_6$, *hv*	R H (60) Me (55)	654
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		743

R^1	R^2	R^3	R^4		
i-Bu	H	Et	H	(91)	
i-Bu	Me	Et	H	(78)	
Me	Me	Et	H	(56)	
MEM	Me	Et	H	(90)	
TBDMS	*t*-Bu	Me	Me	(60)	

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (74) I:II = 85:15	111 438
	Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°	R H (53) Me (52)	419
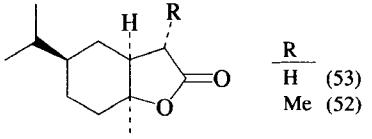
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH, 110°, 8 h	(90)	744
	AIBN, C$_6$H$_6$, 80°	I + II	745

	I:II
Bu$_3$SnH 0.5 M	90:10
Bu$_3$SnH 0.05 M	66:34
Bu$_3$SnH 0.02 M	44:56

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pb(OAc)$_4$		746

R^1	R^2	R^3		
H	H	H	AcOH, 20°	(86)
H	Br	Br	CH$_2$Cl$_2$, 20°	(60)
NH$_2$	H	H	CH$_2$Cl$_2$, 20°	(34)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, Et$_3$B, THF, -78°	(71)	437

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HET EROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	A. AIBN, MeCN, 50-60° B. Carbon anode, Et₄NOTs, MeCN		747
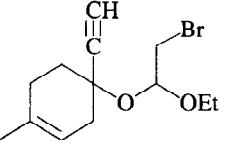
R¹	R²		
Ph	H	A	(66)
		B	(79)
Ph	Me	A	(90)
		B	(48)
CH₂TMS	H	A	(73)
		B	(72)

C₁₃

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH	(70)	748
	Bu₃SnH, AIBN or Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH		749, 738

R¹	R²	X	
Ac	OMe	Br	(96)
Ac	OEt	I	(83)
Ac	OMe	HgOAc	(90)
Ac	H	Br	(55)
Bz	H	Br	(75)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph₃SnH, AIBN, C₆H₆, 80°	 **I + II** (98) **I:II** = 3:1	737
	Ph₃SnH, AIBN, C₆H₆, heat	(88)	112
	Bu₃SnH, AIBN, C₆H₆, 80°		750, 740, 738

R¹	R²	R³		Z:E
H	H	H	(75)	100:0
H	H	CH₂OAc	(77)	5:1
Me	H	H	(65)	5:1
H	Me	H	(63)	4:1

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80° → Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(89)	740
	TsBr, *hv*	(70) *endo:exo* = 7:1	751
	Mn(OAc)$_3$, EtOH, rt, 1 h	(30) + (10)	433
	Et$_3$N, MeCN, *hv*	(50)	752

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(52)	708
+	MeOH, *hv*	CO$_2$Me (70) + CO$_2$Me (25)	727
O–C(=S)–SMe	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(33)	228
	(TMS)$_3$SiH, AIBN, PhMe, 88-90°	O=C–OEt, N–CH$_2$CH$_2$–S–S–Si(TMS)$_3$ (79) 2.4:1	470

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeOH, *hv*	(72)	226
	MeCN, *hv*	(76) 4:3	226
	Bu₃SnH, AIBN, C₆H₆, 80°	R: H (80), *n*-C₆H₁₃ (50)	753
C₁₄ (see structures) + R–CO–Me; R: (CH₂)₃NEt₂, (CH₂)₃Cl, (CH₂)₃CH=CH₂	SmI₂, HMPA, THF, 25°	(76), (10), (38)	176

R structures:
R
H (80)
n-C₆H₁₃ (50)

R values for SmI₂ reaction:
(CH₂)₃NEt₂ — (76)
(CH₂)₃Cl — (10)
(CH₂)₃CH=CH₂ — (38)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R: (CH₂)₃CO₂Et		(40)	176
	CoI(dmgH)₂py, Et₄NOTs, NaOH, MeOH, Pt cathode	(81)	649
	Bu₃SnH, AIBN, C₆H₆, 80°	(80)	48, 497
+ R–CO–R	SmI₂, HMPA, THF, 25°		176

R values for SmI₂ reaction:
Et — (69)
n-C₃H₇ — (81)
(CH₂)₄ — (68)
(CH₂)₅ — (65)
CH(Me)(CH₂)₄ — (70)
(CH₂)₂CH(Bu-*t*)(CH₂)₂ — (67)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R <hr>Cl CO2Me OAc	Bu3SnH, AIBN, C6H6, 80°	 (70) (68) (58)	754
	1. (Bu3Sn)2, *hv* 2. ⟋⟍SnBu3	(72)	593
	Ph3SnH, Et3B, air	(92)	593

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Co(I)(salen)	 **I + II** (70) **I:II** = 74:26	741
	Bu3SnH, AIBN, C6H6, 80°	 **I + II** (91) **I:II** = 74:26	719
	Bu3SnH, AIBN, PhMe, 110°	(85) β:α = 70:30	755, 756
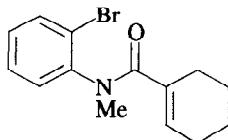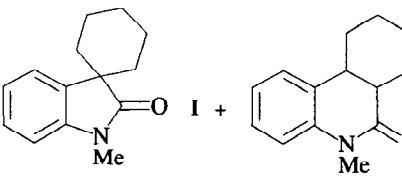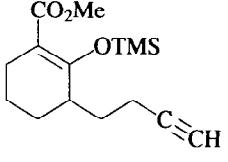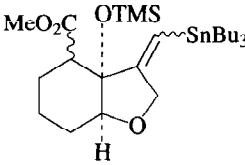
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(acrylate ester with O_2NO, acetonide) $\dfrac{R}{CO_2Me}$ Ph	Bu_3SnH, AIBN	(lactone with R and acetonide) (39) (24)	661
(dihydropyridinone, N-substituted, Ph, Br)	Bu_3SnH, AIBN, C_6H_6, 80°	(bicyclic indolizidinedione, Ph) (80)	757
t-Bu (cyclohexyl ester, vinyl, I)	Ph_3SnH, AIBN	t-Bu (spirolactone) (90)	419
(cyclohexyl, Br, allyl) n-BuO	Polymer-SnCl, AIBN, $NaBH_4$, C_6H_6, EtOH, $h\nu$	n-BuO (spirocyclic) (73)	426

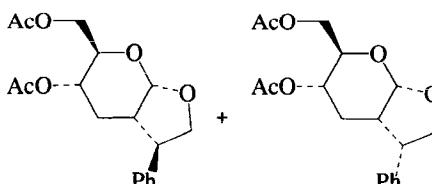TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(cyclohexenyl with isobutyloxy, Br, OEt)	Bu_3SnH, AIBN, C_6H_6, 80°	(bicyclic with isobutyloxy, OEt) (91)	185
	$ClCo(dmgH)_2py$, EtOH, $NaBH_4$, NaOH, 50-60°	" (71)	185
C_{15} n-BuO (with Br, vinyl, cyclohexyl)	Bu_3SnH, AIBN, C_6H_6, 80°	n-BuO (methylene spirocyclic) (64)	443
(aryl Br, N with propargyl, SO_2Ph)	Bu_3SnH, AIBN, C_6H_6, 80°	(methyleneindoline, SO_2Ph) (72)	758
(aryl Br, O-cinnamyl, Ph)	SmI_2, HMPA, THF, MeCN	(dihydrobenzofuran with CH$_2$Ph) (89)	175

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			759
	(TMS)$_3$SiH, AIBN, Et$_3$N, C$_6$H$_6$, 80°	(63)	
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(77)	
	(TMS)$_3$SiH, AIBN, C$_6$H$_6$, 80°	R^1 R^2 H H (80) H Ph (86) Me H (82) Ph H (83)	141, 759
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(60) Δ7:Δ8 = 7:1	665
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(72) + (12)	386, 387

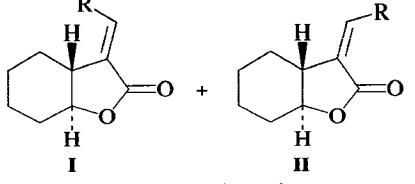TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (70) I:II = 3.7:1	666
ClO$_4^-$	SmI$_2$, CSA, MeCN	I + II I + II (60) I:II = 1:1	664
	CuCl, CuCl$_2$, THF, AcOH, H$_2$O, -45°	I + II I + II (66) I:II = 4.8:1	162
  R H Me	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 (64) (85) two diastereomers 3.7:1	760

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			710
	Bu$_3$SnH, (Bu$_3$Sn)$_2$	$\dfrac{R}{H}$ (70) I (80)	
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(99)	710
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	R^1 R^2 Ac OAc (60) TBDMS H (80)	710

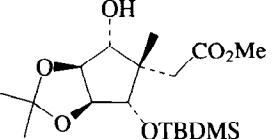TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 **I** + **II** **I:II** (85) 53:47 (80) 75:25	761
$\dfrac{R}{H}$ Ph			
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 **I + II** (53) **I:II** = 9:1	762
C$_{16}$			641
	CuCl, MeCN, 110-140° RuCl$_2$(PPh$_3$)$_3$, C$_6$H$_6$, 110-140°	(85) (88)	

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			641
	CuCl, MeCN, 110-140°	(81)	
	RuCl$_2$(PPh$_3$)$_3$, C$_6$H$_6$, 110-140°	(89)	
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	R X H NH (96) Me NH (56) H O (75)	763
	Bu$_3$SnH, Et$_3$B, THF, -78°	(95)	437
	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	(81) + (5)	313

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

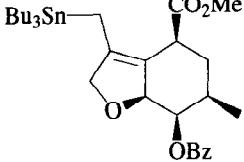| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	(70) + (5)	313
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(32)	331
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (72) I:II = 6:1	764
	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	(67)	482
	Bu$_3$SnH, AIBN, C$_6$H$_6$, heat	+ (19) (10)	765, 766

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(allyl-substituted pyrrolidinone with SPh and CO₂Me)	Bu₃SnH, AIBN, C₆H₆, 80°	**I** (72) + **II + III** (12); *cis:trans* = 1:4 (bicyclic CO₂Me products)	489, 113
(2-methylcyclopentenone with O(CH₂)₄SePh)	Bu₃SnH, AIBN, C₆H₆, 80°	(spirocyclic ketone–tetrahydropyran) (65)	760
(cyclohexane with vinyl and O–C(O)–SePh)	Bu₃SnH, AIBN, C₆H₆, 80°	(oxepanone, 25) + (hexahydrobenzofuran, 32)	386, 392
(2-bromo-N,N-bis(3-methylbut-2-enyl)aniline)	SmI₂, HMPA, THF, MeCN	(3-isopropyl-1-(3-methylbut-2-enyl)indoline) (87)	175

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(diacetoxy glycal with O(CH₂)₂Br) + CH₂=CH–R¹		(bicyclic acetal with R²)	749

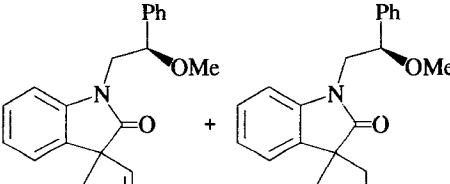| R¹	Conditions	R²	
CO₂Me	Bu₃SnH, AIBN, C₆H₆, 80°	CH₂CH₂CO₂Me	(53)
"	"	CH₂CH(CO₂Me)(CH₂)₂CO₂Me	(7)
CH₂SnBu₃	AIBN, C₆H₆, 80°	CH₂CH=CH₂	(56)
"	"	H	(27)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(Ph-thiazoline with pentenyl and SH)	BPO, *c*-C₆H₁₂, 80°, 2 h	(spiro thiazoline–thiane) (55)	659
(bromomethylene pyran with CO₂Me, AcO, Me, OAc)	Bu₃SnH, AIBN, C₆H₆, 80°	(hexahydrobenzofuran with MeO₂C, AcO, Me, AcO, exo-methylene) (66)	767
(cyclohexane with SePh and N(CN)allyl, R)	Bu₃SnH, AIBN, C₆H₆, 80°	(octahydroindole with R and N–CN); R = H (97), Me (95)	768

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)
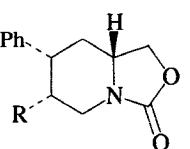
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(structure with R^1, Br, N–Ph, R^2, R^3)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(indolinone structure with R^1, R^3, O, N, Ph, R^2)	769

R^1	R^2	R^3		% de
OMe	Me	H	(64)	2
OMe	Me	Me	(59)	39
H	OMe	H	(83)	7
H	OMe	Me	(79)	14

C$_{17}$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(Ph–N(H)–N=C(Me)–CH=N–aryl structure)	600°, 10^{-2} Torr	(methylindole) (62) + (dimethylquinoxaline) (11)	770, 771
(AcO, allyl, MeO, PhS, pyranone structure)	Bu$_3$SnH, AIBN, C$_6$H$_6$	(AcO, O, OMe bicyclic structure) **I** + (AcO, O, OMe bicyclic structure) **II** I + II (92) I:II = 4:1	764

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(AcO, allyl, MeO, PhS, pyranone structure)	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(OAc, O, OMe bicyclic) **I** + (OAc, O, OMe bicyclic) **II** + (OAc, O, OMe bicyclic) **III** I + II + III (78) I:II:III = 2.5:1.2:1	764
(bicyclic iminium structure with Me, N$^+$, Ph) ClO$_4$$^-$	SmI$_2$, CSA, MeCN	(bicyclic structure with N, Me, H, Ph) (78)	664
(Ts, Me, cyclohexene, O, allyl structure)	TsNa, AcOH, H$_2$O, 100°	(Ts, H, Me, O bicyclic) **I** + (Ts, H, Me, O bicyclic) **II** I + II (78) I:II = 5:2	772, 136
(Ts, Me, cyclohexene, O, propargyl structure)	TsNa, AcOH, H$_2$O, 100°	(Ts, H, Me, O bicyclic) **I** + (Ts, H, Me, O bicyclic) **II** I + II (83) I:II = 10:1	772, 136

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(38)	673
	Bu₃SnH, AIBN, C₆H₆, 80°	(30)	673
	Ph₃SnH, AIBN, C₆H₆, 80°	$\underline{R}$ H (69) *t*-Bu (86)	352
	Bu₃SnH, AIBN, C₆H₆, 80°	(91) + (3)	766
	Bu₃SnH, AIBN, C₆H₆, 80°	(66)	768

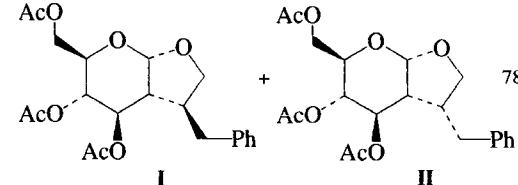TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(68) *cis:trans* = 53:47	479
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II **I + II** (95) **I:II** = 4.3:1	48, 497
	Bu₃SnH, AIBN, C₆H₆, 80°	(75)	773
	ClCo(dmgH)₂py, Et₄NOTs, NaOH, MeOH, Pt-cathode	(75)	649
	Bu₃SnH, AIBN, C₆H₆, 80°	(92)	774

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI$_2$, THF, MeOH, -78°	(69)	775
R = TBDMS *E* *Z*	SmI$_2$, THF, MeOH, -78°	 **I** + **II** **I + II** (64) **I:II** = 4:1 **I + II** (73) **I:II** = 1:100	775
   R Ph 4-ClC$_6$H$_4$ 4-MeOC$_6$H$_4$ 3-O$_2$NC$_6$H$_4$ 2-thienyl 2-naphthyl	DPDC, C$_6$H$_6$	 (64) (64) (55) (50) (30) (50)	776

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{18}$ 	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(95)	777
	SmI$_2$, HMPA, THF, 25°	 R Bn (27) CH$_2$CH=CH$_2$ (38)	176
	MeCN, Et$_4$NClO$_4$, Pt electrode	ClO$_4^-$ (72)	486
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(65) 1:1 ratio	621
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(65)	31

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)
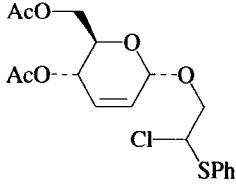
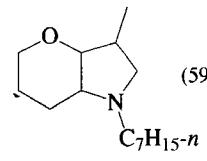| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
α:β = 82:18	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (66) I:II = 97:3	740
α:β = 86:14	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (83) I:II = 88:12	740
	Bu₃SnH, AIBN, PhMe, 110°	R % d.e. H — (0) Me 15 (65)	769
	Bu₃SnH, AIBN, C₆H₆, 80°	(22) + (35)	479
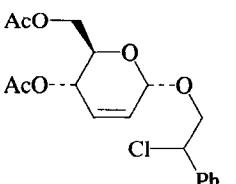
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
		I + II	
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (95) I:II = 3:1	778, 779
	Vitamin B₁₂ (cat.), C felt cathode, LiClO₄, MeOH	I + II (>75) I:II = >95:<5	183, 779
	Me₃SnO OSnMe₃ Ph— —Ph Ph Ph C₆H₆, 80°	I + II (85) I:II = >95:<5	779
R = TMS R = Ph	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (80) I:II = 1:12 I + II (90) I:II = 5:1	496
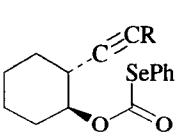
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(93)	780
	SmI$_2$, THF, MeOH, -78°	(65)	781
	Bu$_3$SnH, AIBN		661

R	
CO$_2$Me	(39)
Ph	(23)
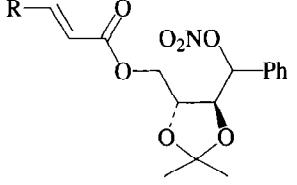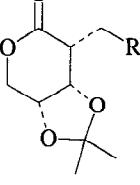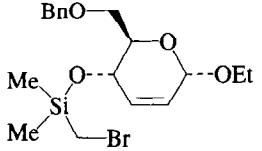
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(>76)	782

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN		82

R^1	R^2	R^3		I + II	I:II
OBn	OBn	OMe		(62)	100:0
H	OBn	H		(67)	92:8
H	H	H		(55)	30:70
OBn	H	H		(32)	23:77
OBn	H	OMe		(51)	14:86

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{19}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(43)	783
	Ph$_3$SnH, AIBN, C$_6$H$_6$, heat	(83)	784

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(AcO-substituted pyranose with allylic iodide, E and Z)	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (95) I:II = 72:28 (E) I + II (85) I:II = 90:10 (Z)	785
(AcO-substituted pyranose with propargyl ether, R = Ph, n-Bu, t-Bu)	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (85) I:II = 74:26 (Ph) I + II (90) I:II = 71:29 (n-Bu) I + II (91) I:II = 36:64 (t-Bu)	761
(BzO-substituted dihydropyran with EtO and Br)	AIBN, C₆H₆, 80° Bu₃SnH, allylSnBu₃	R = H (82) R = CH₂CH=CH₂ (84)	739

$I + II$ (95) I:II = 72:28

$I + II$ (85) I:II = 90:10

R
Ph
n-Bu
t-Bu

$I + II$ (85) I:II = 74:26

$I + II$ (90) I:II = 71:29

$I + II$ (91) I:II = 36:64

R
H (82)
CH₂CH=CH₂ (84)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(TBDMSO pyranone with iodide and OHC, OBu-t)	Bu₃SnH, AIBN, C₆H₆, 80°	(70) 5:1 mixture	42
(thiocarbonyl imidazolide tetrahydropyran with EtO₂C and alkyne CTMS)	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (84) I:II = 3:4	786
(cyclohexenone with aminosilane, Ph, TMS, N-Me)	MeOH, hv	(78) 1:1 ratio	226
(cyclohexenone with aminosilane, TMS, N-Ph)	MeOH, hv	(71)	226, 518, 736

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{20}
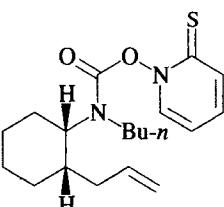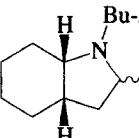
CF$_3$CO$_2$H, *t*-BuSH — (60) — 67
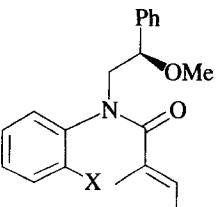
A. Co(I)(salen), 20°
B. Bu$_3$SnH, 20°

I + II + III — 741

X = I	A	I (40) 15% de
X = Br	B	II + III (79), II 15% de

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH, 80° — I + II — 787

R		
CO$_2$Me		
CN		

	I + II	I:II
	(56)	1:4
	(69)	1:2

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

R	
Me	(57)
CH$_2$-CH=CH$_2$	(73)

788

1. Mn(OAc)$_3$
2. H$_3$O$^+$

I + II — 685

I + II (70) I:II = 67:33

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° — CO$_2$Et (38) — 345

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(structure: AcO, Br, OBn, N-OBn, dioxolane)	Bu₃SnH, AIBN, C₆H₆, 80°	(structure) (50)	217, 381
(structure: AcO, Br, OBn, dioxolane)	Bu₃SnH, AIBN, C₆H₆, 80°	**I** (structure) + **II** (structure) I + II (52) I:II = 97:3	217
C₂₁ (structure: cyclohexene, amide, SPh, SPh, Me)	Bu₃SnH, AIBN, C₆H₆, 80°	(structure: H, SPh, O, N, Me) (60)	714
(structure: CPh, SePh)	Bu₃SnH, AIBN, C₆H₆, 80°	(structure: Ph) (75) + (structure: Ph) (15)	465

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROA TOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
(structure: EtO₂C, CO₂Et, O, N, Ph aziridine)	Bu₃SnH, AIBN, C₆H₆, 80°	(structure: CO₂Et, O, Me) (72)	551
(structure: R, N-O, O, pyridine-2-thione, SeBn)	C₆H₆, heat, *hv*	(structure: R, N, Se) — $\dfrac{R}{H\ (54)}$ Me (45) Et (60)	789
(structure: furanone + =SO₂Ph)	Heat, *hv*	(structure: PhO₂S, H, S-pyridine, O) (64)	212
(structure: O, SePh, SPh, dioxolane)	Bu₃SnH, AIBN, C₆H₆, 80°	(structure: O, SPh, O, O) (72)	386

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(81)	69
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II (85) I:II = 75:25	785
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II (86) I:II = 46:54	785
R Ac *p*-BrC$_6$H$_4$CO	THF, *h*v, rt	 (49-64) (69)	150
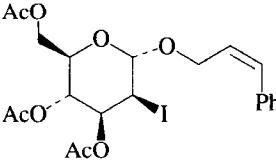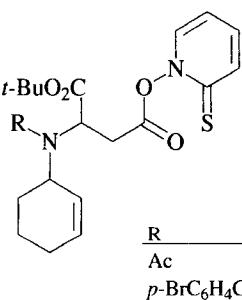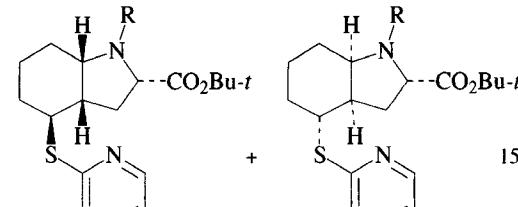
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 (72) β:α = 2:1 (24)	387
	t-BuSH, H$^+$, *h*v	(59)	488
C$_{22}$ X R *p*-OMe Me *p*-OMe Et *p*-OMe Allyl *p*-OMe Bn *m*-OMe Me *m*-OMe Et	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 (57) (60) (60) (62) (58) (63)	790

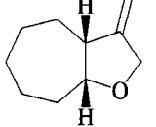TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(88)	791
	Bu₃SnH, AIBN, C₆H₆, 80°	(82)	758
	Bu₃SnH, AIBN, C₆H₆, 80°	$\dfrac{R}{\begin{array}{c}H\ \ (87)\\Me\ \ (85)\end{array}}$	768
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (89) I:II = 43:57	785

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN C₆H₆, 80° PhMe, *hv*, -78°	 I + II (83) I:II = 2.3:1 I + II (88) I:II = 9:1	792
	1. Cp₂TiCl 2. H⁺	(70) *endo:exo* = 83:17	172
C₂₃ Ar =	RuCl₂(PPh₃)₃, C₆H₆, 150°, sealed tube	(57)	793

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{24}$

Bu_3SnH, AIBN,
C$_6$H$_6$, 80°

R^1	R^2
H	H
Me	H
H	Me

(49)
(48)
(43)

431

Ar = 3,4-(MeO)$_2$C$_6$H$_3$

Bu_3SnH, AIBN,
C$_6$H$_6$, 80°

(51)   (30)   712

Bu_3SnH, AIBN,
C$_6$H$_6$, reflux

(56)   (30)   777

Bu_3SnH, AIBN,
C$_6$H$_6$, 80°

(81) 011*E:Z* = 1.2:1   794

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

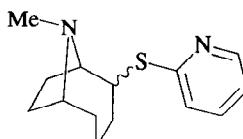| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu_3SnH, AIBN,
PhMe, 110°

I   II

I + II (55)   **I:II** = 1:4.5   690

C$_{25}$

Bu_3SnH, AIBN,
PhMe, 110°

R^1	R^2	
Bz	Et	E
Bn	t-Bu	E
Bn	t-Bu	Z

I   II

I + II	I:II
(91)	1.8:1
(80)	4.5:1
(80)	5.5:1

795,
796

Mg, TMSCl, I$_2$ (cat.),
THF, rt, 60 h

(76) + C-6 and
C-7 epimers

609

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, PhMe, 110°	(100)	696
	Bu₃SnH, AIBN, C₆H₆, 80°	(43)	797
C₂₆	Bu₃SnH, AIBN, C₆H₆, 80°	(62-73)	798
	Bu₃SnH, AIBN, PhMe, heat	(58)	799

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(96) 79 : 21 ratio	785
	C₆H₆, *hv*	(85)	461
C₂₇	Bu₃SnH, AIBN, C₆H₆, 80°	R CH₂CH(CO₂Bu-*t*)₂ (65) H (30)	69

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}	Bu₃SnH, AIBN, C_6H_6, 80°	**I** + **II** I + II (20) I:II = 1:1	764
	Bu₃SnH, AIBN, C_6H_6, 80°		800, 801
R			
CO₂Bu-*t*		(92)	
SO₂Ph		(91)	
C_{29}	C_6H_6, *hv*	(72)	597
C_{30}	Bu₃SnH, AIBN, C_6H_6, 80°	(90) Z:E = 6.5:1	750

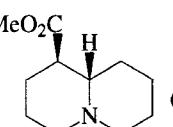TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C_6H_6, 80°	**I** + **II** I + II (80) I:II = 1:1	785
	Bu₃SnH, AIBN, C_6H_6, 80°	(>71)	782
C_{31}	A. Bu₃SnH, AIBN, C_6H_6, reflux B. Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH		738
	A	(85)	
	B	(78)	

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C₃₂

Bu₃SnH, AIBN, PhMe, heat

(50)

360, 82

Bu₃SnH, AIBN, C₆H₆, 80°

(60) *Z:E* = 16:1

750

C₃₃

Bu₃SnH, AIBN, C₆H₆, 80°

(84)

738

C₃₅

AIBN, C₆H₆, 80°

(84)

749

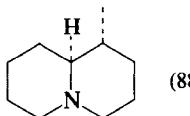TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C₃₆

Bu₃SnH, AIBN

I + II + III

R¹	R²		I + II + III	I:II:III	
H	H	C₆H₆, 80°, 0.01 M	(90)	29:15:56	802,802a
H	H	C₆H₆, 80°, 0.3 M	(95)	48:—:52	792
H	H	PhMe, *h*v, -78°	(88)	55:—:45	792
Me	Me	C₆H₆, 80°	(90)	46:—:54	802,802a
Ph	H	C₆H₆, 80°	(89)	29:—:71	802,802a

Bu₃SnH, AIBN

I + II

792

C₆H₆, 80°   I + II (86) I:II = 6.1:1
PhMe, *h*v, -78°   I + II (95) I:II = 99:1

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

R			
H	C₆H₆, 80°	I + II (92) I:II = 10.1:1	792
H	PhMe, *hv*, -30°	I + II (92) I:II = 32.3:1	792
Me	C₆H₆, 80°	I + II (90) I:II = 62:38	802,802a

C₃₇

	Bu₃SnH, AIBN, C₆H₆, 80°	I, II +	802, 802a

I (*anti*) : II (*syn*) : III
0.01 mol/L   30 : 48 : 22
0.1 mol/L   45 : 50 : 5
0.3 mol/L   50 : 50 : —

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

	Bu₃SnH, AIBN, C₆H₆, 80°	(77)	803

	HgO, I₂, *hv*	(53)	61

C₃₉

	Bu₃SnH, AIBN, C₆H₆, 80°	I +	802, 802a

I + II (95) I:II = 82:18

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

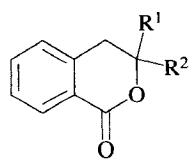| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C43

Bu₃SnH, AIBN, C₆H₆, 80° — (>85) — 696

Bu₃SnH, AIBN, C₆H₆, 80° — (>69) — 696

G. (5+(n+5))-Membered Rings

C8

C₆H₆, *hν* — R: NOH — 164
C₆H₆, O₂, *hν* — H, ONO₂

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C₆H₆, *hν* — (72) — 164

MeOH, HCl, *hν* — I O (11); II (E)-NOH (37); III (Z)-NOH (13) — 413
I, II, III

(t-BuO)₂, O₂ — (29) — 804

C9

Bu₃SnH, AIBN, C₆H₆, 80° — (31) + (53) — 805

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	C_6H_6, $h\nu$	(49)	164
C_{10}	Bu_3SnH, AIBN, C_6H_6, 80°	(88-92)	421
C_{11}	Bu_3SnH, AIBN, C_6H_6, 80°	(25) + (23) + (25)	805
C_{12}	$(Me_3Sn)_2$, $h\nu$	(71)	18

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

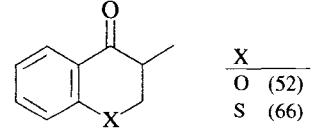| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
		R	
	AcOH, MeCN, 25°	$-SC_5H_4N$ (94)	152
	AcOH, C_6H_6, 4°	$-SC_5H_4N$ (92)	153
	AcOH, C_6H_6, t-BuSH, 4°	H (67)	153
	AcOH, C_6H_6, CBr_4, 4°	Br (60)	503
	AcOH, C_6H_6, $(PhSe)_2$, 4°	SePh (82)	503
C_{15}	AcOH, MeCN, 25°	(60)	152
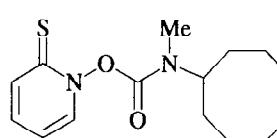
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{16}$	(PhS)$_2$, AIBN, heat	**I** +	806
		II	
		I + II I:II	
	C$_6$H$_6$	(61) 2:1	
	c-C$_6$H$_{12}$	(56) 1:2	
C$_{19}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	**I** + **II**	496
		I + II (92) I:II = 1:10	
	C$_6$H$_6$, hv	(58)	461

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

H. (6+(n+6))-Membered Rings

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_9$	Bu$_3$SnH, AIBN, heat	R^1 R^2 R^3 R^4 H H H H (60) Me H H H (58) H H Me H (58) H H H Me (67)	699
	Ph$_2$SnH$_2$, BPO, C$_8$H$_{18}$, 110°	(62)	272
C$_{10}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	R Me (91) Ph (89) 3,4-(MeO)$_2$C$_6$H$_3$ (91)	757
	FeS$_2$O$_8$	**I** + **II**	807
	pH	I II	
	6.0	(5) (42)	
	5.4	(12) (46)	
	5.1	(17) (45)	
	3.5	(12) (22)	

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS *(Continued)*

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaI, Me$_2$CO, 25°	(65)	707
	1. Ph$_3$GeH, AIBN 2. H$^+$	(85)	54
C$_{11}$	Et$_3$N, MeCN, *h*v	(53)	181
	Bu$_3$SnH, AIBN, PhMe, heat		808

R^1	R^2	
Me	H	(49)
Me	Me	(79)
H	Me	(100)
H	CO$_2$Me	(100)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS *(Continued)*

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH, 80°		809

R	X	Y	
Me	I	O	(64)
Bn	Br	O	(58)
Ac	Br	H$_2$	(70)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		345

R^1	R^2	R^3	
Me	Me	H	(67)
Me	Me	Ph	(60)
Me	Me	CO$_2$Et	(60)
-(CH$_2$)$_2$-		H	(45)
-(CH$_2$)$_3$-		H	(45)
H	H	H	(36)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TsNa, Cu(OAc)$_2$, AcOH, 90°	(73) (68)	280

R
H
CO$_2$Et
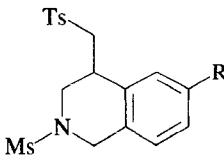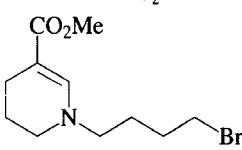
| | Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° | (43) | 723 |

C$_{12}$

| | Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° | | 810 |

R	
i-Pr	(60)
Ph	(70)
C$_6$H$_4$NMe$_2$-*p*	(78)
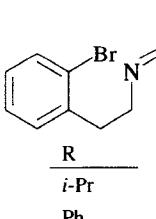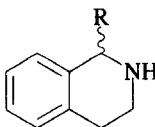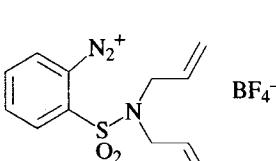
| | NaI, Me$_2$CO, 25° | (57) | 707 |

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{13}$

| | FeCl$_3$, PhC≡CH | | 811 |

R^1	R^2	
H	Ph	(46)
MeO	Ph	(55)
NO$_2$	Ph	(61)
H	Ph	(76)
MeO	Ph	(70)
NO$_2$	Ph	(86)
H	*p*-O$_2$NC$_6$H$_4$	(79)

| | 1,4-Dicyano-naphthalene, *i*-PrOH, *h*v | (88) | 655 |

| | Bu$_3$SnCl, Na(CN)BH$_3$, AIBN, *t*-BuOH, sealed tube, 11 0°, 8 h | (80) | 744 |

| | MeOH, *h*v | (91) 1.2:1 mixture | 226, 518 |
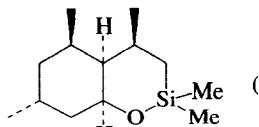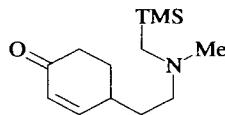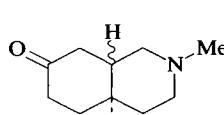
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}	Ph_3SnH, AIBN, C_6H_6, heat	(99)	112
			812

R^1	R^2		
Me	H	$CHCl_3$, *hv*	(62)
p-MeC$_6$H$_4$	H	$CHCl_3$, *hv*	(46)
Me	Me	$CHCl_3$, *hv*	(64)
$-(CH_2)_5-$		$CHCl_3$, *hv*	(42)
Ph	Ph	HgO, I_2, C_6H_6, *hv*	(64)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
$\dfrac{n}{4}$ $\;5$	MeCN, H_2O, *hv*	 **I** **II** (15) (6) (23) (20)	813

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}	Bu_3SnH, AIBN, C_6H_6, 80°, 8 h	(>84)	59
C_{16}	Bu_3SnH, AIBN, C_6H_6, 80°, 8 h	 X O (52) S (66)	814
	1. *hv*, 8° 2. $(PhSe)_2$, *hv*, 8°	(61)	815
	Bu_3SnH, AIBN, C_6H_6, 80°, 8 h	 R^1 R^2 H H (90) H Me (87) Me H (79) H Ph (91)	367
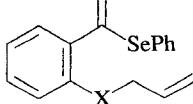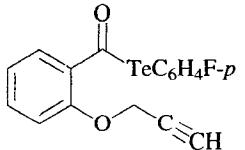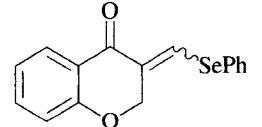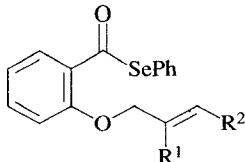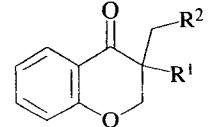
TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETE ROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

DPDC, C_6H_6, 60°

R^1	R^2	
H	CN	(63)
H	Ph	(42)
H	CO_2Me	(41)
Cl	CN	(34)
OMe	CN	(57)
OMe	Ph	(42)
OMe	CO_2Me	(44)
Mc	CN	(55)

816

C_{17}

DPDC, C_6H_6, 60°

R	R^1	R^2	
H	CO_2Me	CO_2Me	(37)
H	CN	CN	(38)
OMe	Ph	Ph	(20)
OMc	CN	CN	(42)
H	Ph	Ph	(40)

816

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

$R^1C{\equiv}CH$, DPDC, C_6H_6, 60°

R	R^1	
Ph	Ph	(75)
m-$O_2NC_6H_4$	Ph	(65)
p-ClC_6H_4	Ph	(65)
p-$MeOC_6H_4$	Ph	(75)
Ph	COMe	(70)
p-ClC_6H_4	COMe	(65)
p-$MeOC_6H_4$	COMe	(85)
Ph	CO_2Et	(75)
p-ClC_6H_4	CO_2Et	(75)
p-$MeOC_6H_4$	CO_2Et	(80)

817

H_2O, heat

R	
Ph	(91)
o-MeC_6H_4	(75)

818

Bu_3SnH, AIBN, C_6H_6, 80°, 8 h

(61)

127

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeCN, $h\nu$	(65)	819
C$_{18}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°, 8 h	**I** + **II** **I** + **II** (83) **I:II** = 1:12.5	764
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°, 8 h	**I** + **II** **I** + **II** (71) **I:II** = 11:3	764
	$h\nu$	(74)	528

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	DPDC, C$_6$H$_6$, 60°		820

X	R^1	R^2	
CH	Ph	H	(45)
CH	Ph	OMe	(72)
CH	p-MeOC$_6$H$_4$	H	(47)
CH	p-MeOC$_6$H$_4$	OMe	(73)
CH	t-Bu	OMe	(57)
N	Ph	OMe	(47)
N	Ph	OMe	(47)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, PhMe, 110°	**I** + **II**	821

R^1	R^2	I	II
–OCH$_2$O–		(56)	(10)
OMe	OMe	(51)	(9)

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{19}$

	HgO, EtOH, 78°	$\dfrac{R}{\text{H} \quad (51)}$ OMe (89)	822
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(69)	33
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(61) *cis:trans* = 7:1 + (29)	489

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	DCA, MeCN, *hv*	(89)	226

C$_{20}$

| | (TMS)$_3$SiH, AIBN, PhMe, 85°, 10 h | (55) | 127, 823 |
| | Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° | R   R^1
Ac CH$_2$OMe (67)
Boc H (55)
Ac CO$_2$Et (25) | 824 |

C$_{21}$

| | Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° | (73) 3:1 | 551 |

TABLE IV. BICYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{25}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(>73)	696
C$_{34}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I 7:1 mixture II 5:1 mixture I + II (100)	795, 796
C$_{39}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I 5:1 mixture II 3:1 mixture (83) $\frac{I + II}{(82)}$	795, 796

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	A. Tricyclic Systems		

C$_9$

Bu$_3$SnH, AIBN, C$_6$H$_6$, $h\nu$
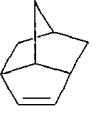
 (60)

366
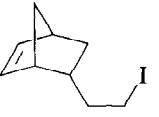
Bu$_3$SnH, AIBN, C$_6$H$_6$, 65°
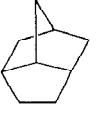
 (98)

825

C$_{10}$
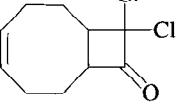
Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°
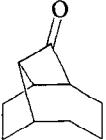
 (85)

535
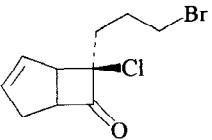
Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°
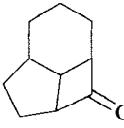
 (74)

601

C$_{11}$
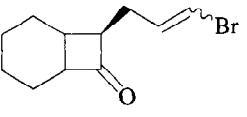
Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°
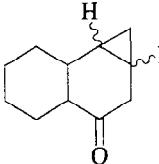
 (45)

826

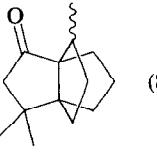TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)
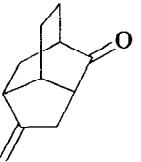
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(75)	827
C₁₂	Bu₃SnH, AIBN, C₆H₆, 80°	(40)	826
	Bu₃SnH, AIBN, C₆H₆, 80°	(61)	535
	Bu₃SnH, AIBN, C₆H₆, 80°	(88)	546
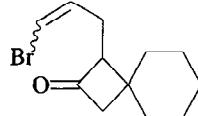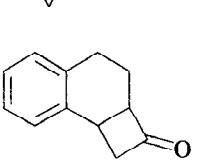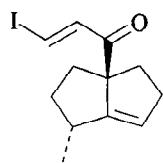
TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(51) ratio 87:13	535
	Bu₃SnH, AIBN, C₆H₆, 80°	(77) + (10)	107
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II (63) I:II = 4:1	828
C₁₃	Bu₃SnH, AIBN, C₆H₆, 80°	(84) 4 isomers: 6.3:5:3.3:1	294
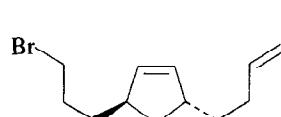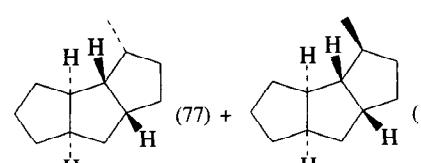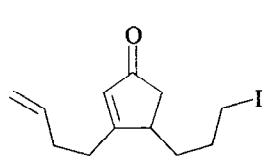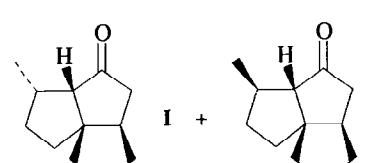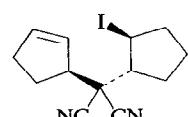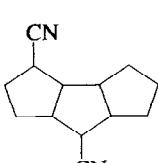
TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(85)	546
	K₃Fe(CN)₆, KOH, CH₂Cl₂	(70)	829
	Bu₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH, 85°	(77)	830
C₁₄	Et₄NOTs, *i*-PrOH, Sn cathode, rt	(74)	610

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, C₆H₆, PhCO₃Bu-*t*, *hv*, 36°	I + II I + II (62) I:II = 3:2	831
	Mn(OAc)₃•H₂O, AcOH, 35°, 15 h	(79)	196
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II (95) I:II = 9:1	832
	Et₄NOTs, *i*-PrOH, Sn cathode, rt	(45)	610
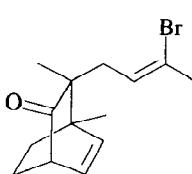
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(70)	27
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(80)	833
	K$_3$Fe(CN)$_6$, KOH, CH$_2$Cl$_2$	(66)	829
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(53)	834
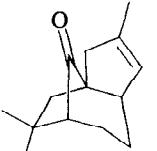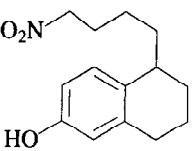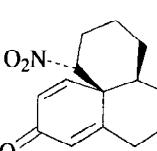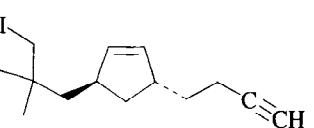
TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeCN, Et$_3$N, *hv*	(58)	835, 836
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(85) *anti:syn* = 4:1	537
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II **I + II** (81) **I:II** = 1.5:1	291
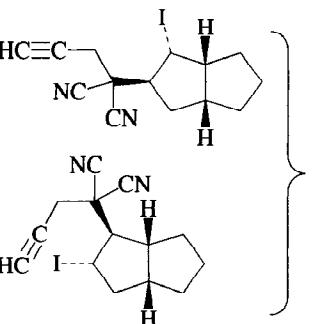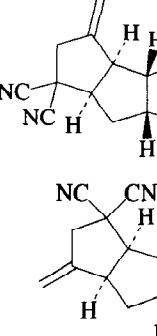
TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhI(OAc)$_2$, I$_2$, *hv*	(58)	837
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(52)	838
	Mn(OAc)$_3$•H$_2$O, AcOH, 35°, 17 h	(81)	196
+ TsCN	AIBN	(72) + (6)	839
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 65°	(85)	567

C$_{15}$

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(55-65) R^1 R^2 H H Me Me H OMe Me OMe	840
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(86)	19
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(97)	570
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(92)	570

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(PhS)$_2$, AIBN, C$_6$H$_6$, *hv*, 80°	(60)	541
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(61)	841
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(64)	107
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(73)	559
	(TMS)$_3$SiH, AIBN, PhMe, 90°	(72)	559
	(Me$_3$Sn)$_2$, C$_6$H$_6$, 80°	(74) *E:Z* = 6:1	159

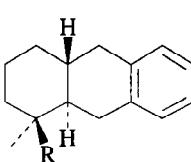| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SmI$_2$, HMPA, THF, 25-30°, 1 h	(69)	559
	NaC$_{10}$H$_8$	(40)	842
	(*t*-BuO)$_2$, *c*-C$_6$H$_{12}$, 150°, sealed tube	I + II I + II (60) I:II = 3:1	104
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	I + II I + II (66) I:II = 3:1	158, 828

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Mn(OAc)₃, Cu(OAc)₂,	(73)	574
	Mn(OAc)₃, Cu(OAc)₂, AcOH, 25°	(61)	569
	(t-BuO)₂, MeCHO, 130°, sealed tube	**I** + **II**	843

I + II + III + IV (54)   I:II:III:IV = 5:1:1:5

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeSH, (MeS)₂, C₆H₆, hν	(100) X = H and SMe ratio 1:1	279
	1,4-CHD, PhCl, 191–210°	(see table below)	844
	Bu₃SnH, AIBN, C₆H₆, 80°	(50)	845
C₁₆	Bu₃SnH, AIBN, C₆H₆, 80°	(see table below)	846

Products for ref. 844:

R¹	R²	
CO₂Me	Me	(93)
Me	CO₂Me	(53)
CH₂OH	H	(>99)
OAc	H	(83)
OMe	H	(95)

Products for ref. 846:

R	
Ph	(85)
p-MeC₆H₄	(93)
p-MeOC₆H₄	(85)
o-MeC₆H₄	(60)
PhC≡C	(82)

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1,4-CHD, PhCl, 210°, 19-24 h		847

R	n
H	1
CH₂OTBDMS	1
H	2

(72)
(58)
(53)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°		832

R	
Me	(95)
CO₂Me	(85)
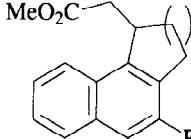
| | Bu₃SnH, AIBN, C₆H₆, 80° | (75) | 560, 561 |

| | Bu₃SnH, AIBN, C₆H₆, 80° | I + II | 34 |

I + II (65)   I:II = 1:5

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₇	Bu₃SnH, AIBN, C₆H₆, 80°, 10 h	(67)	840
	Bu₃SnH, AIBN, C₆H₆, 80°	(75)	848
	1. SmI₂, solvent, 0° 2. TsOH, Me₂CO	I R¹ = OH, R² = H II R¹ = H, R² = OH	849
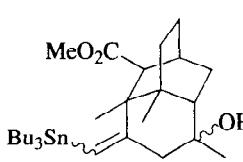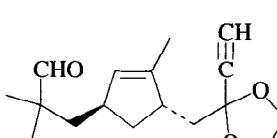
	I + II	I:II
THF, HMPA (20:1)	(63)	100:0
THF, DMPU (20:1)	(69)	91:9
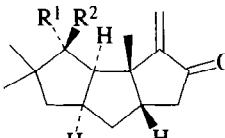
| | Bu₃SnH, AIBN, C₆H₆, 80° | (72) | 546 |

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II 34	
		+ III I + II + III (62) I:II:III = 1:5:2	
C₁₈	1. Ph₃SnH, AIBN, PhMe, 110° 2. Silica gel	(79)	548
	Bu₃SnH, AIBN, C₆H₆, 80°	(78)	828

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	BPO, *c*-C₆H₁₂, 80°	(89)	850
	1,4-CHD, PhCl, 245°, 3 h	(98) 1:1 ratio	586
C₁₉	Bu₃SnH, AIBN, PhMe, 110°	I + II I + II (46) I:II = 1:1	851
C₂₀	Bu₃SnH, AIBN, C₆H₆, 80°	(86)	33

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
$\dfrac{R}{\begin{array}{c}H\\Me\end{array}}$	C_6H_6, 80°	(69) (63)	852
	$NaC_{10}H_8$, THF, 25°	(41)	853, 854
	Bu_3SnH, AIBN, C_6H_6, 80°, 8 h	(62)	855
C$_{21}$	Ph_3SnH, AIBN, C_6H_6, 80°	(80)	340
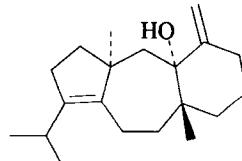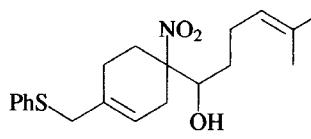
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
$\dfrac{n}{\begin{array}{c}1\\2\end{array}}$	Cu_2O, Cu(OTf)$_2$	I + II (90) I:II 20:1 (87) 20:1	348
C$_{22}$	Bu_3SnH, AIBN, C_6H_6, 80°	(75) 1:1 mixture	199
C$_{23}$	Bu_3SnH, AIBN	$\dfrac{R}{\begin{array}{ll}CO_2Me & (50)\\CN & (58)\\COMe & (30)\\Ph & (60)\end{array}}$	856, 857
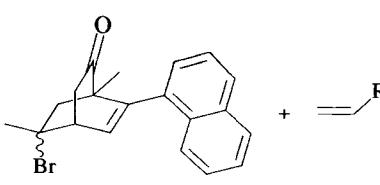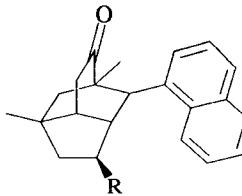
TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)
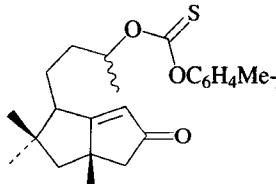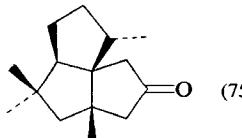
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(75)	858, 859
	Mn(OAc)₃, AcOH, rt	(70)	860
	Bu₃SnH, AIBN, C₆H₆, 80°	(65)	34
	TsI, CH₂Cl₂, 40°	(80)	139
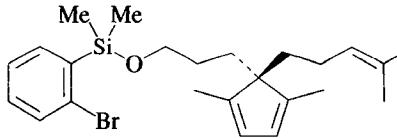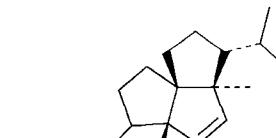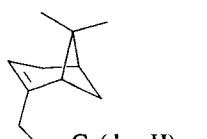
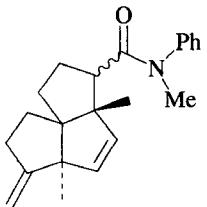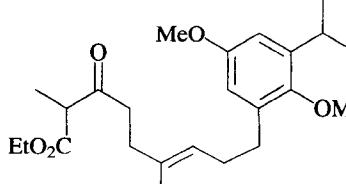TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₂₅	Bu₃SnH, AIBN, C₆H₆, 80°	(35)	199
	Bu₃SnH, AIBN, C₆H₆, 80°	(42)	861
C₂₆	NaC₁₀H₈, THF, MeOH, 25°	(50)	862
	Ph₃SnH, AIBN, C₆H₆, 80°	(91)	352, 585
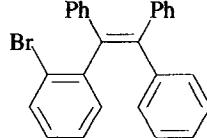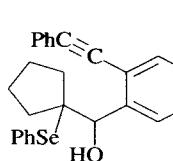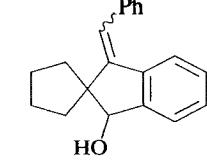
TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}	1. *N*-Methyl- carbazole, 1,4-CHD, THF, H_2O, *hv*, 55°, 5 h 2. PhSH, C_7H_{16}, AIBN, 50°, 30 min	(46)	863

B. Tetracyclic Systems

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}	$(Me_3Sn)_2$, C_6H_6, *hv*	(59)	864
	Bu_3SnH, AIBN, C_6H_6, *hv*	R = H (100) R = OTBDMS (100)	366
C_{11}	Bu_3SnH, AIBN, C_6H_6, 80°	(58)	601

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}	Bu_3SnH, AIBN, C_6H_6, 80°	(85)	827
C_{15}	*t*-BuOH, C_6H_6, *hv*	(90)	865
	Bu_3SnH, AIBN, C_6H_6, 80°	(86)	827
C_{16}	DMF, TBAL, e⁻	I + II	866

n	X	Y
2	Cl	Cl
3	Br	Br

	I	II
	(57)	(0)
	(0)	(55)

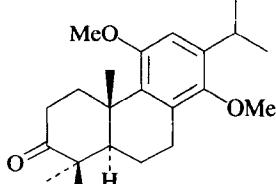TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}	$K_3Fe(CN)_6$, Na_2CO_3	(46)	867
	$K_3Fe(CN)_6$, KOH	(88)	868
C_{19}	Bu_3SnH, AIBN, C_6H_6, 80°	(67)	869
	$(PPh_3)_2ReCl_3$, CCl_4, reflux	(79) *cis:trans* = 4.2:1	282

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$KC_{10}H_8$, THF	(69)	870
C_{22}	Bu_3SnCl, $NaBH_4$, EtOH, *hv*	(67)	871
C_{25}	$Mn(OAc)_3$·2 H_2O, $Cu(OAc)_2$·H_2O, AcOH, rt, 20 h	(31)	872

TABLE V. OLIGOCYCLIC RINGS CONTAINING ONLY CARBON (*Continued*)

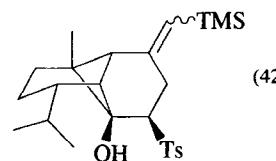| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{28}$	NaC$_{10}$H$_8$, THF	(89)	870
C$_{29}$	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, rt	(79)	873
C$_{33}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(79)	585, 874
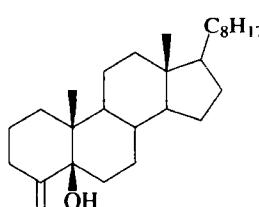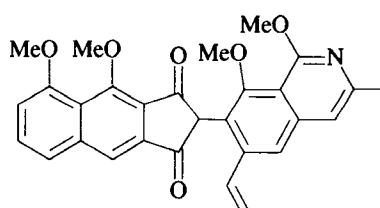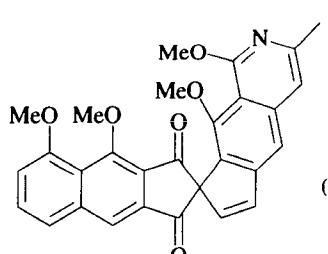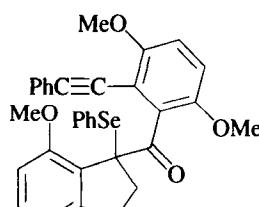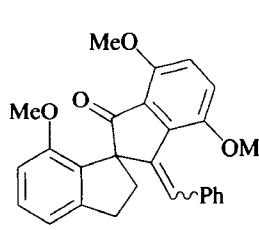
TABLE VI. OLIGOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

A. Tricyclic Systems

C_8

RuCl$_2$(PPh$_3$)$_3$,
C$_6$H$_6$, 160°,
sealed tube

(88)

221

C_9

Mn$_2$(OAc)$_7$,
AcOH, 23°

(63)

191

Mn$_2$(OAc)$_7$,
AcOH, 23°

(61)

191

C_{10}

Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°

R	
H	(86)
Me	(58)

875

Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°

(70)

642

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et₃B, O₂, PhMe, 100°	(38) + (5)	731
	Mn₂(OAc)₇, AcOH, 23°	(63)	191
C₁₁ + CS₂	NaI, Me₂CO, rt	(45)	876
Y ⎯⎯ O NCO₂Et	ClCo(dmgH)₂py, NaBH₄, MeOH, NaOH, 50°	(90) (95)	877

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(30)	878
	Bu₃SnH, AIBN, C₆H₆, 80°	(62)	642
R ⎯⎯ Me OMe H	Bu₃SnH, AIBN	I + II I + II I:II (66) 2:1 (68) 1.7:1 (88) 2.1:1	879
	Me₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH	I, II I + II (86) I:II = 2:1	218

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	ClCo(dmgH)$_2$py, NaBH$_4$, MeOH, NaOH, 50°	 **I** **II** **I + II** (48)	731
	Et$_3$B, O$_2$, PhMe, 100°	 **I** **II** **I + II** (50)	731
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 **I** **II** **+** **III** **I + II + III** (90), **I:II** = 76:24, **(I, II):III** = 85:15	671

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(55)	880
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 **I** **II** **I + II** (64) **I:II** = 1:3	671

C$_{12}$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°		881

Y	X	R	
I	O	Me	(63)
Br	CH$_2$	Me	(40)
I	NMe	Me	(39)
I	O	OMe	(24)
I	O	F	(50)
I	NMe	F	(44)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	BPO, CHCl₃, *hv*	R = H (40) R = Me (40)	882
	ClCo(dmgH)₂py, NaBH₄, MeOH, NaOH, 50°	I (95)	877
	Ni(II)complex, Hg cathode, NH₄ClO₄, DMF	I (86)	702
	Bu₃SnH, AIBN, C₆H₆, 80°		883

R	R¹	R²	R³	
OMe	H	H	H	(85)
Me	H	H	H	(82)
Cl	H	H	H	(82)
OMe	Me	H	H	(80)
OMe	H	Me	H	(78)
OMe	H	H	Me	(75)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°		884

R¹	R²	
H	H	(6)
H	CN	(81)
H	CO₂Me	(73)
OMe	H	(62)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°		885

R	X	
H	I	(79)
OMe	Br	(74)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II (80) I:II = 6:1	878

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(73)	886
	Bu₃SnH, AIBN, C₆H₆, 80°	(63)	887
	Bu₃SnH, AIBN, C₆H₆, 80°	 I + II + III (83) I:II:III = 6:1:2	888

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Me₃SnCl, Na(CN)BH₃, AIBN, *t*-BuOH	(85)	330
	Bu₃SnH, AIBN, C₆H₆, 80°		889

R
———
OH
OBz

	I	II	I, α:β ratio
	(33)	(44)	70:30
	(34)	(46)	—

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	(*t*-BuO)₂, PhCl, 132°	(50)	890
	Bu₃SnH, AIBN, C₆H₆, 80°	(66)	891

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{13}$

| | Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° | R
Ph (91)
Me (86) | 757 |

| | MeOH, *hv* | I + II (40) I:II = 3:1 | 892 |

| | MeOH, *hv* | I + II (55) I:II = 6:1 | 892 |

| | 1. Hg(OAc)$_2$
2. NaBH$_4$ | (72) | 893 |
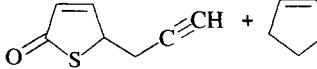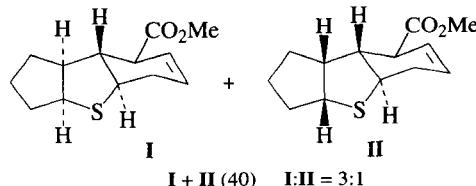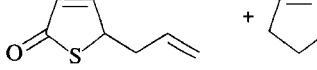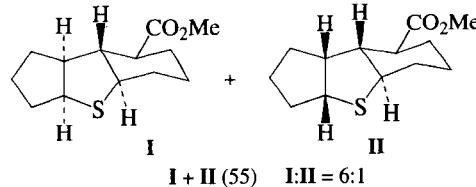
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

| | K$_3$Fe(CN)$_6$, KOH | (84) | 868 |

| | SmI$_2$, HMPA, THF | (31) | 175 |

| | SmI$_2$, HMPA, THF, MeCN | (89) | 175 |

| | (*t*-BuO)$_2$, PhCl, 110° | | 894 |

R^1	R^2	R^3	R^4	
H	H	H	H	(83)
Cl	H	H	H	(85)
MeO	H	H	H	(90)
H	H	NO$_2$	H	(55)
H	Me	H	Me	(95)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
  R —— Me Ph H	Bu₃SnH, AIBN, C₆H₆, 80°	 I + II I II —— (42) (35) (0) (76) (50) (0)	714, 715
	ClCo(dmgH)₂py, NaBH₄, MeOH, NaOH, 50°	(80)	877
	ClCo(dmgH)₂py, NaBH₄, MeOH, NaOH, 50°	(62)	877
	(Bu₃Sn)₂, *hv*, 150°	(70)	895

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(46)	718
	Bu₃SnH, AIBN, C₆H₆, 80°	(70)	896
	Bu₃SnH, AIBN, C₆H₆, 80°	(34)	897
	Bu₃SnH, AIBN, C₆H₆, 80°	(36)	878

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R = OMe R = SPr-*i*	Bu₃SnH, DIPHOS, AIBN, C₆H₆, 80°	I + II I + II (85) I:II = 5:1 I + II (80) I:II = 8:1	878
	Bu₃SnH, AIBN, C₆H₆, 80°	(68)	898
+ ⟶OH	(Bu₃Sn)₂, C₆H₆, *hv*	n = 1 (75) n = 2 (66)	256
	Bu₃SnH, AIBN, C₆H₆, heat	(25)	889
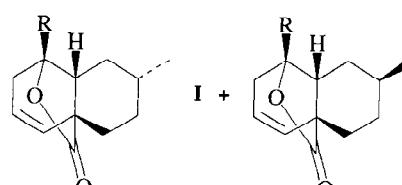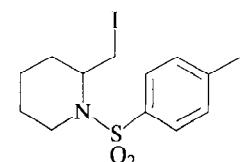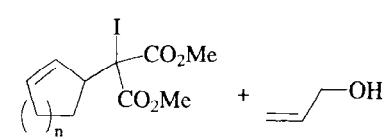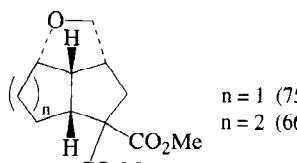
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°		399

R¹	R²
H	CO₂Et
CO₂Me	CO₂Me
CO₂Me	CO₂Me
Me	CO₂Me

R³	R⁴	
CH₂CO₂Et	H	(69)
CO₂Me	CH₂CO₂Me	(67)
CH₂CO₂Me	CO₂Me	(15)
Me, CH₂CO₂Me	Me, CH₂CO₂Me	(89)
diastereomeric mixture, ca. 4:1		

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R: OH / OBz	Bu₃SnH, AIBN, C₆H₆, 80°	α:β (82) 85:15 (80) 80:20	889
	Bu₃SnH, AIBN, C₆H₆, 80°	(31) *endo:exo* = 82:18	671

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, PhMe, 110°	**I** **II** I + II (81) I:II = 86:14 I + II (79) I:II = 47:53	419, 899
	Bu$_3$SnH, AIBN, PhMe, 110°	(75)	900
	Na, NH$_3$, (NH$_4$)$_2$SO$_4$	(90)	901
	Bu$_3$SnH, AIBN, xylenes, 155°	(77)	902

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(60)	722
	Ph$_3$SnH, AIBN, PhMe, 100°	**I** + **II** I + II (85) I:II = 1:3.25	903
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(60)	897
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(100)	904

R
—
H
Me

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			905
	Bu₃SnH, AIBN, C₆H₆, 80°	R = H (85)	
	Bu₃SnH, ⟍CN, AIBN, C₆H₆, 80°	R = (CH₂)₂CN (80)	
	Bu₃Sn⟍⟍, AIBN, C₆H₆, 80°	R = CH₂CH=CH₂ (70)	
	Bu₃SnH, AIBN, C₆H₆, 80°	(100)	904
C₁₄	Bu₃SnH, AIBN, C₆H₆, 80°	(90)	757
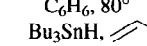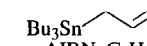
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	t-BuOI, *t*-BuOH, *h*v Pb(OAc)₄	(76) (68)	906
	Bu₃SnH, AIBN, C₆H₆, 80°	(81)	907
MeC≡C⟍⟍I +	(Bu₃Sn)₂, AIBN, *h*v, 150°	I + I + II (62) I:II = 79:21 II	895

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
  R $\overline{\text{CH}_2\text{Cl}}$ CHCl_2 CCl_3	MeCN, H$_2$O, *hv*	 Y = H, X = H (34) Y = OH, X = H (58) YX = O (—)	908
	MeCN, *hv*		908
	H$_2$O MeOH NH$_2$OH	Y = OH (58) Y = OMe (63) Y = NHOH (51)	
	Bu$_3$SnH, AIBN	(45)	909

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
  R $\overline{n\text{-Bu}}$ Et Me	Bu$_3$SnH, AIBN	 I + II + III	910
		I — II — III — I:II (30) — (11) — (9) — 2.3:1 (31) — (13) — (28) — 2.9:1 (12) — (—) — (28) — >10:1	
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	 I + II I + II (63) I:II = 1:3.2	723
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 25°, *hv*		911
	ClCH$_2$SO$_2$Ph PhSCH$_2$CO$_2$Me PhSCH$_2$CN	R $\overline{\text{SO}_2\text{Ph}}$ (84) CO$_2$Me (62) CN (76)	

The I:II header row for the second table: columns I, II, III, I:II.

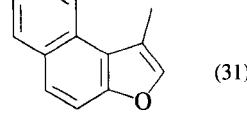| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 E *Z*	Bu₃SnH, AIBN, C₆H₆, 80°	 **I** + **II** (89) **I:II** = 8:1 **I** + **II** (97) **I:II** = 100:0	795
	Bu₃SnH, AIBN, C₆H₆	(41)	714
 R¹ — R² H — CO₂Et Me — CO₂Me	Bu₃SnH, AIBN, C₆H₆, 80°	 (75) 5:1 mixture of isomers (77) 9:1 mixture of isomers	399

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(65)	57
 E:Z = 1:1 R OMe CO₂Me	Bu₃SnH, AIBN, C₆H₆, 80°	 **I** **II** **I + II** **I:II** (84) 92:8 (86) 93:7	217
	Bu₃SnH, AIBN, C₆H₆, 80°	(80)	399

Reactant	Conditions	Pr oduct(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	I +	880

Z R = Me
E R = Et

I + II (85) I:II = 9:1
I + II (74) I:II = 2:1

C₁₅

| | Bu₃SnH, AIBN, C₆H₆, 60° | I, II +   III, IV | 912 |

	R¹	R²
I, III	Me	CO₂Et
II, IV	CO₂Et	Me

Y
―
O
CH₂

I-IV (92) I:II:III:IV = 83:1:11:4
I-IV (79) I:II:III:IV = 61:7:24:8

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II	913
	Bu₃SnH, AIBN, C₆H₆, 80°	(97)	914
	A: Pt foil anode, CH₂(CO₂R)₂, n-Bu₄NBr, MeCN	I + II	915

I + II (84) I:II = 7.4:1

A
A + LiClO₄
A + Mg(ClO₄)₂

I + II (90) I:II = 1:1
I + II (77) I:II = 3:1
I + II (62) I:II = 11.4:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$S_2O_8^{2-}$, Fe^{2+}	R H (71) Me (60) Ph (66)	916
	Bu_3SnCl, $Na(CN)BH_3$, AIBN, *t*-BuOH, 80°	(85)	713
	Bu_3SnH, AIBN, C_6H_6, 80°	(73)	497, 48
	Bu_3SnH, AIBN, C_6H_6, 80°	(95)	917

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R H Me	$Mn(OAc)_3$, AcOH, NaOAc, 110°	I + II I:II (38) 1.8:1 (77) 2.7:1	918
$R^1 = CO_2Et$, $R^2 = Me$ $R^1 = Me$, $R^2 = CO_2Et$	Bu_3SnH, AIBN, C_6H_6, 80°	R^3 R^4 I II Me H (4) (4) H Me (4) (81) Me H (12) (1) H Me (15) (37)	98, 912
	Bu_3SnH, AIBN, C_6H_6, 80°	I + II (67) I:II = 65:35	111, 438

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 E *E/Z* mixture 5:1	Bu₃SnH, AIBN, C₆H₆, 80°	 **I** + **II** | I + II	I:II
---	---
(61)	10:1
(56)	4.5:1		919
	Bu₃SnH, AIBN, C₆H₆, 80°	 R = CO₂Me, one diastereomer, (61) R = Me, one diastereomer, (61)	399
	Bu₃SnH, AIBN, C₆H₆, 80°	 **I** + **II** **I + II** (—) **I:II** = 7:3	671

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 R OC(S)SMe OC(S)Im	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + **II** | I + II	I:II
---	---
(73)	88:12
(88)	88:12		671
	(Me₃Sn)₂, *hv*	(42)	18
	Mn(OAc)₃, AcOH, O₂, rt	(30)	618

Reac tant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, c-C$_6$H$_{12}$, heat	R^1 R^2 Me H **I** **I + II** (67) H Me **II** **I:II** = 3:7	23
	Bu$_3$SnH, Et$_3$B	(67)	920
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(52)	723
	Bu$_3$SnH, AIBN	(72)	921
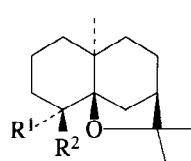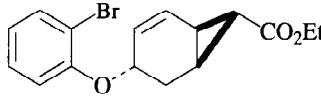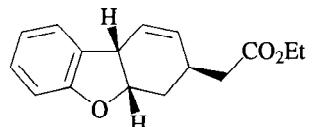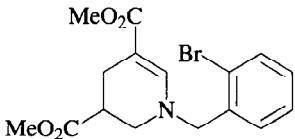
C$_{16}$

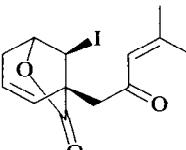TABLE VI. OLIGOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

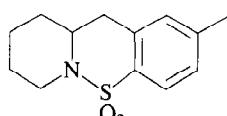| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
R = α-Me	Bu$_3$SnH, AIBN	(95)	914, 922
R = β-Me		(95)	
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(50)	897
	Bu$_3$SnH, AIBN, PhMe, 110°, 2 h	CO$_2$Et (81)	923
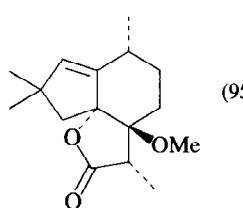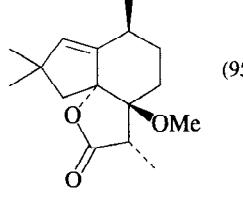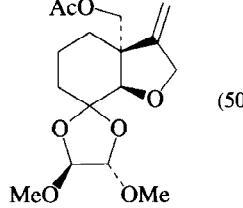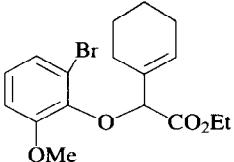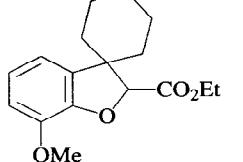
C$_{17}$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(68)	924
	Bu₃SnH, AIBN, C₆H₆, 80°	$\dfrac{R}{\begin{array}{ll} H & (45) \\ TMS & (60) \end{array}}$	925
	Bu₃SnH, AIBN, xylene, 140°	(60)	463
	Bu₃SnH, AIBN, C₆H₆, 80°	(80)	905

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(73)	888
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II (89) I:II = 4:1	99
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II (75) I:II = 91:9	217
	UV, (450-W Hanovia), THF, rt, 45 min	(33)	926

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	4 isomers in ratio 68:14:12:6	671

R
OC(S)SMe
OC(S)Im

(83)
(76)
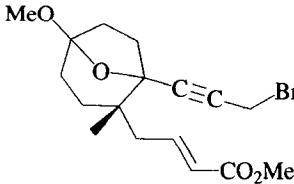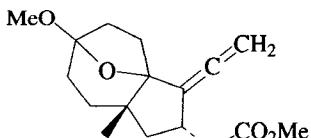
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°, 2 h	(93) >10:1	542
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(>90)	122

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. KOH, MeOH, 2. Mn$_3$(OAc)$_7$, AcOH	(68)	927
	Pt-foil anode, CH$_2$(CO$_2$R)$_2$, n-Bu$_4$NBr, MeCN	I + II I + II (90) I:II = 1:1	915
C$_{18}$	RuCl$_2$(PPh$_3$)$_3$, C$_6$H$_6$, 80°, 72 h	(93)	928
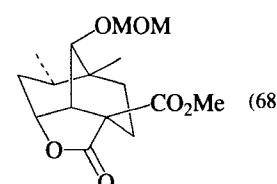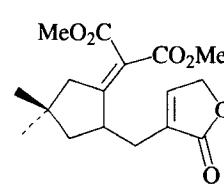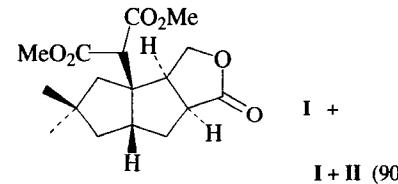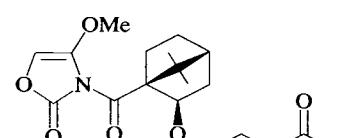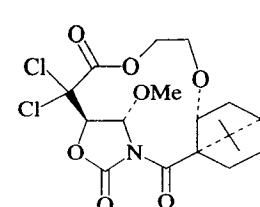
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN	**I** + **II**	99
	NaI, Me₂CO, -20°	R = 4-MeC₆H₄ (84) R = 4-ClC₆H₄ (90)	929, 930
PhC≡C—CH₂CH₂—I +	(Bu₃Sn)₂, *hv*, 150°	**I** + **II** **I** + **II** (57) **I:II** = 93:7	895
	Bu₃SnH, AIBN, PhMe, 110°	(71)	931

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(47)	560, 561
	Bu₃SnH, AIBN, C₆H₆, DIPHOS	(60) 1 : 1 mixture of isomers	878
(1:1)	Bu₃SnH, AIBN, C₆H₆, 80°	(30) α:β = 90:10	889
	Bu₃SnH, AIBN, C₆H₆, 80°	(>69)	753

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
			932

n	R		
1	Me	MeOH, hv	(87)
1	CH₂CO₂Et	MeCN, hv	(70)
2	CH₂CO₂Et	MeOH, hv	(71)
3	Me	MeOH, hv	(66)

| | Bu₃SnH, AIBN | | 23 |

C_{19}

| | Bu₃SnH, AIBN PhMe, 110° | | 715 |

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	DPDC, C₆H₆, 60°		933

R	R¹		
H	Ph		(85)
Cl	Ph		(90)
OMe	4-ClC₆H₄		(85)
H	4-O₂NC₆H₄		(86)
H	4-MeOC₆H₄		(86)
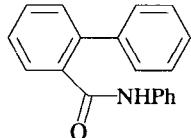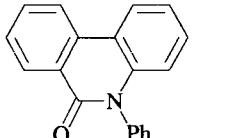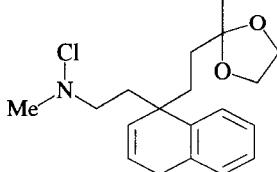
| | K₂S₂O₈, H₂O, 100° | (97) | 934 |

| | CuCl₂, CuCl, THF, AcOH, H₂O | | 163 |
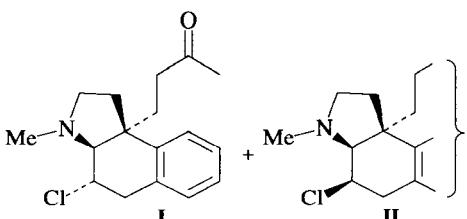
I + II (84) **I:II** = 2.2:1

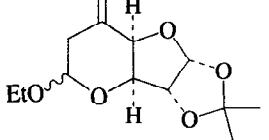TABLE VI. OLIGOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO, MeO-substituted tetrahydroisoquinoline with N-C(O)CCl₃ and CH₂CH=CHCO₂Et side chain	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + (structure, MeO, MeO, N, O, H, CH₂CO₂Et) and **II** (structure, MeO, MeO, N, O, H, CH₂CO₂Et); I + II (60), I:II = 3.3:1	935
TBDMSO, HC≡C-, MesO, dioxaspiro cyclopentane	1. NaI 2. Bu₃SnH, AIBN	TBDMSO, (=CH₂) fused bicyclic with dioxane spiro (91)	555
Indole 2-Ts, N-(CH₂)₄I	Bu₃SnH, AIBN, C₆H₆, 80°	fused indolizidine-type tricyclic (71)	931

TABLE VI. OLIGOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

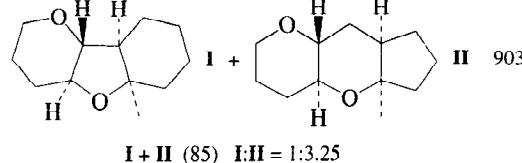| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
2-Br-benzoyl on N of oxazolidine with Me, Ph, vinyl substituents	Bu₃SnH, AIBN, C₆H₆, 80°	**I** + (tricyclic with 6, O, N, Me, Ph, H) and **II** (tricyclic with 6, O, N, Me, Ph, H); I + II (50), I:II = 85:15	936
octahydronaphthalene with C(CH₃)(C=O)OCH₂SePh	Bu₃GeH, AIBN, C₆H₆, 80°	**I** (H, fused lactone, Me, O, O) + **II** (H, fused lactone, Me, O, O); I + II (73) I:II = 1:2.4	50
Ph-benzylidene acetal pyranose, OHC, MeO, OMe, CH₂CH₂I	Bu₃SnH, AIBN, C₆H₆, 80°	Ph, O, O, HO, OMe, OMe bicyclic (85)	42

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₂₀	Bu₃SnH, C₆H₆, *hv*	R = Ph or SPh (60-85)	937
	Bu₃SnH, AIBN, C₆H₆, 80°	(85) 2:1 ratio	42
C₂₁	Bu₃GeH, AIBN, C₆H₆, 80°	(83)	50
	MeCN, *hv*	(47) *trans:cis* = 3:1	908

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN	I +	938
		II	
	Bu₃SnH, AIBN, C₆H₆, 80°	I +	671
		I + II (45) I:II = 83:17	
		II	

R	I	II
Me	(30)	(50)
Ph	(75)	(13)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(85)	79
	MeOH, *hv*	(60)	932, 939
	t-BuSH, *hv*	(57)	940
	Ph₃SnH, AIBN, C₆H₆, heat	(77)	112

C₂₂ appears at left margin near second structure.

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 R Y H CH₂ NMe₂ S	A: (Ph₂S)₂, AIBN, C₆H₆, 40°, *hv* B: (Ph₂COSnMe₃)₂, C₆H₆, 80° A (94) B (85)		941
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II (92) I:II = 10:1	942
	Bu₃SnH, AIBN, C₆H₆, 80°	(98)	943
	Bu₃SnH, AIBN, C₆H₆, 80°	(36)	345

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{23}$

Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

R	
H	(57)
3-OMe	(63)
4-OMe	(65)

944
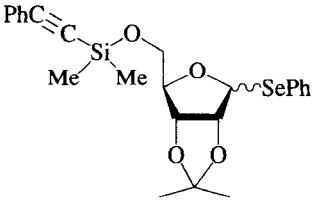
Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°
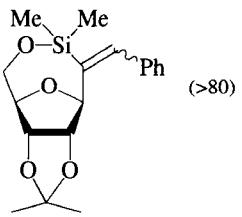
   (>80)

696
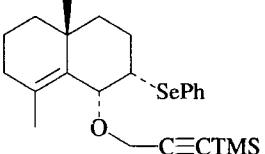
Bu$_3$SnH, Et$_3$B, C$_6$H$_{14}$, rt

 TMS

I, II   I + II (75)
I:II = 1:1

945

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

 TMS   I

945

1. Ph$_3$SnH, AIBN, C$_6$H$_6$, 80°
2. [O]

I (52)

1. Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°
2. CrO$_3$, py, CH$_2$Cl$_2$

I (58) E:Z = 5.5:1

134

C$_{25}$
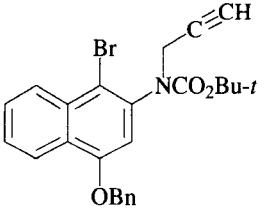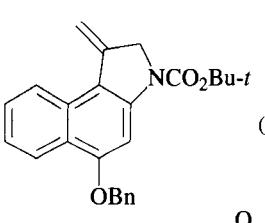
Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°

   (>62)

946
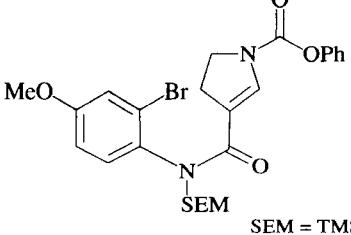
Bu$_3$SnH, AIBN, PhMe, 110°
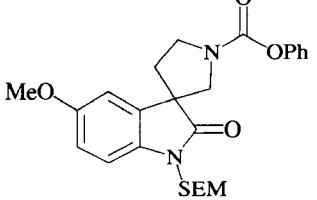
   (70)

947

SEM = TMS(CH$_2$)$_2$OCH$_2$

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{26}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(66)	50
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(75) *E:Z* = 1:1	948
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	R H (65) OBn (70)	948

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{29}$	Bu$_3$SnH, AIBN,	I +	792
		II	
	C$_6$H$_6$, 80°	I + II (95) I:II = 1.6:1	
	PhMe, –78°, *h*v	I + II (95) I:II = 3.8:1	
	Bu$_3$SnH, AIBN,	I +	792
		II	
	C$_6$H$_6$, 80°	I + II (96) I:II = 8.1:1	
	PhMe, –78°, *h*v	I + II (96) I:II = >150:1	

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{37}$	Bu$_3$SnH, AIBN, PhMe, 90°	(80)	949
C$_{41}$	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(70)	905
C$_{44}$	K$_2$Fe(CN)$_6$, OH$^-$	(95)	950
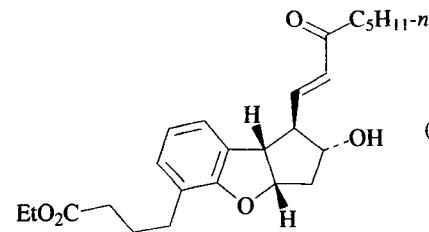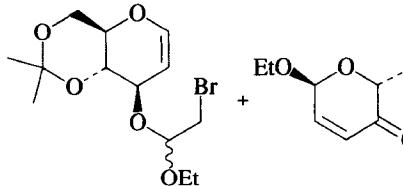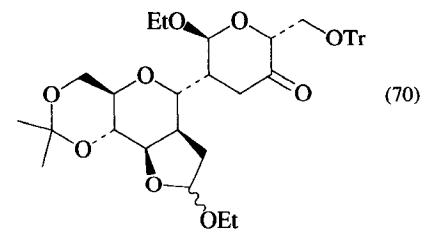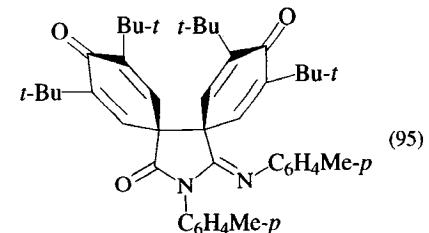
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{48}$	Bu$_3$SnH, Et$_3$B	I + + II	527
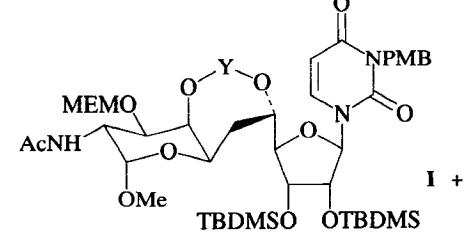
Y		I + II	I:II
SiMe$_2$	MeCN, -10 to 23°	(80)	1:3.4
SiMe$_2$	PhMe, 0°	(74)	6:1
Si(OMe)$_2$	PhMe, 0°	(—)	3:1
Me$_2$SiOSiMe$_2$	PhMe, 0°	(—)	>95:5

TABLE VI. OLIGOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C₅₆

C₅₇

Bu₃SnH, AIBN, C₆H₆, 80° (>40) 951

Bu₃SnH, AIBN, PhMe, 110° (>35) 952

TABLE VI. OLIGOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)
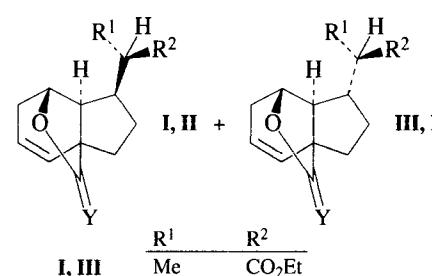
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C₆₀

Bu₃SnH, Et₃B, 0°   I + 953
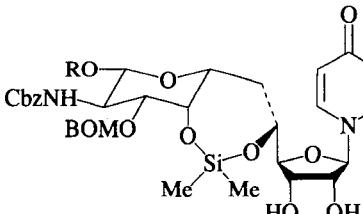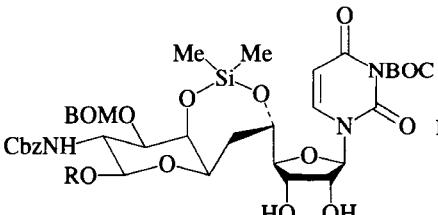
	I + II	I:II
PhMe	(>68)	7.5:1
MeOH	(—)	1.6:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	B. Tetracyclic Systems		

C_{13}

| | 1. Bu_3SnH, AIBN, C_6H_6, 80°
2. AcOH, H_2O | (35) | 954 |

C_{14}

| | Bu_3SnH, AIBN, C_6H_6, 80° | (66) | 955 |

| | NH_3, K, THF, $(NH_4)_2SO_4$ | (75) | 956 |

C_{15}

| | $(Me_3Sn)_2$, C_6H_6, *h*v, 80° | (40) | 957 |

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu_3SnH, AIBN, C_6H_6, 80°		958

R	R^1	R^2	
H	H	H	(82)
OMe	–CH=CHCH=CH–		(90)
Cl	–CH=CHCH=CH–		(88)

| | Bu_3SnH, AIBN, C_6H_6, heat | (51) | 887 |

| | Bu_3SnH, AIBN, C_6H_6, 80° | (68) | 887 |

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₆	Bu₃SnH, AIBN, C₆H₆, 80°, *hv*	(53)	959
	Bu₃SnH, AIBN, C₆H₆, 80°, *hv*	(35)	959
	Bu₃SnH, AIBN, C₆H₆, 80°	(55)	887

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(81)	960
	Bu₃SnH, AIBN, C₆H₆, 80°	(31) + (40)	961
C₁₇	Bu₃SnH, AIBN, C₆H₆, 80°	(67)	962
	K₃Fe(CN)₆, KOH	(57)	868

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Bu₃SnH, AIBN 2. [O]	(82) 3.8:1 mixture	963
	Carbon felt anode		964

R		Y	
Ac		OH	(70)
CO₂Bu-*t*		OH	(70)
Me		OAc	(73)

| | Bu₃SnH, AIBN | I + II | 158, 828, 965 |

I + II (65) I:II = 2.5:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₈	Bu₃SnH, AIBN, C₆H₆, 80°	(90)	686
	Bu₃SnH, AIBN	(62)	966
	1. Cycloaddition 2. Bu₃SnH, AIBN	(70)	962
	Bu₃SnH, AIBN, C₆H₆, 80°	I + II	345
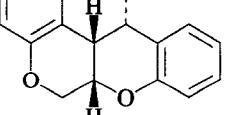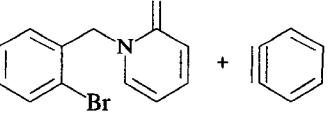
Y	Z		I	II
H	H		(21) *cis* Me, H	(35) *trans* Me, H
TMS	H		(—)	(54)
H	CO₂Et		(36)	(36)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{19}

Bu₃SnH, AIBN, C₆H₆, 80°

R^1	R^2	R^3
OMe	OMe	OMe
H	H	H
H		-OCH₂O-

R^1	R^2	R^3	
OMe	OMe	OMe	(60)
H	H	H	(60-80)
H		-OCH₂O-	(60-80) 6:1
-OCH₂O-		H	

967

Bu₃SnH, AIBN, *o*-xylene, 140°

(91)

923

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

Bu₃SnH, AIBN PhMe, 110°

R = H (61)
R = OMe (62)

968
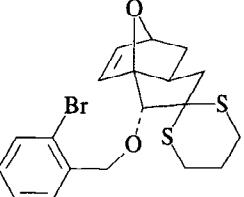
Bu₃SnH, AIBN C₆H₆, 80°
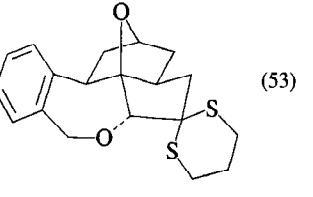
(53)

887
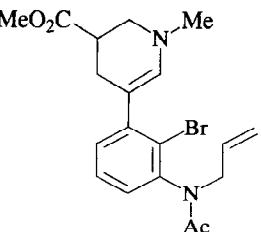
Bu₃SnH, AIBN PhMe, 110°, 20 h
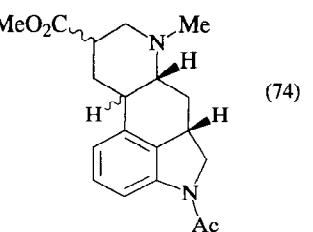
(74)

969

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{20}

| | 1. Bu₃SnH, AIBN
2. H⁺ | (80) | 943 |
| Ph, O, O, NC, OMe, I (structure) | | Ph, O, O, O=, OMe, H (structure) | |

| | Bu₃SnH, AIBN,
C₆H₆, 80° | I + II (91) I:II = 1:4 | 970 |
| Ph, O, O, OHC, OMe, I (structure) | | **I** (HO, H, H, OMe)   **II** (HO, OMe) | |

| | (Me₃Sn)₂, *hv*, 80° | (45) | 957 |
| HC≡C—N, O, Br, CO₂Me, Et (structure) + NC—Ph (phenyl isocyanide) | | quinoline-fused structure with CO₂Me, Et | |

| | Bu₃SnH, AIBN,
C₆H₆, 80° | | 971, 972 |
| MeO, MeO, O, X, Br, OMe, MeO (structure) | | MeO, MeO, O, X, MeO, MeO (structure)   X: O (49), NH (60) | |

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{21}

| | Bu₃SnH, AIBN,
C₆H₆, 80° | I + II (84) I:II = 1:1 | 917 |
| Br, Me—N, OMe, O, MeO (structure) | | **I** (Me—N, O, MeO, OMe)   **II** (Me—N, MeO, O, OMe) | |

| | Bu₃SnH, AIBN,
C₆H₆, 80° | (91) | 970 |
| Ph, O, O, HC≡C, OMe, I (structure) | | Ph, O, O, O, OMe, H (structure) | |

| | 1. Bu₃SnH, AIBN,
C₆H₆, 80°
2. CH₂Cl₂, silica gel | (85) | 973 |
| Ph, O, O, NC, OMe, HC≡C (structure) | | Ph, O, O, O=, OMe, H (structure) | |

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO, MeO (tetrahydroisoquinoline with N-CH₂-benzyl, Br, R, R)	Bu₃SnH, AIBN, PhMe, 110°	MeO, MeO (fused polycyclic) R = –CH₂O– (51), R = Me (32)	968
Ph pyrazole with X, Ph. X = Cl, Br, I, OAc, OMe	MeOH, *hv*	Ph (fused pyrazolophenanthridine) (80), (84), (83), (61), (52)	974, 975
Ph–O, O, O= ketone, OMe, I	Bu₃SnH, AIBN, C₆H₆, 80°	Ph–O, O, O=, OMe (94)	943

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
naphthalimide with N-CH₂CH₂CH=CH-Ph	MeOH, MeCN (1:1) *hv*	Ph, HO, OMe (55) + Ph, HO, OMe (16)	976
naphthalimide (angular) with N-CH₂CH₂CH=CH-Ph	MeOH, MeCN (1:1) *hv*	Ph, HO, OMe (57) + (angular product) HO, Ph, OMe (34)	976

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{22}$

	1. Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° 2. CH$_2$Cl$_2$, silica gel	(92)	973
	1. Bu$_3$SnH, AIBN, C$_6$H$_6$, 80° 2. CH$_2$Cl$_2$, silica gel	(91)	977
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(82)	978
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(>63)	979

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{23}$

	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(94)	980
	1. Bu$_3$SnH, AIBN, PhMe, 110° 2. DDQ	R = Ph (84) R = H (86)	981
	1. Bu$_3$SnCl, NaH 2. Bu$_3$SnH, AIBN, PhMe, 110°	(73)	981

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{24}$			
	Bu$_3$SnH, AIBN	(51) +	982
		(28)	
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(65)	71
C$_{25}$			
	Bu$_3$SnH, AIBN	(48)	982

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(50)	983
C$_{26}$			
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(70)	984
	SmI$_2$, THF, 25°	(92)	985

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₃₀	Bu₃SnH, AIBN, C₆H₆, 80°, 18 h	(52)	969
C₃₁	Bu₃SnH, AIBN, C₆H₆, heat, 35 h	(35)	986
	Bu₃SnH, AIBN, C₆H₆, 80°	(70)	987, 988

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₃₃	Bu₃SnH, AIBN, C₆H₆, 80°	R = H (57) R = Me (82)	987, 988
C₃₈	Bu₃SnH, AIBN, C₆H₆, 80°	(65)	133

C. Polycyclic Systems

C₁₆	Bu₃SnH, AIBN, C₆H₆, 80°	(59)	887
C₁₇	Bu₃SnH, AIBN, C₆H₆, 80°	X = O (76) X = NMe (54) X = SO (67)	887, 962

TABLE VI. OLIGOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(67)	962
	Ph₃SnH, AIBN, C₆H₆, 80°	(55) (37)	989
C₂₀	Bu₃SnH, AIBN, C₆H₆, 80°	(56)	886

TABLE VI. OLIGOCYCLIC RINGS CONTAINING ONE OR MORE HETEROATOMS (*Continued*)

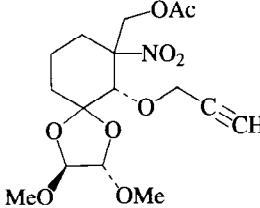| Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C₂₂	Bu₃SnH, AIBN, xylene	(80)	990
C₂₅	MeOH, MeCN (1:1), *hv*	(49)	976
E *Z*	Bu₃SnH, AIBN, C₆H₆, 80°	I + II I + II (>55) I:II = 49:51 I + II (>48) I:II = 43:57	991

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, PhMe, 110°	R = H (68) R = OAc (70)	992
C₂₇	Bu₃SnH, AIBN, C₆H₆, 80°	(52) + (16)	993
C₂₉	*t*-BuSH, THF, *h*ν, 80°	(60)	994

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu₃SnH, AIBN, C₆H₆, 80°	(70)	58
	Bu₃SnH, AIBN, C₆H₆, 80°	(65)	58
	Bu₃SnH, AIBN, C₆H₆, 80°	(>75)	101

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{30}

A: Li/NH$_3$, THF, -78°
B: Bu$_3$SnH, AIBN,
   PhMe, 110°

995

R	X		
H	F	A	(82)
H	Cl	A	(81)
H	Br	A	(85)
H	Br	B	(89)
OMe	Br	A	(89)
OMe	Br	B	(92)

C_{31}

R = TBDMS

Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°

(73)   996

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{30}

Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°

I +   II   991

R^1	R^2		
H	(CH$_2$)$_2$Pr-*i*	I + II (>62)	I:II = 100:0
(CH$_2$)$_2$Pr-*i*	H	I + II (>56)	I:II = 0:100

C_{33}

Bu$_3$SnH, AIBN,
C$_6$H$_6$, 80°

I +   997

II

I + II (65) I:II = 4:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{34}$			
	Bu$_3$SnH, AIBN, PhMe, 110°	(50)	991
C$_{36}$			
	Bu$_3$SnH, AIBN, C$_6$H$_6$, 80°	(46)	917
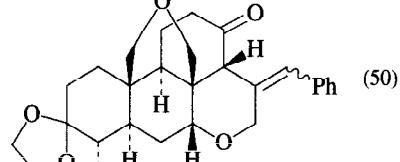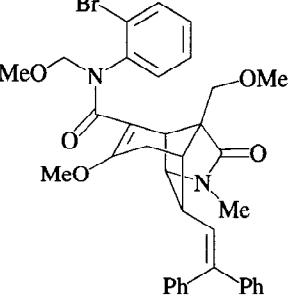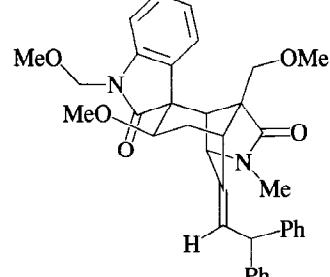
References

1. J.-M. Surzur in *Reactive Intermediates*, R. A. Abramovitch, Ed., **Vol.2**, Plenum Press, New York, 1982, p. 121.
2. D. P. Curran, Synthesis, **417**, 489 (1988).
3. M. Ramaiah, Tetrahedron, **43**, 3541 (1987).
4. D. P. Curran in *Comprehensive Organic Synthesis*, B. M. Trost, and I. Fleming, Eds.; **Vol.IV**, Pergamon Press, London, 1991, p. 779.
5. C. P. Jasperse, D. P. Curran, and T. L. Fevig, Chem. Rev., **91**, 1237 (1991).
6. B. Giese in "Radicals" in *Organic Synthesis, Formation of Carbon-Carbon Bonds*, Pergamon Press, Oxford, 1986.
7. M. Regitz and B. Giese in Houben-Weyl, Methoden der Organischen Chemie, Vol. **E19a**, G. Thieme Verlag, Stuttgart, 1989.
8. M. B. Motherwell and D. Crich in *Best Synthetic Methods, Free Radical Chain Reactions in Organic Synthesis*, Academic Press, London, 1991.
9. A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Serelis, J. Am. Chem. Soc. **102**, 1734 (1980).
10. A. L. J. Beckwith and K. U. Ingold in *Rearrangements in Ground and Excited States*, P. de Mayo, Ed., Academic Press, New York, 1980.
11. Z. Cekovic and R. Saicic, Tetrahedron Lett., **31**, 6085 (1990).
12. M. E. Jung, J. D. Trifunovich, and N. Lensen, Tetrahedron Lett., **33**, 6719 (1992).
13. A. L. J. Beckwith and C. H. Schiesser, Tetrahedron, **41**, 3925 (1985).
14. A. L. J. Beckwith, Tetrahedron, **37**, 3073 (1981).
15. D. C. Spellmeyer and K. N. Houk, J. Org. Chem., **52**, 959 (1987).
16. A. L. J. Beckwith, J. C. Christopher, T. Lawrence, and A. K. Serelis, Aust. J. Chem., **36**, 545 (1983).
17. S. Hanessian, D. S. Dhanoa, and P. L. Beaulieu, Can. J. Chem., **65**, 1859 (1987).
18. D. P. Curran and C.-T. Chang, J. Org. Chem., **54**, 3140 (1989).
19. D. L. J. Clive and D. R. Cheshire, J. Chem. Soc., Chem. Commun., **1987**, 1520.
20. M. Julia, Acc. Chem. Res., **4**, 386 (1971).
21. M. Julia, Pure Appl. Chem., **40**, 553 (1974).
22. M. Julia and M. Maumy, Org. Synth., **55**, 57 (1976); Org. Synth., Coll. Vol., **6**, 586 (1988).
23. G. Büchi and H. Wüest, J. Org. Chem., **44**, 546 (1979).
24. G. Stork and N. H. Baine, J. Am. Chem. Soc., **104**, 2321 (1982).

25. G. Stork and R. Mook, Jr., Tetrahedron Lett., **27**, 4529 (1986).

26. A. L. J. Beckwith and D. M. O'Shea, Tetrahedron Lett., **27**, 4525 (1986).

27. K. Nozaki, K. Oshima, and K. Utimoto, J. Am. Chem. Soc., **109**, 2547 (1987).

28. G. Stork and N. H. Baine, Tetrahedron Lett., **26**, 5927 (1985).

29. A. L. J. Beckwith and W. B. Gara, J. Chem. Soc., Perkin. Trans. 2, **1975**, 795.

30. H. Urabe and I. Kuwajima, Tetrahedron Lett., **27**, 1355 (1986).

31. K. A. Parker, D. M. Spero, and K. C. Inman, Tetrahedron Lett., **27**, 2833 (1986).

32. A. N. Abeywickrema, A. L. J. Beckwith, and S. Gerba, J. Org. Chem., **52**, 4072 (1987).

33. D. L. Boger and R. J. Mathvink, J. Org. Chem., **57**, 1429 (1992).

34. C. E. Schwartz and D. P. Curran, J. Am. Chem. Soc., **112**, 9272 (1990).

35. D. L. Boger and R. J. Mathvink, J. Org. Chem., **53**, 3377 (1988).

36. M. D. Bachi and E. Bosch, Heterocycles, **28**, 579 (1989).

37. P. A. Bartlett, K. L. McLaren, and P. C. Ting, J. Am. Chem. Soc., **110**, 1633 (1988).

38. D. L. J. Clive, P. L. Beaulieu, and L. Set, J. Org. Chem., **49**, 1313 (1984).

39. A. L. J. Beckwith and B. P. Hay, J. Am. Chem. Soc., **111**, 230 (1989).

40. R. Tsang, J. K. Dickson, Jr., H. Pak, R. Walton, and B. Fraser-Reid, J. Am. Chem. Soc., **104**, 3484 (1987).

41. R. A. Walton and B. Fraser-Reid, J. Am. Chem. Soc., **113**, 5791 (1991).

42. R. Tsang and B. Fraser-Reid, J. Am. Chem. Soc., **108**, 8102 (1986).

43. A. Padera, H. Nimmesgern, and G. S. K. Wong, Tetrahedron Lett., **26**, 957 (1985).

44. T. W. Smith and G. B. Butler, J. Org. Chem., **43**, 6 (1978).

45. A. L. J. Beckwith, I. A. Blair, and G. Phillipou, Tetrahedron Lett., **96**, 1613 (1974).

46. A. L. J. Beckwith and S. A. Glover, Aust. J. Chem., **40**, 157 (1987).

47. A. Padwa, W. Dent, H. Nimmesgern, M. K. Venkatramanan, and G. S. K. Wong, Chem. Ber., **119**, 813 (1986).

48. V. H. Rawal, S. P. Singh, C. Dufour, and C. Michoud, J. Org. Chem., **56**, 5245 (1991).

49. D. L. J. Clive and P. L. Beaulieu, J. Chem. Soc., Chem. Commun., **1983**, 307.

50. A. L. J. Beckwith and P. E. Pigou, J. Chem. Soc., Chem. Commun., **1986**, 85.

51. D. P. Curran and J. Tamine, J. Org. Chem., **56**, 2746 (1991).

52. G. Stork, R. Mook, Jr., S. A. Biller, and S. D. Rychnovsky, J. Am. Chem. Soc., **105**, 3741 (1983).

53. Y. Ueno, K. Chinom, M. Watanabe, O. Moriya, and M. Okawara, J. Am. Chem. Soc., **104**, 5565 (1982).

54. G. Stork and R. Mah, Heterocycles, **28**, 723 (1989).

55. J. W. Wilt, Tetrahedron, **41**, 3979 (1985).

56. H. Nishiyama, T. Kitajima, M. Matsumoto, and K. Itoh, J. Org. Chem., **49**, 2298 (1984).

57. G. Stork and M. Kahn, J. Am. Chem. Soc., **107**, 500 (1985).

58. M. Koreeda and I. A. George, J. Am. Chem. Soc., **108**, 8098 (1986).

59. M. T. Crimmins and R. O'Mahony, J. Org. Chem., **54**, 1157 (1989).

60. J. M. Surzur, M. P. Bertrand, and R. Nouguier, Tetrahedron Lett., **1969**, 4197.

61. G. A. Kraus and J. Thurston, Tetrahedron Lett., **28**, 4011 (1987).

62. A. L. J. Beckwith and B. P. Hay, J. Am. Chem Soc., **110**, 4415 (1988).

63. M. Newcomb, M. T. Burchill, and T. M. Deeb, J. Am. Chem. Soc., **110**, 3163 (1988).

64. R. Sutcliffe and K. U. Ingold, J. Am. Chem. Soc., **104**, 6071 (1982).

65. F. Minisci, Synthesis, **1973**, 1.

66. F. Stella, Angew. Chem., **95**, 368 (1983); Angew. Chem. Int. Ed. Engl., **22**, 337 (1983).

67. M. Newcomb and T. M. Deeb, J. Am. Chem. Soc., **109**, 3163 (1987).

68. M. Newcomb and K. A. Weber, J. Org. Chem., **56**, 1309 (1991).

69. J. Boisin, E. Fouquet, and S. Z. Zard, Tetrahedron Lett., **31**, 3545 (1990).

70. B. B. Snider and J. E. Merritt, Tetrahedron, **47**, 8663 (1991).

71. J. H. Rigby and M. N. Qabar, J. Org. Chem., **58**, 4473 (1993).

72. M. Koreeda and L. G. Hamann, J. Am. Chem. Soc., **112**, 8175 (1990).

73. P. Dowd and W. Zhang, Chem. Rev., **93**, 2091 (1993).

74. P. Dowd and S.-C. Choi, J. Am. Chem. Soc., **109**, 3493 (1987).

75. P. Dowd and S.-C. Choi, Tetrahedron, **45**, 77 (1989).

76. J. Baldwin, R. M. Adlington, and J. Robertson, Tetrahedron, **45**, 909 (1989).

77. N. A. Porter and V. H. T. Chang, J. Am. Chem. Soc., **109**, 4976 (1987).

78. N. A. Porter, V. H.-T. Chang, D. R. Magnin, and B. T. Wright, J. Am. Chem. Soc., **110**, 3554 (1988).

79. F. E. Ziegler and Z. L. Zheng, Tetrahedron Lett., **28**, 5973 (1987).

80. G. E. Keck and A. M. Tafesh, Synlett, **1990**, 257.

81. P. Renaud, Tetrahedron Lett., **31**, 4601 (1990).

82. T. V. RajanBabu, T. Fukunaga, and G. S. Reddy, J. Am. Chem. Soc., **111**, 1759 (1989).

83. T. V. RajanBabu, Acc. Chem. Res., **24**, 139 (1991).

84. M.-Y. Chen, J.-M. Fang, Y.-M. Tsai, and R.-L. Yeh, J. Chem. Soc., Chem. Commun., **1991**, 1603.

85. D. P. Curran, W. Shen, J. Zhang, and T. A. Heffner, J. Am. Chem. Soc., **112**, 6738 (1990).

86. E. Nakamura, D. Machii, and T. Inubushi, J. Am. Chem. Soc., **111**, 6849 (1989).

87. F. Soucy, D. Wernic, and P. Beaulieu, J. Chem. Soc., Perkin Trans. 1, **1991**, 2885.

88. J. H. Byers, T. G. Gleason, and K. S. Knight, J. Chem. Soc., Chem. Commun., **1991**, 354.

89. T. Sato, Y. Wada, M. Nishimoto, H. Ishibashi, and M. Ikeda, J. Chem. Soc., Perkin Trans. 1, **1989**, 879.

90. H. Nagashima, K. Seki, N. Ozaki, H. Wakamatsu, K. Itoh, Y. Tomo, and J. Tsuji, J. Org. Chem., **55**, 985 (1990).

91. H. Nagashima, N. Ozaki, M. Ishii, K. Seki, M. Washiyama, and K. Itoh, J. Org. Chem., **58**, 464 (1993).

92. A. V. R. Rao, G. V. M. Sharma, and M. N. Bhanu, Tetrahedron Lett., **33**, 3907 (1992).

93. M. Ikara, K. Yasai, N. Tanigachi, and K. Fukumoto, J. Chem. Soc., Perkin Trans. 1, **1990**, 1469.

94. S. D. Burke and J. Rancourt, J. Am. Chem. Soc., **113**, 2335 (1991).

95. N. A. Porter, B. Lacher, V. H.-T. Chang, and D. R. Magnin, J. Am. Chem. Soc., **111**, 8309 (1989).

96. V. H. Rawal, R. C. Newton, and V. Krishnamurthy, J. Org. Chem., **55**, 5181 (1990).

97. A. L. J. Beckwith, G. Phillipou, and A. K. Serelis, Tetrahedron Lett., **29**, 2811 (1981).

98. D. J. Hart and H. C. Huang, Tetrahedron Lett., **26**, 3749 (1985).

99. C.-P. Chuang, J. C. Galluci, and D. J. Hart, J. Org. Chem., **53**, 3210 (1988).

100. G. Stork, P. M. Sher, and H.-L. Chen, J. Am. Chem. Soc., **108**, 6384 (1986).

101. G. Stork and M. J. Sofia, J. Am. Chem. Soc., **108**, 6826 (1986).

102. A. Y. Mohammed and D. L. J. Clive, J. Chem. Soc., Chem. Commun., **1986**, 588.

103. N. Iwasawa, M. Funahashi, S. Hayakawa, and K. Narasaka, Chem.

Lett., **1993**, 545.

104. J. D. Winkler and V. Sridar, J. Am. Chem. Soc., **108**, 1708 (1986).

105. J. D. Winkler and V. Sridar, Tetrahedron Lett., **29**, 6219 (1988).

106. D. P. Curran and D. Kim, Tetrahedron Lett., **27**, 5821 (1986).

107. D. P. Curran and D. M. Rakiewicz, Tetrahedron, **41**, 3943 (1985).

108. W. P. Neumann, Synthesis, **1987**, 665.

109. C. Walling, Tetrahedron, **41**, 3890 (1985).

110. K. Miura, Y. Ichinose, K. Nozaki, K. Fugami, K. Oshima, and K. Utimoto, Bull. Chem. Soc. Jpn., **62**, 143 (1989).

111. N. Ono, H. Miyake, and A. Kaji, Chem. Lett., **1985**, 635.

112. D. L. J. Clive and R. J. Bergstra, J. Org. Chem., **55**, 1786 (1990).

113. P. M. Esch, H. Hiemstra, R. F. De Boer, and W. N. Speckamp, Tetrahedron, **48**, 4659 (1992).

114. D. Crich and L. Quintero, Chem. Rev., **89**, 1413 (1988).

115. E. J. Enholm and G. Prasad, Tetrahedron Lett., **30**, 4939 (1989).

116. V. Yadav and A. G. Fallis, Tetrahedron Lett., **30**, 3283 (1989).

117. V. Yadav and A. G. Fallis, Can. J. Chem., **69**, 779 (1991).

118. G. Stork and R. Mook Jr., J. Am. Chem. Soc., **109**, 2829 (1987).

119. R. Mook and P. M. Sher, Org. Synth., **66**, 75 (1987).

120. J. Ardisson, J. P. Férézou, M. Julia, L. Lenglet, and A. Pancrazi, Tetrahedron Lett., **28**, 1997 (1987).

121. E. J. Corey and J. W. Suggs, J. Org. Chem., **40**, 2554 (1975).

122. G. Stork and P. M. Sher, J. Am. Chem. Soc., **108**, 303 (1986).

123. J. M. Berge and S. M. Roberts, Synthesis, **1979**, 471.

124. J. Lusztyk, B. Maillard, S. Deycard, D. A. Lindsay, and K. U. Ingold, J. Org. Chem., **52**, 3509 (1987).

125. C. Chatgilialoglu, J. Dickhaut, and B. Giese, J. Org. Chem., **56**, 6399 (1991).

126. C. Chatgilialoglu, Acc. Chem. Res., **25**, 188 (1992).

127. S. A. Hitchcock and G. Pattenden, J. Chem. Soc., Perkin Trans. 1, **1992**, 1323.

128. G. A. Russel and D. Guo, Tetrahedron Lett., **25**, 5239 (1984).

129. B. Giese and G. Kretzschmar, Chem. Ber., **117**, 3160 (1984).

130. J. Barluenga and M. Yus, Chem. Rev., **88**, 487 (1988).

131. K. Weinges and W. Sipos, Chem. Ber., **121**, 363 (1988).

132. G. E. Keck and E. J. Enholm, Tetrahedron Lett., **26**, 3311 (1985).

133. S. J. Danishefsky and J. S. Panek, J. Am. Chem. Soc., **109**, 917 (1987).

134. D. L. J. Clive and A. C. Joussef, J. Org. Chem., **55**, 1096 (1990).

135. J. W. Harvey and G. H. Whitman, J. Chem. Soc., Perkin Trans. 1, **1993**, 185.

136. T. A. K. Smith and G. H. Whitham, J. Chem. Soc., Chem. Commun., **1985**, 897.

137. G. N. Schrauzer, Angew. Chem., Int. Ed. Engl., **15**, 417 (1976).

138. M. R. Ashcraft, A. Buny, C. J. Cooksey. A. G. Davies, B. D. Gupta, M. D. Johnson, and H. Morris, J. Organomet. Chem., **195**, 89 (1980).

139. M. R. Ashcroft, P. Bougeard, A. Bury, C. J. Cooksey, and M. D. Johnson, J. Organomet. Chem., **289**, 403 (1985).

140. P. Bougeard, C. J. Cooksey, M. D. Johnson, M. J. Lewin, S. Mitchell, and P. A. Owens, J. Organomet. Chem., **288**, 389 (1985).

141. C. H. Schiesser and K. Sutej, Tetrahedron Lett., **33**, 5137 (1992).

142. K. J. Kulicke, C. Chatgilialoglu, B. Kopping, and B. Giese, Helv. Chim. Acta, **75**, 935 (1992).

143. D. Crich, Aldrichim. Acta, **20**, 35 (1987).

144. D. H. R. Barton and S. Z. Zard, Pure Appl. Chem., **58**, 675 (1986).

145. D. H. R. Barton and M. Samadi, Tetrahedron, **48**, 7083 (1992).

146. D. H. R. Barton, Y. Herv, P. Potier, and J. Thierry, Tetrahedron, **47**, 6127 (1987).

147. D. H. R. Barton, N. Ozbalik, and B. Vacher, Tetrahedron, **44**, 3501 (1988).

148. D. H. R. Barton, D. Crich, and P. Potier, Tetrahedron Lett., **26**, 5943 (1985).

149. D. H. R. Barton, D. Bridon, E. Fernandez-Picot, and S. Z. Zard, Tetrahedron, **43**, 2733 (1987).

150. D. H. R. Barton, J. Guilhem, Y. Herv, P. Potier, and J. Thierry, Tetrahedron Lett., **28**, 1413 (1987).

151. M. Newcomb, S.-U. Park, J. Kaplan, and D. J. Marquardt, Tetrahedron Lett., **26**, 5651 (1985).

152. M. Newcomb, D. J. Marquardt, and T. M. Deeb, Tetrahedron, **46**, 2329 (1990).

153. M. Newcomb and D. J. Marquardt, Heterocycles, **28**, 129 (1989).

154. J. Iqbal, B. Bhatia, and N. K. Nayyar, Chem. Rev., **94**, 519 (1994).

155. G. M. Lee, M. Parvez, and S. M. Weinreb, Tetrahedron, **44**, 4671 (1988).

156. D. P. Curran and C. T. Chang, Tetrahedron Lett., **28**, 2477 (1987).

157. D. P. Curran, E. Bosch, J. Kaplan, and M. Newcomb, J. Org. Chem., **54**, 1826 (1989).

158. D. P. Curran and S. C. Kuo, J. Am. Chem. Soc., **108**, 1106 (1986).

159. D. P. Curran, M. H. Chen, and D. Kim, J. Am. Chem. Soc., **108**, 2489

(1986).

160. G. Haaima and R. T. Weavers, Tetrahedron Lett., **29**, 1085 (1988).

161. L. Stella, Angew. Chem., **95**, 368 (1982); Angew. Chem. Int. Ed. Engl., **22**, 337 (1982).

162. C. A. Broka and K. K. Eng, J. Org. Chem., **51**, 5043 (1986).

163. C. A. Broka and J. F. Gerlits, J. Org. Chem., **53**, 2144 (1988).

164. Y. L. Chow and R. A. Perry, Can. J. Chem., **63**, 2203 (1985).

165. D. H. R. Barton and M. Akthar, J. Am. Chem. Soc., **86**, 1528 (1964).

166. A. J. Bloodworth, R. J. Curtis, and N. Mistry, J. Chem. Soc., Chem. Commun., **1989**, 954.

167. L. Becking and H. J. Schäfer, Tetrahedron Lett., **29**, 2797 (1988).

168. D. C. Harrowven and G. Pattenden, Tetrahedron Lett., **32**, 243 (1991).

169. V. F. Patel and G. Pattenden, Tetrahedron Lett., **28**, 1451 (1987).

170. G. Pattenden, Chem. Soc. Rev., **17**, 361 (1988).

171. H. Fischer, J. Am. Chem. Soc., **108**, 3925 (1986).

172. W. A. Nugent and T. V. RajanBabu, J. Am. Chem. Soc., **110**, 8561 (1988).

173. T. V. RajanBabu and W. A. Nugent, J. Am. Chem. Soc., **111**, 4525 (1989).

174. D. P. Curran, T. L. Fevig, and M. J. Totleben, Synlett, **1990**, 773.

175. J. Inanaga, O. Ujikawa, and M. Yamaguchi, Tetrahedron Lett., **32**, 1737 (1991).

176. G. A. Molander and L. S. Harring, J. Org. Chem., **55**, 6171 (1990).

177. H. B. Kagan and J. L. Namy, Tetrahedron, **42**, 6573 (1986).

178. G. A. Molander and J. A. McKie, J. Org. Chem., **57**, 3132 (1992).

179. G. A. Molander and C. Kenny, J. Org. Chem., **56**, 1439 (1991).

180. D. Belotti, J. Cossy, J. P. Pete, and C. Portella, J. Org. Chem., **51**, 4966 (1986).

181. J. Mattay, A. Banning, E. W. Bischof, A. Heidbreder, and J. Runsink, Chem. Ber., **125**, 2119 (1992).

182. R. Scheffold, S. Abrecht, R. Orlinski, H.-R. Ruf, P. Stamouli, O. Tinembart, L. Walder, and C. Weymoth, Pure Appl. Chem., **59**, 363 (1987).

183. J. H. Hutchinson, G. Pattenden, and P. L. Myers, Tetrahedron Lett., **28**, 1313 (1987).

184. B. Giese, P. Erdmann, T. Gkbel, and R. Springer, Tetrahedron Lett., **33**, 4545 (1992).

185. M. Ladlow and G. Pattenden, Tetrahedron Lett., **25**, 4317 (1984).

186. H. Bhandal, V. F. Patel, G. Pattenden, and J. J. Russel, J. Chem. Soc.,

Perkin Trans. 1, **1990**, 2691.

187. L. Becking and H. J. Schfer, Tetrahedron Lett., **29**, 2801 (1988).

188. Y. T. Jeon, C. P. Lee, and P. S. Mariano, J. Am. Chem. Soc., **113**, 8847 (1991).

189. B. B. Snider, R. Mohan, and S. A. Kates, Tetrahedron Lett., **28**, 841 (1987).

190. J.-M. Surzur and M. P. Bertrand, Pure Appl. Chem., **60**, 1659 (1988).

191. E. J. Corey and M. Kang, J. Am. Chem. Soc., **106**, 5384 (1984).

192. S. A. Kates, M. A. Dombroski, and B. B. Snider, J. Org. Chem., **55**, 2427 (1990).

193. J. E. Merritt, M. Sasson, S. A. Kates, and B. B. Snider, Tetrahedron Lett., **29**, 5209 (1988).

194. B. B. Snider and J. E. Meritt, Tetrahedron, **47**, 8663 (1991).

195. G. Stork and R. Mook, Jr., J. Am. Chem. Soc., **105**, 3720 (1983).

196. B. B. Snider, Q. Zhang, and A. M. Dombroski, J. Org. Chem., **57**, 4195 (1992).

197. D. P. Curran, D. Kim, H. T. Liu, and W. Shen, J. Am. Chem. Soc., **110**, 5900 (1988).

198. A. Johns and J. A. Murphy, Tetrahedron Lett., **29**, 837 (1988).

199. D. P. Curran, A. C. Abraham, and H. Lin, J. Org. Chem., **56**, 4335 (1991).

200. A. L. J. Beckwith, D. M. O'Shea, and S. W. Westwood, J. Am. Chem. Soc., **110**, 2565 (1988).

201. W. B. Motherwell and J. D. Harling, J. Chem. Soc., Chem. Commun., **1988**, 1380.

202. R. A. Batey, J. D. Harling, and W. B. Motherwell, Tetrahedron, **48**, 8031 (1992).

203. R. A. Batey and W. B. Motherwell, Tetrahedron Lett., **32**, 6649 (1991).

204. A. Johns, J. A. Murphy, and M. S. Sherburn, Tetrahedron, **45**, 7835 (1989).

205. G. E. Keck and D. A. Burnett, J. Org. Chem., **52**, 2958 (1987).

206. G. Stork and P. M. Sher, J. Am. Chem. Soc., **105**, 6765 (1983).

207. H. Togo and O. Kikuchi, Tetrahedron Lett., **29**, 4133 (1988).

208. D. P. Curran and C. M. Seong, J. Am. Chem. Soc., **112**, 9401 (1990).

209. D. L. Boger and R. J. Mathvink, J. Am. Chem. Soc., **112**, 4003 (1990).

210. C.-P. Chuang, Synlett, **1991**, 859.

211. B. B. Snider and B. D. Buckman, Tetrahedron, **45**, 6969 (1989).

212. J. Boivin, E. Crepon, and S. Z. Zard, Tetrahedron Lett., **32**, 199 (1991).

213. V. H. Rawal and S. Iwasa, Tetrahedron Lett., **33**, 4687 (1992).

214. D. A. Singleton and K. M. Church, J. Org. Chem., **55**, 4780 (1990).

215. M. Journet and M. Malacria, J. Org. Chem., **57**, 3085 (1992).

216. D. A. Singleton, K. M. Church, and M. J. Lucero, Tetrahedron Lett., **31**, 5551 (1990).

216a. C. Thebtaranonth and Y. Thebtaranonth, Tetrahedron, **46**, 1385 (1990) and references cited therein.

216b. J. K. Sutherland in *Comprehensive Organic Synthesis*, B. M. Trost, I. Fleming, Eds., **Vol.3**, Pergamon Press, New York, 1991, p. 341.

216c. W. F. Bailey, J. J. Patricia, V. C. DelGobbo, R. M. Jarret, and P. J. Okarma, J. Org. Chem., **50**, 1999 (1985).

216d. W. F. Bailey, T. T. Nurmi, J. J. Patricia, and W. Wang, J. Am. Chem. Soc., **109**, 2442 (1987).

216e. R. D. Little, M. R. Masjedizadeh, O. Wallquist, and J. I. McLaughlin, Org. React., **47**, 315 (1995) and references cited therein.

216f. B. M. Trost, Angew. Chem., Int. Ed. Engl., **29**, 1173 (1989).

217. J. Marco-Contelles, C. Pozuelo, M. L. Jimeno, L. Martinez, and A. Martinez-Grau, J. Org. Chem., **57**, 2625 (1992).

218. S. Hanessian and R. J. Leger, Synlett, **1992**, 402.

219. I. De Riggi, S. Gastaldi, J. M. Surzur, M. P. Bertrand, and A. Virgili, J. Org. Chem., **57**, 6118 (1992).

220. D. H. R. Barton, D. Crich, and G. Kretzschmar, J. Chem. Soc., Perkin Trans. 1, **1986**, 39.

221. T. K. Hayes, R. Villani, and S. M. Weinreb, J. Am. Chem. Soc., **110**, 5533 (1988).

222. J. A. Seijas, M. P. Vazquez-Tato, L. Castedo, R. J. Estevez, M. G. Onega, and M. Ruiz, Tetrahedron, **48**, 1637 (1992).

223. M. Okabe, M. Abe, and M. Tada, J. Org. Chem., **47**, 1775 (1982).

224. S. Busato, O. Tinembert, Z. Zhang, and R. Scheffold, Tetrahedron, **46**, 3155 (1990).

225. G. Pattenden and G. M. Robertson, Tetrahedron, **41**, 4001 (1985).

226. W. Xu, X. M. Zhang, and P. S. Mariano, J. Am. Chem. Soc., **113**, 8863 (1991).

227. K. S. Feldmann, H. M. Berven, and P. H. Weinreb, J. Am. Chem. Soc., **115**, 11364 (1993).

228a. S. Iwasa, M. Yamamoto, S. Kohmoto, and K. Yamada, J. Org. Chem., **56**, 2849 (1991).

228b. S. Iwasa, M. Yamamoto, S. Kohmoto, and K. Yamada, J. Chem. Soc., Perkin Trans. 1, **1991**, 1173.

228. A. Bury and M. D. Johnson, J. Chem. Soc., Chem. Commun., **1980**, 498.

229. A. Bury, M. D. Johnson, and M. J. Stewart, J. Chem. Soc., Chem.

Commun., **1980**, 622.

230. A. Bury, S. T. Corker, and M. D. Johnson, J. Chem. Soc., Perkin Trans. 1, **1982**, 645.

231. S. U. Park, T. R. Varick, and M. Newcomb, Tetrahedron Lett., **31**, 2975 (1990).

232. K. Ogura, N. Sumitani, A. Kuyano, H. Iguchi, and M. Fujita, Chem. Lett., **1992**, 1487.

233. E. Hasegawa and D. P. Curran, Tetrahedron Lett., **34**, 1717 (1993).

234. E. J. Walsh, Jr., J. M. Messinger, II, D. A. Grusdoski, and C. A. Allchin, Tetrahedron Lett., **27**, 4409 (1980).

235. M. Ballestri, C. Chatgilialoglu, N. Cardi, and A. Sommazzi, Tetrahedron Lett., **33**, 1787 (1992).

236. D. P. Curran, M.-H. Chen, and D. Kim, J. Am. Chem. Soc., **108**, 2489 (1986); J. Am. Chem. Soc., **111**, 6265 (1989).

237. C. Bonini, R. Di Fabio, S. Merozzi, and G. Righi, Tetrahedron Lett., **31**, 5369 (1990).

238. C. Walling and A. Cioffari, J. Am. Chem. Soc., **94**, 6059 (1972).

239. M. Julia and E. Colomer, C. R. Acad. Sci., Ser. C, **270**, 1305 (1970).

240. Y. Watanabe, T. Yokozawa, T. Takata, and T. Endo, J. Fluorine Chem., **39**, 431 (1988).

241. J. M. Aurrecoechea and A. Fernandez-Acebes, Tetrahedron Lett., **34**, 549 (1993).

242. R. N. Saicic and Z. Cekovic, Tetrahedron, **46**, 3627 (1990).

243. J. E. Swartz, T. J. Mahachi, and E. Kariv-Miller, J. Am. Chem. Soc., **110**, 3622 (1988).

244. E. Kariv-Miller and T. J. Mahachi, J. Org. Chem., **51**, 1041 (1986).

245. T. Shono, I. Nishiguchi, H. Ohmizu, and M. Mitani, J. Am. Chem. Soc., **100**, 545 (1978).

246. W. R. Bowman and S. W. Jackson, Tetrahedron Lett., **30**, 1857 (1989).

247. D. P. Curran, M.-H. Chen, and D. Kim, J. Am. Chem. Soc., **111**, 6265 (1989).

248. I. Ryu, K. Kusano, M. Hasegawa, N. Kambe, and N. Sonoda, J. Chem. Soc., Chem. Commun., **1991**, 1018.

249a. A. L. J. Beckwith, I. A. Blair, and G. Phillipou, Tetrahedron Lett., **1974**, 2251.

249. N. O. Brace, J. Org. Chem., **32**, 2711 (1967).

250. D. P. Curran and M. Shu, Bull. Soc. Chim. Fr., **130**, 314 (1993).

251. T. Inokuchi, H. Kawafuchi, and S. Torii, J. Org. Chem., **56**, 4983 (1991).

252. G. Pandey and B. B. V. Setzhar, J. Chem. Soc., Chem. Commun., **1993**,

780.

253. J. Hatem, C. Henriet-Bernard, J. Grimaldi, and R. Maurin, Tetrahedron Lett., **33**, 1057 (1992).

254. J. E. Forbes, C. Tailhan, and S. Z. Zard, Tetrahedron Lett., **31**, 2565 (1990).

255. D. P. Curran, M.-H. Chen, E. Spletzer, C. M. Seong, and C.-T. Chang, J. Am. Chem. Soc., **111**, 8872 (1989).

256. E. Lee, C. H. Hur, and J. H. Park, Tetrahedron Lett., **30**, 7219 (1989).

257. A. L. J. Beckwith and G. Moad, J. Chem. Soc., Perkin Trans. 2, **1975**, 1726.

258. I. De Riggi, R. Mouguier, J. M. Surzur, C. Lesueur, M. Bertrand, C. Jaime, and A. Virgili, Bull. Soc. Chim. Fr., **130**, 229 (1993).

259. E. Nakamura, T. Inubushi, S. Aoki, and D. Machii, J. Am. Chem. Soc., **113**, 8980 (1991).

260. J. K. Crandall and M. Mualla, Tetrahedron Lett., **27**, 2243 (1986).

261. T. Lübbers and H. J. Schäfer, Synlett, **1990**, 861.

262. G. A. Molander and C. Kenny, J. Am. Chem. Soc., **111**, 8236 (1989).

263. J. E. Forbes and S. Z. Zard, J. Am. Chem. Soc., **112**, 2034 (1990).

264. Y. Ichinose, K. Oshima, and K. Utimoto, Chem. Lett., **1988**, 1437.

265. C. B. Ziegler, Jr., J. Org. Chem., **55**, 2983 (1990).

266. M. Julia and M. Barreau, C. R. Hebd. Seances Acad. Sci., Ser. C, **280**, 957 (1975).

267. M. Yamamoto, A, Furusawa, S. Iwasa, S. Kohmoto, and K. Yamada, Bull. Chem. Soc. Jpn., **65**, 1550 (1992).

268. E. J. Enholm and K. S. Kinter, J. Am. Chem. Soc., **113**, 7784 (1991).

269. K. S. Feldman, A. L. Romanelli, R. E. Ruckle, Jr., and G. Jean, J. Org. Chem., **57**, 100 (1992).

270. B. B. Snider, R. Mohan, and S. A. Kates, J. Org. Chem., **50**, 3661 (1985).

271. C.-P. Chuang and V.-J. Jiang, J. Chin. Chem. Soc., **36**, 177 (1989).

272. S. A. Dodson and R. D. Stipanovic, J. Chem. Soc., Perkin Trans. 1, **1975**, 410.

273. J. K. Crandall and W. I. Michaely, J. Org. Chem., **49**, 4244 (1984).

274. Y. Ichinose, S. Matsanuga, K. Fugami, K. Oshima, and K. Utimoto, Tetrahedron Lett., **30**, 3155 (1989).

275. J. K. Crandall and D. J. Keyton, Tetrahedron Lett., **21**, 1653 (1969).

276. N. O. Brace and J. E. Van Elswyk, J. Org. Chem., **41**, 766 (1976).

277. I. De Riggi, J.-M. Surzur, M. P. Bertrand, A. Archavlis, and R. Faure, Tetrahedron, **46**, 5285 (1990).

278. M. E. Kuehne and R. E. Damon, J. Org. Chem., **42**, 1825 (1977).

279. C.-P. Chuang, Tetrahedron Lett., **33**, 6311 (1992).

280. C.-P. Chuang, Synth. Commun., **22**, 3151 (1992).

281. R. Grigg, J. Devlin, A. Ramasubbu, R. M. Scott, and P. Stevenson, J. Chem. Soc., Perkin Trans. 1, **1987**, 1515.

282. K. Weinges and W. Sipos, Angew. Chem., **99**, 1177 (1987); Angew. Chem., Int. Ed. Engl., **27**, 1152 (1987).

283. Z. Cekovic and R. Saicic, Tetrahedron Lett., **27**, 5981 (1986).

284. V. K. Yadav and A. G. Fallis, Tetrahedron Lett., **29**, 897 (1988).

285. G. A. Molander and C. Kenny, Tetrahedron Lett., **28**, 4367 (1987).

286. J. K. Crandall and T. A. Ayers, Tetrahedron Lett., **32**, 3659 (1991).

287. F. Barth and C. O-Yang, Tetrahedron Lett., **32**, 5873 (1991).

288. K. Miura, K. Fugami, K. Oshima, and K. Utimoto, Tetrahedron Lett., **29**, 5135 (1988).

289. C.-P. Chuang and T. H. J. Ngoi, J. Chem. Res. (S), **1991**, 1.

290. D. P. Curran and C. M. Seong, Tetrahedron, **48**, 2157 (1992).

291. M. Julia, B. Mansour, and D. Mansuny, Tetrahedron Lett., **1976**, 3443.

292. G. Stork and M. E. Reynolds, J. Am. Chem. Soc., **110**, 6911 (1988).

293. D. P. Curran and C. M. Seong, Tetrahedron, **48**, 2175 (1992).

294. D. P. Curran and W. Shen, J. Am. Chem. Soc., **115**, 6051 (1993).

295. B. B. Snider, J. E. Merritt, M. A. Dombroski, and B. O. Buckman, J. Org. Chem., **56**, 5544 (1991).

296. K. S. Feldman, R. E. Ruckle, Jr., and A. L. Romanelli, Tetrahedron Lett., **30**, 5845 (1989).

297. T. Harrison, P. L. Myers, and G. Pattenden, Tetrahedron, **45**, 5247 (1989).

298. S. Danishefsky, S. Chackalamannil, and B. J. Uang, J. Org. Chem., **47**, 2231 (1982).

299. T. Harrison, G. Pattenden, and P. L. Myers, Tetrahedron Lett., **29**, 3869 (1988).

300. J. E. Brumwell, N. S. Simpkins, and N. K. Terrett, Tetrahedron Lett., **34**, 1215 (1993).

301. J. E. Brumwell, N. S. Simpkins, and N. K. Terrett, Tetrahedron Lett., **34**, 1219 (1993).

302. G. A. Kraus and S. Liras, Tetrahedron Lett., **31**, 5265 (1990).

303. A. Ogawa, H. Yokoyama, K. Yokoyama, T. Masawaki, N. Kambe, and N. Sonoda, J. Org. Chem., **56**, 5721 (1991)

304. A. Arnone, P. Bravo, G. Cavicchio, M. Frigerio, and F. Viani, Tetrahedron, **48**, 8523 (1992).

305. A. Arnone, P. Bravo, G. Cavicchio, M. Frigerio, and F. Viani, Tetrahedron, **49**, 6873 (1993).

306. T. Kataoka, M. Yoshimatsu, Y. Noda, T. Sato, H. Shimizu, and M. Hori, J. Chem. Soc., Perkin Trans. 1, **1993**, 121.

307. L. Moens, M. M. Baizer, and R. D. Little, J. Org. Chem., **51**, 4497 (1986).

308. R. Mook, Jr. and P. M. Sher, Org. Synth., **66**, 75 (1988).

309. C. G. Sowell, R. L. Wolin, and R. D. Little, Tetrahedron Lett., **31**, 485 (1990).

310. B. B. Snider, L. Armanetti, and R. Baggio, Tetrahedron Lett., **34**, 1701 (1993).

311. C. Chatgilialoglu, B. Giese, and B. Kopping, Tetrahedron Lett., **31**, 6013 (1990).

312. T. Morikawa, T. Nishiwaki, and Y. Kobayashi, Tetrahedron Lett., **30**, 2407 (1989).

313. S. Kim and S. Lee, Tetrahedron Lett., **32**, 6575 (1991).

314. A. Srikrishna and G. Sundarababu, Tetrahedron, **46**, 3601 (1990).

315. T. A. K. Smith and G. H. Whitham, J. Chem. Soc., Perkin Trans. 1, **1989**, 319.

316a. T. A. K. Smith and G. H. Whitham, J. Chem. Soc., Perkin Trans. 1, **1989**, 313.

316. T. Morikawa, Y. Kodama, J. Uchida, M. Takano, Y. Washio, and T. Taguchi, Tetrahedron, **48**, 8915 (1992).

317. M. J. Begley, N. Housden, A. Johns, and J. A. Murphy, Tetrahedron, **47**, 8417 (1991).

318. F. E. Ziegler, C. A. Metcalf, III, and G. Schulte, Tetrahedron Lett., **33**, 3117 (1992).

319. S. Kim and J. R. Cho, Synlett, **1992**, 629.

320. J. R. Peterson, R. S. Egler, D. B. Horsley, and T. J. Winter, Tetrahedron Lett., **28**, 6109 (1987).

321. C.-P. Chuang, S.-S. Hou, and T. H. J. Ngoi, J. Chin. Chem. Soc., **37**, 85 (1990).

322. C.-P. Chuang, S.-S. Hou, and T. H. J. Ngoi, J. Chem. Res. (S), **1991**, 216.

323. Y.-M. Tsai, B.-W. Ke, and C.-H. Lin, Tetrahedron Lett., **31**, 6074 (1990).

324a. D. A. Singleton and K. M. Church, J. Org. Chem., **55**, 4780 (1990).

324. J. M. Fang, H. T. Chang, and C. C. Lin, J. Chem. Soc., Chem. Commun., **1988**, 1385.

325. Y.-M. Tsai, F.-C. Chang, J. Huang, and C.-L. Shiu, Tetrahedron Lett., **30**, 2121 (1989).

326. K. S. Feldman, A. L. Romanelli, R. E. Ruckle, Jr., and R. F. Miller, J. Am.

Chem. Soc., **110**, 3300 (1988).

327. D. A. Singleton, C. C. Huval, K. M. Church, and E. S. Priestley, Tetrahedron Lett., **32**, 5765 (1991).

328. D. P. Curran and P. A. van Elburg, Tetrahedron Lett., **30**, 2501 (1989).

329. S. Hanessian and R. J. Leger, J. Am. Chem. Soc., **114**, 3115 (1992).

330. D. Crich and S. M. Fortt, Tetrahedron Lett., **28**, 2895 (1987).

331. A. D. Borthwick, S. Caddick, and P. J. Parsons, Tetrahedron Lett., **31**, 6911 (1990).

332. A. Srikrishna and G. Sundarababu, Tetrahedron, **47**, 481 (1991).

333. A. Srikrishna and G. Sunderbabu, Tetrahedron Lett., **30**, 3561 (1989).

334. A. L. J. Beckwith, D. M. Cliff, and C. H. Schiesser, Tetrahedron, **48**, 4641 (1992).

335. T. Morikawa, M. Uejima, and Y. Kobayashi, Chem. Lett., **1989**, 623.

336. Y.-M. Tsai and C.-D. Cherng, Tetrahedron Lett., **32**, 3515 (1991).

337. D. P. Curran, W.-T. Jiaang, M. Palovich, and Y.-M. Tsai, Synlett, **1993**, 403.

338. D. A. Singleton, K. M. Church, and M. I. Lucero, Tetrahedron Lett., **31**, 5551 (1990).

339. D. L. J. Clive and T. L. B. Boivin, J. Org. Chem., **54**, 1997 (1989).

340. E. J. Enholm, J. A. Burroff, and L. M. Jaramillo, Tetrahedron Lett., **31**, 3727 (1990).

341. Y. M. Tsai, K. H. Tang, and W. T. Jiaang, Tetrahedron Lett., **34**, 1303 (1993).

342. S. Kim, I. S. Kee, and S. Lee, J. Am. Chem. Soc., **113**, 9882 (1991).

343. I. Rochigneux, M. L. Fontanel, J. C. Malanda, and A. Doutheau, Tetrahedron Lett., **32**, 2017 (1991).

344. V. Snieckus, J. C. Cuevas, C. P. Sloan, H. Lin, and D. P. Curran, J. Am. Chem. Soc., **112**, 896 (1990).

345. T. B. Lowinger and L. Weiler, Can. J. Chem., **68**, 1636 (1990).

346. J. G. Stack, D. P. Curran, S. V. Geib, J. Rebek, Jr., and P. Ballester, J. Am. Chem. Soc., **114**, 7007 (1992).

347. B. B. Snider and T. Kwon, J. Org. Chem., **57**, 2399 (1992).

348. C.-P. Chuang, Tetrahedron, **47**, 5425 (1991).

349. S. Kiyooka, Y. Kaneko, H. Matsue, and R. Fujiyama, J. Org. Chem., **55**, 5562 (1990).

350. C.-P. Chuang, Synlett, **1990**, 527.

351. L. Set, D. R. Cheshire, and D. L. J. Clive, J. Chem. Soc., Chem. Commun., **1985**, 1205.

352. D. L. J. Clive, T. L. B. Boivin, and A. G. Angoh, J. Org. Chem., **52**, 4943

(1987).

353. A. G. Angoh and D. L. J. Clive, J. Chem. Soc., Chem. Commun., **1985**, 941.

354a. A. G. Angoh and D. L. J. Clive, J. Chem. Soc., Chem. Commun., **1985**, 980.

354. D. J. Coveney, V. F. Patel, and G. Pattenden, Tetrahedron Lett., **28**, 5949 (1987).

355. J. J. Gaudino and C. S. Wilcox, Carbohydr. Res., **206**, 233 (1990).

356. C. S. Wilcox and J. J. Gaudino, J. Am. Chem. Soc., **108**, 3102 (1986).

357. N. S. Simpkins, S. Stokes, and A. J. Whittle, Tetrahedron Lett., **33**, 793 (1992).

358. S. M. Roberts and K. A. Shoberu, J. Chem. Soc., Perkin Trans. 1, **1992**, 2625.

359. T. V. RajanBabu, J. Am. Chem. Soc., **109**, 609 (1987).

360. C. A. Broka and D. E. C. Reichert, Tetrahedron Lett., **28**, 1503 (1987).

361. E. Lee and C. U. Hur, Tetrahedron Lett., **32**, 5101 (1991).

362. B. B. Snider and J. J. Patricia, J. Org. Chem., **54**, 38 (1989).

363. D. P. Curran, T. M. Morgan, C. E. Schwartz, B. B. Snider, and M. A. Dombroski, J. Am. Chem. Soc., **113**, 6607 (1991).

364. R. D. Little, D. P. Fox, L. Van Hijfte, R. Dannecker, G. Sowell, R. L. Wolin, L. Moens, and M. M. Baizer, J. Org. Chem., **53**, 2287 (1988).

365. R. C. Denis, J. Rancourt, E. Ghiro, F. Boutonnet, and D. Gravel, Tetrahedron Lett., **34**, 2091 (1993).

366. M. D. Bachi and D. Denenmark, Heterocycles, **28**, 583 (1989).

367. C. Destabel, J. D. Kilburn, and J. Knight, Tetrahedron Lett., **34**, 3151 (1993).

368. M. Harendza, K. Lexmann, and W. P. Neumann, Synlett, **1993**, 283.

369. J. Marco-Contelles and B. Snchez, J. Org. Chem., **58**, 4293 (1993).

370. P. Gottschalk and D. C. Neckers, J. Org. Chem., **50**, 3498 (1985).

371. A. Heidbrecher and J. Mattay, Tetrahedron Lett., **33**, 1973 (1992).

372. M. Journet, E. Magnuol, G. Aguel, and M. Malacria, Tetrahedron Lett., **31**, 4445 (1990).

373. A. Arnone, P. Bravo, G. Cavicchio, M. Frigerio, and F. Viani, Tetrahedron: Asymmetry, **3**, 9 (1992).

374. A. Arnone, P. Bravo, and F. Viani, Tetrahedron: Asymmetry, **2**, 399 (1992).

375. J. E. Ward and B. F. Kaller, Tetrahedron Lett., **32**, 843 (1991).

376. W. F. Bailey and A. D. Khanolkar, Tetrahedron, **47**, 7727 (1991).

377. K. Ogura, A. Kayano, T. Fujino, N. Sumitani, and M. Fujita, Tetrahedron

Lett., **34**, 8313 (1993).

378. D. H. R. Barton, P. J. Dalko, and S. D. Gero, Tetrahedron Lett., **32**, 4713 (1991).

379. M. Chatzopoulos and J. P. Montheard, Rev. Roum. Chim., **26**, 275 (1981).

380. J. Marco-Contelles, L. Martinez, A. Martinez-Grau, C. Pozuelo, and M. L. Jimeno, Tetrahedron Lett., **32**, 6437 (1991).

381. F. L. Harris and L. Weiler, Tetrahedron Lett., **28**, 2941 (1987).

382. J. Marco-Contelles, B. Snchez, and P. Ruiz, Natural Product Letters 1, **1992**, 167.

383. C. Chen and D. Crich, Tetrahedron Lett., **33**, 1945 (1993).

384. C. Destabel and J. D. Kilburn, J. Chem. Soc., Chem. Commun., **1992**, 596.

385. D. Crich, K. A. Eustache, S. M. Fortt, and T. J. Ritchie, Tetrahedron, **46**, 2135 (1990).

386. D. Crich and S. M. Fortt, Tetrahedron, **45**, 6581 (1989).

387. D. Batty, D. Crich, and S. M. Fortt, J. Chem. Soc., Chem. Commun. **1989**, 1366.

388. D. Batty, D. Crich, and S. M. Fortt, J. Chem. Soc., Perkin Trans 1, **1990**, 2875.

389. D. Batty and D. Crich, J. Chem. Soc., Perkin Trans. 1, **1991**, 2894.

390. M. Apparu and J. K. Crandall, J. Org. Chem., **49**, 2125 (1984).

391. D. Crich and S. M. Fortt, Tetrahedron Lett., **29**, 2585 (1988).

392. N. A. Porter, D. R. Magnin, and B. T. Wright, J. Am. Chem. Soc., **108**, 2787 (1986).

393. N. J. G. Cox, G. Pattenden, and S. D. Mills, Tetrahedron Lett., **30**, 621 (1989).

394. N. J. G. Cox, S. D. Mills, and G. Pattenden, J. Chem. Soc., Perkin Trans. 1, **1992**, 1313.

395. M. P. Astley and G. Pattenden, Synlett, **1991**, 335.

396. H. S. Dang and B. P. Roberts, J. Chem. Soc., Perkin Trans. 1, **8**, 891 (1993).

397. D. L. Flynn and D. L. Zabrowski, J. Org. Chem., **55**, 3673 (1990).

398. Y. Araki, T. Endo, Y. Arai, M. Tanji, and Y. Ishido, Tetrahedron Lett., **30**, 2892 (1989).

399. S. L. Fremont, J. L. Belletiere, and D. M. Ho, Tetrahedron Lett., **32**, 2335 (1991).

400. H. Ishibashi, C. Kameoka, A. Yoshikawa, R. Ueda, K. Kodama, T. Sato, and M. Ikeda, Synlett, **1993**, 649.

401. G. B. Gill, G. Pattenden, and S. J. Reynolds, Tetrahedron Lett., **30**, 3229 (1989).

402. M. Tada, T. Nakamura, and M. Matsumoto, Chem. Lett., **1987**, 409.

403. P. Kanshal and B. P. Roberts, J. Chem. Soc., Perkin Trans. 2, **1989**, 1559.

404. R. D. Rieke and N. A. Moore, Tetrahedron Lett., **25**, 2035 (1969).

405. M. Kaafarani, M. P. Crozet, and J. M. Surzur, Bull. Soc. Chim. Fr., **1981**, 449.

406. M. P. Crozet, M. Kaafarani, and J. M. Surzur, Bull. Soc. Chim. Fr., **1984**, 390.

407. E. Lee, S. B. Ko, K. W. Jung, and M. H. Chang, Tetrahedron Lett., **30**, 827 (1989).

408. I. De Riggi, J. M. Surzur, and M. P. Bertrand, Tetrahedron, **44**, 7119 (1988).

409. A. Naim, G. Mills, and P. B. Shevlin, Tetrahedron Lett., **33**, 6779 (1992).

410. A. C. Serra, C. M. M. da Silva Corraa, M. A. M. S. A. Viera, and M. A. Gomes, Tetrahedron, **46**, 3061 (1990).

411. T. J. Barton and A. Revis, J. Am. Chem. Soc., **106**, 3802 (1984).

412. R. A. Perry, S. C. Chen, B. C. Menon, K. Hanaya, and Y. L. Chow, Can. J. Chem., **54**, 2385 (1976).

413. H. Nagashima, N. Ozaki, K. Seki, M. Ishii, and K. Itoh, J. Org. Chem., **54**, 4497 (1989).

414. S. Takano, S. Nishizawa, M. Akiyama, and K. Ogasawara, Synthesis, **1984**, 949.

415. J. L. Bougeois, L. Stella, and J. M. Surzur, Tetrahedron Lett., **22**, 61 (1981).

416. J. H. Udding, H. Hiemstra, M. N. A. van Zanden, and W. N. Speckamp, Tetrahedron Lett., **32**, 3123 (1991).

417. K. Mochida and K. Asami, J. Organomet. Chem., **232**, 13 (1982).

418. S. Hanessian, R. Di Fabio, J.-F. Marcoux, and M. Prud'homme, J. Org. Chem., **55**, 3436 (1990).

419. F. Barth and C. O-Yang, Tetrahedron Lett., **31**, 1121 (1990).

420. J. P. Dulcere, J. Rodriguez, M. Santelli, and J. P. Zahra, Tetrahedron Lett., **28**, 2009 (1987).

421. J. L. Courtneidge, M. Bush, and L. S. Loh, Tetrahedron, **48**, 3835 (1992).

422. A. L. J. Beckwith and R. D. Wagner, J. Chem. Soc., Chem. Commun., **1980**, 485.

423. E. Lee, J. S. Tae, C. Lee, and C. M. Park, Tetrahedron Lett., **34**, 4831 (1993).

424. J. M. Clough, G. Pattenden, and P. G. Wight, Tetrahedron Lett., **30**, 7469 (1989).

425. Y. Ueno, O. Moriya, K. Chino, M. Watanabe, and M. Okawara, J. Chem. Soc., Perkin Trans. 1, **1986**, 1351.

426. A. Srikrishna and K. Krishnan, J. Org. Chem., **54**, 3981 (1984).

427. M. Yamamoto, T. Uruma, S. Iwasa, S. Kohmoto, and K. Yamada, J. Chem. Soc., Chem. Commun., **1989**, 1265.

428. E. Magnol and M. Malacria, Tetrahedron Lett., **27**, 2255 (1986).

429. J. M. Surzur, L. Stella, and P. Tordo, Bull. Soc. Chim. Fr., **1975**, 1429.

430. O. Moriya, M. Kakihana, Y. Urata, T. Sugizaki, T. Kageyama, Y. Ueno, and T. Endo, J. Chem. Soc., Chem. Commun., **1985**, 1401.

431. O. Moriya, Y. Urata, Y. Ikeda, Y. Ueno, and T. Endo, J. Org. Chem., **51**, 4708 (1986).

432. J. Cossy and C. Leblanc, Tetrahedron Lett., **30**, 4531 (1989).

433. K. S. Feldman, R. E. Simpson, and M. Parvez, J. Am. Chem. Soc., **108**, 9328 (1986).

434. K. S. Feldman and R. E. Simpson, J. Am. Chem. Soc., **111**, 4878 (1989).

435. M. Newcomb, M. U. Kumar, J. Boivin, E. Crpon, and S. Z. Zard, Tetrahedron Lett., **32**, 45 (1991).

436. K. Nozaki, K. Oshima, and K. Utimoto, Bull. Chem. Soc. Jpn., **63**, 2578 (1990).

437. N. Ono, H. Miyake, A. Kamimura, I. Itamamoto, R. Tamura, and A. Kaji, Tetrahedron, **41**, 4013 (1985).

438. R. Kiesewettter and P. Margaretha, Helv. Chim. Acta, **70**, 125 (1987).

439a. J. E. Baldwin, M. G. Molonay, and A. F. Passons, Tetrahedron, **47**, 155 (1991).

439. T. Naito, Y. Houda, O. Miyata, and I. Ninomiya, Heterocycles, **32**, 2319 (1991).

440. B. Maillard, C. Gardrat, and M. J. Bourgeois, J. Organomet. Chem., **236**, 61 (1982).

441. M. D. Bachi and D. G. Lasanow, Synlett, **1990**, 551.

442. O. Moriya, M. Okawara, and Y. Ueno, Chem. Lett., **1984**, 1437.

443. J. S. Yadav and V. R. Gadgil, J. Chem. Soc., Chem. Commun., **1989**, 1824.

444. R. C. Gash, F. MacCorquodale, and J. C. Walton, Tetrahedron, **45**, 5531 (1989).

445. A. Sririshina and G. Sunderababu, Chem. Lett., **1988**, 371.

446. K. S. Feldman and C. M. Kraebel, J. Org. Chem., **57**, 4574 (1992).

447. T. Lpbbers and H. J. Schfer, Synlett, **1990**, 44.

448. C. Hackmann and H. J. Schfer, Tetrahedron, **49**, 4559 (1993).

449. T. Sato, N. Machigashira, H. Ishibashi, and M. Ikeda, Heterocycles, **33**, 139 (1992).

450. Y. Watanabe and T. Endo, Tetrahedron Lett., **29**, 321 (1988).

451. A. Padwa, H. Nimmesgern, and G. S. K. Wong, J. Org. Chem., **50**, 5620 (1985).

452. E. Castagnino, S. Corsano, and D. H. R. Barton, Tetrahedron Lett., **30**, 2983 (1989).

453. A. Citterio, M. Ramperti, and E. Vismara, J. Heterocycl. Chem., **18**, 763 (1981).

454. A. L. J. Beckwith, B. P. Hay, and G. M. Williams, J. Chem. Soc., Chem. Commun., **1989**, 1202.

455. J. H. Udding, J. M. Tuijp, H. Hiemstra, and W. N. Speckamp, J. Chem. Soc., Perkin Trans. 2, **1992**, 857.

456. J. L. Courtneidge, J. Chem. Soc., Chem. Commun., **1992**, 1270.

457. M. Journet and M. Malacria, Tetrahedron Lett., **33**, 1893 (1992).

458. M. Journet, E. Magual, W. Smadja, and M. Malacria, Synlett, **1991**, 58.

459. G. Agnel and M. Malacria, Synthesis, **1989**, 687.

460. A. Ali, D. C. Harrowven, and G. Pattenden, Tetrahedron Lett., **33**, 2851 (1992).

461. Y. Ueno, R. K. Khare, and M. Okawara, J. Chem Soc., Perkin Trans. 1, **1983**, 2637.

462. M. D. Bachi, E. Bosch, D. Denenmark, and D. Girsh, J. Org. Chem., **57**, 6803 (1992).

463. K. Yamamoto, S. Abrecht, and R. Scheffold, Chimia, **45**, 86 (1991).

464. M. D. Bachi and E. Bosch, J. Org. Chem., **57**, 4696 (1992).

465. A. L. J. Beckwith and G. E. Davison, Tetrahedron Lett., **32**, 49 (1991).

466. M. D. Bachi and E. Bosch, J. Org. Chem., **54**, 1234 (1989).

467. M. Tokuda, Y. Yamada, T. Takagi, H. Suginome, and A. Furusaki, Tetrahedron, **43**, 281 (1987).

468. M. Tokuda, Y. Yamada, T. Takagi, H. Suginome, and A. Furusaki, Tetrahedron Lett., **26**, 6085 (1985).

469. P. Arya and D. D. M. Wayner, Tetrahedron Lett., **32**, 6265 (1991).

470. A. Serra and C. M. M. da Silva Correa, Tetrahedron Lett., **32**, 6653 (1991).

471. A. Srikrishna, Ind. J. Chem., **29B**, 479 (1990).

472. K. S. Feldman and T. E. Fisher, Tetrahedron, **45**, 2969 (1989).

473. J. L. Belletire and N. O. Mahmoodi, J. Nat. Prod., **55**, 194 (1992).

474. G. Cavicchio, V. Marchetti, A. Arnone, P. Bravo, and V. Fiorenza, Tetrahedron, **47**, 9439 (1991).

475. G. Cavicchio, V. Marchetti, A. Arnone, P. Bravo, and F. Viani, Gazz. Chim. Ital., **121**, 423 (1991).

476. S. Adhikari and S. Roy, Tetrahedron Lett., **33**, 6025 (1992).

477. S. Iwasa, M. Yamamoto, A. Furusawa, S. Kohmoto, and K. Yamada, Chem. Lett., **1991**, 1457.

478. L. D. M. Lolkema, H. Hiemstra, A. A. A. Ghouch, and W. N. Speckamp, Tetrahedron Lett., **32**, 1491 (1991).

479. M. Newcomb and J. L. Esker, Tetrahedron Lett., **32**, 1035 (1991).

480. R. Kiesewetter and P. Margaretha, Helv. Chim. Acta, **72**, 83 (1989).

481. T. Morikawa, T. Nishiwaki, Y. Iitaka, and Y. Kobayashi, Tetrahedron Lett., **28**, 671 (1987).

482. M. Newcomb and C. Ha, Tetrahedron Lett., **32**, 6493 (1991).

483. J. L. Esker and M. Newcomb, Tetrahedron Lett., **34**, 6877 (1993).

484. J. Boivin, E. Fouquet, and S. Z. Zard, Tetrahedron Lett., **32**, 4299 (1991).

485. J. Gunic. I. Tabakovic, and Z. Samicanin, Electrochim. Acta, **35**, 225 (1990).

486. A. Srikrishna and G. Sundarababu, Tetrahedron, **46**, 7901 (1990).

487. M. Newcomb and M. U. Kumar, Tetrahedron Lett., **31**, 1675 (1990).

488. P. M. Esch, H. Hiemstra, and W. N. Speckamp, Tetrahedron Lett., **31**, 759 (1990).

489. S. C. Roy and S. Adhikari, Tetrahedron Lett., **49**, 8415 (1993).

490. B. B. Snider and B. A. McCarthy, Tetrahedron, **49**, 9447 (1993).

491. C. H. Schiesser and K. Sutej, J. Chem. Soc., Chem. Commun., **1992**, 57.

492. L. Bejamin, C. H. Schiesser, and K. Sutej, Tetrahedron, **49**, 2557 (1993).

493. J. F. Lavallee and G. Just, Tetrahedron Lett., **32**, 3469 (1991).

494. J. E. Baldwin, M. G. Moloney, and A. F. Parsons, Tetrahedron, **46**, 7263 (1990).

495. M. D. Bachi and E. Bosch, Tetrahedron Lett., **27**, 641 (1986).

496. V. H. Rawal, S. P. Singh, C. Dufour, and C. Michoud, J. Org. Chem., **58**, 7718 (1993).

497. J. H. Byers and G. C. Lane, J. Org. Chem., **58**, 3355 (1993).

498. M. R. Ashcroft, P. Bougeard, A. Bury, C. J. Cooksey, M. D. Johnson, J. M. Hungerford, and G. M. Lampman, J. Org. Chem., **49**, 1751 (1984).

499. Y. Ueno, C. Tanaka, and M. Okawara, Chem. Lett., **1983**, 795.

500. R. M. Adlington and S. J. Mantell, Tetrahedron, **48**, 6529 (1992).

501. J. E. Baldwin and C. S. Li, J. Chem. Soc., Chem. Commun., **1987**, 166.

502. M. Newcomb, D. J. Marquardt, M. U. Kumar, and M. Udaya, Tetrahedron, **46**, 2345 (1990).

503. C.-P. Chuang, Tetrahedron, **47**, 5425 (1991).

504. S. Hatakeyama, K. Sugawara, and S. Takano, J. Chem. Soc., Chem. Commun., **1993**, 125.

505. P. N. Culshaw and J. C. Walton, J. Chem. Soc., Perkin Trans. 2, **1991**, 1201.

506. C. Dupuy, M. P. Crozet, and J. M. Surzur, Bull. Soc. Chim. Fr., **1980**, 361.

507. M. O. Funk, R. Isaac, and N. A. Porter, J. Am. Chem. Soc., **97**, 1281 (1975).

508. M. P. Crozet, J. M. Surzur, and C. Dupuy, Tetrahedron Lett., **23**, 2031 (1971).

509. W. B. Motherwell, A. M. K. Pennell, and F. Ujjainwalla, J. Chem. Soc., Chem. Commun., **1992**, 1067.

510. S. P. Munt and E. J. Thomas, J. Chem. Soc., Chem. Commun., **1989**, 480.

511. R. D. Walkup, N. U. Obeyekesere, and R. R. Kane, Chem. Lett., **1990**, 1055.

512. K. S. Feldmann and H. M. Berven, Synlett, **1993**, 827.

513. I. Lakomy and R. Scheffold, Helv. Chim. Acta, **76**, 804 (1993).

514. S. Hatakeyama, N. Ochi, H. Numata, and S. Takano, J. Chem. Soc., Chem. Commun., **1988**, 1202.

515. N. A. Porter, N. A. Roe, and A. T. McPhail, J. Am. Chem. Soc., **102**, 7574 (1980).

516. M. D. Bachi and D. Denenmark, J. Org. Chem., **55**, 3442 (1990).

517. W. Xu, T. Y. Jeon, E. Hasegawa, U. C. Yoon, and S. P. Mariano, J. Am. Chem. Soc., **111**, 406 (1989).

518. M. Ihara, K. Yasai, N. Taniguchi, K. Fukumoto, and T. Kametani, Tetrahedron Lett., **29**, 4963 (1988).

519. G. Pandey, G. Kumaraswamy, and U. T. Bhalerao, Tetrahedron Lett., **30**, 6059 (1989).

520. L. Stella, B. Raynier, and J. M. Surzur, Tetrahedron Lett., **31**, 2721 (1977).

521. M. Ihara, N. Taniguchi, K. Kukumoto, and T. Kametani, J. Chem. Soc., Chem. Commun., **1987**, 1438.

522. S. Yoo, K. Y. Yi, S.-H. Li, and N. Jeong, Synlett, **1990**, 575.

523. T. Yamada, Y. Iwahara, H. Nishino, and K. Kurosawa, J. Chem. Soc., Perkin Trans. 1, **1993**, 609.

524. M. Kaafarani, M. P. Crozet, and J. M. Surzur, Bull. Soc. Chim. Fr., **1987**, 885.

525. J. H. Hutchinson, T. S. Daynard, and J. W. Gillard, Tetrahedron Lett., **32**, 573 (1991).

526. A. G. Myers, D. Y. Gin, and K. L. Widdowson, J. Am. Chem. Soc., **113**, 9661 (1991).

527. G. A. Kraus and Y. Wu, J. Am. Chem. Soc., **114**, 8705 (1992).

528. E. I. Troyansky, M. I. Lazareva, D. V. Demchuk, V. V. Samoshiu, Y. A. Strelenko, and G. I. Nikishiu, Synlett, **1992**, 233.

529. D. L. Boger and R. J. Mathvink, J. Am. Chem. Soc., **112**, 4008 (1990).

530. J. E. Baldwin, R. M. Adlington, M. B. Mitchell, and J. Robertson, J. Chem. Soc., Chem. Commun., **1990**, 1574.

531. K. J. Shea, R. O'Dell, and D. Y. Sasaki, Tetrahedron Lett., **33**, 4699 (1992).

532. C. Descoins, M. Julia, and H. van Sang, Bull. Soc. Chim. Fr., **1971**, 4087.

533. S. Wolf and W. C. Agosta, J. Org. Chem., **45**, 3139 (1980).

534. P. Dowd and W. Zhang, J. Am. Chem. Soc., **114**, 10084 (1992).

535. T. Shono and N. Kise, Tetrahedron Lett., **31**, 1303 (1990).

536. C. K. Sha, T. S. Jean, and D. C. Wang, Tetrahedron Lett., **31**, 3745 (1990).

537. S. Wolf and W. C. Agosta, J. Chem. Res. (S), **1981**, 78.

538. M. Nagai, J. Lazor, and C. S. Wilcox, J. Org. Chem., **55**, 3440 (1990).

539. E. J. Corey and S. G. Pyne, Tetrahedron Lett., **24**, 2821 (1983).

540. V. H. Rawal and V. Krishnamurthy, Tetrahedron Lett., **33**, 3439 (1992).

541. F. H. Wartenberg, H. Junga, and S. Blechert, Tetrahedron Lett., **34**, 5251 (1993).

542. B. B. Snider and B. O. Buckman, J. Org. Chem., **57**, 322 (1992).

543. E. J. Eukden and J. A. Burroff, Tetrahedron Lett., **33**, 1835 (1992).

544. J. D. Kilburn, Tetrahedron Lett., **31**, 2193 (1990).

545. C. P. Jasperse and D. P. Curran, J. Am. Chem. Soc., **112**, 5601 (1990).

546. A. J. Bloodworth, D. Crich, and T. Melvin, J. Chem. Soc., Chem. Commun., **1987**, 786.

547. D. L. J. Clive and H. W. Manning, J. Chem. Soc., Chem. Commun., **1993**, 666.

548. D. L. J. Clive, D. R. Cheshire, and L. Set, J. Chem. Soc., Chem. Commun., **1987**, 353.

549a. D. P. Curran, A. C. Abraham, and H. Liu, J. Org. Chem., **56**, 4335 (1991).

549. M. Journet, W. Smadja, and M. Malacria, Synlett, **1990**, 320.

550. S. Kim and J. S. Kee, Tetrahedron Lett., **34**, 4213 (1993).

551. G. V. M. Sharma and S. R. Vepachedu, Tetrahedron Lett., **31**, 4931 (1990).

552. W. R. Leonard and T. Livinghouse, Tetrahedron Lett., **26**, 6431 (1985).

553. D. H. R. Barton, E. da Silva, and S. Z. Zard, J. Chem. Soc., Chem. Commun., **1988**, 285.

554. H. Hemmerle and H. J. Gais, Angew. Chem., **101**, 362 (1989); Angew. Chem., Int. Ed. Engl., **28**, 349 (1989).

555. M. Suzuki, H. Koyano, and R. Noyori, J. Org. Chem., **52**, 5583 (1987).

556. F. MacCorquodale and J. C. Walton, J. Chem. Soc., Chem. Commun., **1987**, 1456.

557. F. MacCorquodale and J. C. Walton, J. Chem. Soc., Perkin Trans. 1, **1989**, 347.

558. K. Weinges, H. Reichert, U. Huber-Patz, and H. Irngartinger, Liebigs Ann. Chem., **1993**, 403.

559. S. B. Booth, P. R. Jenkins, C. J. Swain, and J. B. Sweeney, J. Chem. Soc., Chem. Commun., **1991**, 1656.

560. S. B. Booth, P. R. Jenkins, and C. J. Swain, J. Chem. Soc., Chem. Commun., **1991**, 1248.

561. N. N. Marinovic and H. Ramanathan, Tetrahedron Lett., **24**, 1872 (1983).

562. J. K. Mcleod and L. C. Monahan, Tetrahedron Lett., **29**, 391 (1988).

563. E. W. Della, A. M. Knill, and P. E. Pigou, J. Org. Chem., **58**, 2110 (1993).

564. A. L. J. Beckwith and S. Gerba, Aust. J. Chem., **45**, 289 (1992).

565. J. K. MacLeod and L. C. Monahan, Aust. J. Chem., **43**, 329 (1990).

566. A. L. J. Beckwith, D. M. O'Shea, and D. H. Roberts, J. Chem. Soc., Chem. Commun., **1983**, 1445.

567. G. A. Kraus and S. Liras, Tetrahedron Lett., **31**, 5265 (1990).

568. M. A. Dombroski, S. A. Kates, and B. B. Snider, J. Am. Chem. Soc., **112**, 2759 (1990).

569. A. L. J. Beckwith and D. H. Roberts, J. Am. Chem. Soc., **108**, 5893 (1986).

570. V. H. Rawal, V. Krishnamurthy, and A. Fabre, Tetrahedron Lett., **34**, 2899 (1993).

571. S. Kim and J. S. Koh, J. Chem. Soc., Chem. Commun., **1992**, 1377.

572. J. Cossy, J. P. Pete, and C. Portella, Tetrahedron Lett., **30**, 7361 (1989).

573. B. B. Snider and M. A. Dombroski, J. Org. Chem., **52**, 5487 (1987).

574. W. F. Berkowitz and P. J. Wilson, J. Org. Chem., **56**, 3097 (1991).

575. M. Julia and F. LeGoffic, Bull. Soc. Chim. Fr., **1965**, 1555.

576. D. F. Taber, Y. Wang, and S. J. Stachel, Tetrahedron Lett., **34**, 6209 (1993).

577. Y. Hanzawa, H. Ito, N. Kohara, H. Sasaki, H. Fukuda, T. Morikawa, and T. Taguchi, Tetrahedron Lett., **32**, 4143 (1991).

578. P. A. Zoretic, M. Ramachandani, and M. C. Caspar, Synth. Commun., **21**, 923 (1991).

579. T. V. RajanBabu and T. Fukunaga, J. Am. Chem. Soc., **111**, 296 (1989).

580. J. E. Einhorn, C. Einhorn, and J. L. Luche, Tetrahedron Lett., **29**, 2183 (1988).

581. B. B. Snider and Q. Zhang, Tetrahedron Lett., **33**, 5921 (1993).

582. B. B. Snider, B. Y.-F. Wan, B. O. Buckman, and B. M. Fox, J. Org. Chem., **56**, 328 (1991)

583. B. B. Snider and Q. Zhang, Tetrahedron Lett., **33**, 5921 (1992).

584. D. L. J. Clive, Pure Appl. Chem., **60**, 1645 (1988).

585. J. W. Grissom, T. L. Calkins, and H. A. McMillen, J. Org. Chem., **58**, 6556 (1993).

586. P. J. Wagner and B. S. Park, Tetrahedron Lett., **32**, 165 (1991).

587. S. Kim and J. S. Koh, Tetrahedron Lett., **33**, 7391 (1992).

588. D. L. Boger and R. J. Mathvink, J. Org. Chem., **55**, 5442 (1990).

589. A. Srikrishna and P. Hemamalini, Tetrahedron, **48**, 9337 (1992).

590. E. J. Corey, C. Shih, N. Y. Shih, and K. Shimaji, Tetrahedron Lett., **25**, 5013 (1984).

591. E. J. Corey, K. Shimaji, and C. Shih, J. Am. Chem. Soc., **106**, 6425 (1984).

592. D. L. J. Clive, H. W. Manning, T. L. B. Boivin, and M. H. D. Postema, J. Org. Chem., **58**, 6857 (1993).

593. D. L. J. Clive and M. H. D. Postema, J. Chem. Soc., Chem. Commun., **5**, 429 (1993).

594. S. Satoh, M. Sodeoka, H. Sasai, and M. Shibasaki, J. Org. Chem., **57**, 2278 (1991).

595. J. D. Harling and W. B. Motherwell, J. Chem. Soc., Chem. Commun., **1988**, 1380.

596. D. L. J. Clive, H. W. Manning, and T. L. B. Boivin, J. Chem. Soc., Chem. Commun., **1990**, 972.

597. P. A. Zoretic, X. Weng, C. K. Biggers, M. S. Biggers, M. L. Caspar, and G. D. Davis, Tetrahedron Lett., **33**, 2637 (1992).

598. D. Colclough, J. B. White, W. B. Smith, and Y. Chu, J. Org. Chem., **58**, 6303 (1993).

599. P. Dowd and W. Zhang, J. Am. Chem. Soc., **113**, 9875 (1991).

600. P. Dowd and W. Zhang, J. Org. Chem., **57**, 7163 (1992).

601. K. Weinges, W. Maurer, H. Reichert, G. Schilling, T. Oeser, and H. Irngartinger, Chem. Ber., **123**, 901 (1990).

602. C. Ellwood and G. Pattenden, Tetrahedron Lett., **32**, 1591 (1991).

603. T. Sugimura, T. Futagawa, and A. Tai, Chem. Lett., **1990**, 2295.

604. T. Satoh, M. Itoh, and K. Yamakawa, Chem. Lett., **1987**, 1949.

605. W. Fan and J. B. White, Tetrahedron Lett., **34**, 957 (1993).

606. H. Nishida, H. Takahashi, H. Takeda, N. Takada, and O. Yonemitsu, J. Am. Chem. Soc., **112**, 902 (1990).

607. F. Lombardo, R. A. Newmark, and E. Kariv-Miller, J. Org. Chem., **56**, 2422 (1991).

608. T. Ikeda, S. Yue, and C. R. Hutchinson, J. Org. Chem., **50**, 5193 (1985).

609. T. Shono, N. Kise, T. Suzumoto, and T. Morimoto, J. Am. Chem. Soc., **108**, 4676 (1986).

610. A. Srikrishna and P. Hemamalini, J. Chem. Soc., Perkin Trans. 1, **1989**, 2511.

611. J. C. Chottard, M. Julia, and J. M. Salard, Tetrahedron, **25**, 4967 (1969).

612. M. Kawaguchi, S. Satoh, M. Mori, and M. Shibasaki, Chem. Lett., **1992**, 395.

613. P. A. Zoretic, M. Ramchandani, and M. L. Caspar, Synth. Commun., **21**, 915 (1991).

614. G. H. Posner, E. Asirvatham, T. G. Hamill, and K. S. Webb, J. Org. Chem., **55**, 3132 (1989).

615. J. D. Winkler, V. Sridar, and M. G. Siegel, Tetrahedron Lett., **30**, 4943 (1989).

616. J. D. White, T. C. Somers, and K. M. Yager, Tetrahedron Lett., **31**, 59 (1990).

617. M. I. Colombo, S. Signorella, M. P. Mischue, M. Gonzales-Sierra, and E. A. Ruveda, Tetrahedron, **46**, 4149 (1990).

618. J. L. Stein and M. P. Crozet, C. R. Acad. Sci., Ser. 2, **300**, 59 (1985).

619. J. L. Stein, L. Stella, and J. M. Surzur, Tetrahedron Lett., **21**, 287 (1980).

620. W.-W. Weng and T.-Y. Luh, J. Org. Chem., **58**, 5574 (1993).

621. J. Knight and P. J. Parsons, J. Chem. Soc, Perkin Trans. 1, **1987**, 1237.

622. J. Knight, P. J. Parsons, and R. Southgate, J. Chem. Soc., Chem. Commun., **1986**, 78.

623. M. D. Bachi, A. DeMesmaeker, and N. Stevenart-DeMesmaeker, Tetrahedron Lett., **28**, 2887 (1987).

624. M. D. Bachi, A. DeMesmaeker, and N. Stevenart-DeMesmaeker,

Tetrahedron Lett., **28**, 2637 (1987).

625. J. Anaya, D. H. R. Barton, S. D. Gero, M. Grande, N. Martin, and C. Tachdijian, Angew. Chem. Int. Ed. Engl., **32**, 867 (1993).

626. G. I. Nikishin, E. I. Troyanskii, and M. I. Lazareva, Tetrahedron, **41**, 4279 (1985).

627. T. Kametani and T. Honda, Heterocycles, **19**, 1861 (1982).

628. T. Kametani, D. C. Shih, A. Itoh, S. Maeda, and T. Honda, Heterocycles, **27**, 875 (1988).

629. A. L. J. Beckwith and D. R. Boate, Tetrahedron Lett., **26**, 1761 (1985).

630. T. Kametani, S. D. Chu, A. Itoh, S. Maeda, and T. Honda, J. Org. Chem., **53**, 2683 (1988).

631. M. D. Bachi and C. Hoornaert, Tetrahedron Lett., **1982**, 2505.

632. W. Cabri, I. Candiani, A. Bedeschi, and R. Santi, Tetrahedron Lett., **33**, 4783 (1992).

633. W. Cabri, D. Borghi, E. Arlandini, P. Sbraletta, and A. Bedeschi, Tetrahedron, **49**, 6837 (1993).

634. V. M. Girijavallabhan and A. K. Ganguly, Heterocycles, **28**, 47 (1989).

635. M. D. Bachi, F. Frolow, and C. Hoornaert, J. Org. Chem., **48**, 1841 (1983).

636. M. D. Bachi and C. Hoornaert, Tetrahedron Lett., **1981**, 2693.

637. M. D. Bachi and C. Hoornaert, Tetrahedron Lett., **1981**, 2689.

638. K. Miura, K. Oshima, and K. Utimoto, Chem. Lett., **1992**, 2477.

639. M. Pezechk, A. P. Brunetiere, and J. Y. Lallemand, Tetrahedron Lett., **27**, 3715 (1986).

640. H. Nagashima, K. Ara, H. Wakamatsu, and K. Itoh, J. Chem. Soc., Chem. Commun., **1985**, 518.

641. S. Knapp, F. S. Gibson, and Y. H. Choe, Tetrahedron Lett., **31**, 5397 (1990).

642. T. Sato, K. Tsujimoto, K. Matsubayashi, H. Ishibashi, and M. Ikeda, Chem. Pharm. Bull., **40**, 2308 (1992).

643. P. F. Keusenkothen and M. B. Smith, Tetrahedron, **48**, 2977 (1992).

644. P. F. Keusenkothen and M. B. Smith, Tetrahedron Lett., **30**, 3369 (1989).

645. R. S. Jolly and T. Livinghouse, J. Am. Chem. Soc., **110**, 7536 (1988).

646. J. M. Surzur and L. Stella, Tetrahedron Lett., **1974**, 2191.

647. R. J. Kolt, D. Griller, and D. D. M. Wayner, Tetrahedron Lett., **31**, 7539 (1990).

648. S. Torii, T. Inokuchi, and T. Yukawa, J. Org. Chem., **50**, 5875 (1985).

649. H. Ishibashi, T. Sato, M. Irie, S. Harada, and M. Ikeda, Chem. Lett.,

1987, 795.

650. C. D. S. Brown, N. S. Simpkins, and K. Clinch, Tetrahedron Lett., **34**, 131 (1993).

651. S. Iwasa, M. Yamamoto, S. Kohmoto, and K. Yamada, J. Org. Chem., **56**, 2849 (1991).

652. A. Srikrishna, S. Nagaraju, and G. V. R. Sharma, J. Chem. Soc., Chem. Commun., **1993**, 285.

653. A. Nishida, M. Nishida, and O. Yonemitsu, Tetrahedron Lett., **31**, 7035 (1990).

654. G. Pandey and G. D. Reddy, Tetrahedron Lett., **33**, 6533 (1992).

655. G. Stork and O. Ouerfelli, New J. Chem., **16**, 95 (1992).

656. C. S. Wilcox and L. M. Thomasco, J. Org. Chem., **50**, 546 (1985).

657. M. F. Jones and S. M. Roberts, J. Chem. Soc., Perkin Trans. 1, **1988**, 2927.

658. C. Jenny, P. Wipf, and H. Heimgartner, Helv. Chim. Acta, **72**, 838 (1989).

659. S. Takano, K. Ohashi, T. Sugihara, and K. Ogasawara, Chem. Lett., **1991**, 203.

660. M. J. Begley, R. J. Fletcher, J. A. Murphy, and M. S. Sherburn, J. Chem. Soc., Chem. Commun., **1993**, 1723.

661. C. Gennari, G. Poli, C. Scolastico, and M. Vassallo, Tetrahedron Asymmetry, **2**, 793 (1991).

662. L. Belsivi, C. Gennari, G. Poli, C. Scolastico, B. Salom, and M. Vassallo, Tetrahedron, **48**, 3945 (1992).

663. S. F. Martin, C. P. Yang, W. L. Laswell, and H. Rueger, Tetrahedron Lett., **29**, 6685 (1988).

664. D. A. Burnett, J. K. Choi, D. J. Hart, and Y. M. Tsai, J. Am. Chem. Soc., **106**, 8201 (1984).

665. D. J. Hart and Y. M. Tsai, J. Am. Chem. Soc., **104**, 1430 (1982).

666. A. Srikrishna, G. V. R. Sharma, and S. Nagaraju, Synth. Commun., **22**, 1221 (1992).

667. J.-K. Choi and D. J. Hart, Tetrahedron, **41**, 3959 (1985).

668. D. J. Hart and Y. M. Tsai, J. Am. Chem. Soc., **106**, 8209 (1984).

669. A. G. H. Wee, Tetrahedron, **46**, 5065 (1990).

670. J. Marco-Contelles, P. Ruiz, L. Martinez, and A. Martinez-Grau, Tetrahedron, **49**, 6669 (1993).

671. J. E. Baldwin, M. G. Molonay, and A. F. Passons, Tetrahedron, **48**, 9373 (1992).

672. D. S. Middleton, N. S. Simpkins, and N. K. Terrett, Tetrahedron Lett., **30**, 3865 (1989).

673. J. Cossy and A. Bouzide, J. Chem. Soc., Chem. Commun., **1993**, 1218.

674. H. Urbach and R. Henning, Heterocycles, **28**, 957 (1989).

675. K. Matsumoto, K. Miura, K. Oshima, and K. Utimoto, Tetrahedron Lett., **33**, 7031 (1992).

676. Y. M. Tsai, B. W. Ben, C. T. Yang, and C. H. Lin, Tetrahedron Lett., **33**, 7895 (1992).

677. S. Kano, Y. Yuasa, K. Asami, and S. Shibuya, Chem. Lett., **1986**, 735.

678. C. L. Tu and P. S. Mariano, J. Am. Chem. Soc., **109**, 5287 (1987).

679. J. M. Contelles, P. Ruiz, B. Snchez, and M. L. Jimeno, Tetrahedron Lett., **33**, 5261 (1993).

680. J. K. Choi, D. J. Hart, and Y. M. Tsai, Tetrahedron Lett., **23**, 4765 (1982)

681. D. P. Curran, W.-T. Jiaang, M. Palovich, and Y.-M. Tsai, Synlett, **1993**, 403.

682. R. Mahler and J. O. Metzger, Fat. Sci. Technol., **95**, 337 (1993).

683. C. E. McDonald and R. W. Dugger, Tetrahedron Lett., **29**, 2413 (1988).

684. J. Cossy, A. Bouzide, and C. Leblanc, Synlett, **1993**, 202.

685. W. R. Bowman, D. N. Clark, and R. J. Marmon, Tetrahedron Lett., **34**, 4993 (1992).

686. D. R. Artis, J. S. Cho, and J. M. Muchowski, Can. J. Chem., **70**, 1838 (1992).

687. D. L. Flynn, D. L. Zabrowski, and R. Nosal, Tetrahedron Lett., **33**, 7281 (1992).

688. J. E. Baldwin and C. S. Li, J. Chem. Soc., Chem. Commun., **1988**, 261.

689. J. P. Marino, E. Laborde, and R. S. Paley, J. Am. Chem. Soc., **110**, 966 (1988).

690. J. J. Gaudino and C. S. Wilcox, J. Am. Chem Soc., **112**, 4374 (1990).

691. W. Koof, R. VanGinkel, M. Kranenburg, H. Hiemstra, S. Louwrier, M. J. Molenaar, and W. N. Speckamp, Tetrahedron Lett., **32**, 401 (1991).

692. J. M. Dener and D. J. Hart, Tetrahedron, **44**, 7037 (1988).

693. S. Velázquez, S. Huss, and M.-J. Camarasa, J. Chem. Soc., Chem. Commun., **1991**, 1263.

694. G. E. Keck, E. N. K. Cressman, and E. J. Enholm, J. Org. Chem., **54**, 4345 (1989).

695. G. Stork, H. S. Suh, and G. Kim, J. Am. Chem. Soc., **113**, 7054 (1991).

696. M. Kaafarani, M. P. Crozet, and J. M. Surzur, Bull. Soc. Chim. Fr., **1989**, 114.

697. H. Nagashima, H. Wakamatsu, N. Ozaki, T. Ishii, M. Watanabe, T. Tajima, and U. Itoh, J. Org. Chem., **57**, 1682 (1992).

698. J. A. Murphy and M. S. Sherburn, Tetrahedron, **47**, 4077 (1991).

699. J. A. Murphy and M. S. Sherburn, Tetrahedron Lett., **31**, 3495 (1990).

700. L. Benati, P. C. Montevecchi, and P. Sagnolo, J. Chem. Soc., Perkin Trans. 1, **1991**, 2103.

701. S. Ozaki, H. Matsushita, and H. Ohmori, J. Chem. Soc., Chem. Commun., **1992**, 1120.

702. G. Boisvert and R. Giasson, Tetrahedron Lett., **33**, 6587 (1992).

703. A. L. J. Beckwith and G. F. Meijs, J. Chem. Soc., Chem. Commun., **1981**, 595.

704. G. F. Meijs and A. L. J. Beckwith, J. Am. Chem. Soc., **108**, 5890 (1986).

705. G. F. Meijs and A. L. J. Beckwith, J. Chem. Soc., Chem. Commun., **1981**, 136.

706. A. L. J. Beckwith and G. F. Meijs, J. Org. Chem., **52**, 1922 (1987).

707. Y. Yuasa, S. Kano, and S. Shibuya, Heterocycles, **32**, 2311 (1991).

708. K. Nozaki, K. Oshima, and K. Utimoto, Tetrahedron, **45**, 923 (1989).

709. C. Audin, J.-M. Lancelin, and J.-M. Beau, Tetrahedron Lett., **29**, 3691 (1988).

710. H. Ishibashi, T. S. So, T. Sato, K. Kuroda, and M. Ikeda, J. Chem. Soc., Chem. Commun., **1989**, 762.

711. H. Ishibashi, T. S. So, K. Okochi, T. Sato, N. Nakamura, H. Nakatani, and M. Ikeda, J. Org. Chem., **56**, 95 (1991).

712. A. Srikrishna, J. Chem. Soc., Chem. Commun., **1987**, 587.

713. H. Ishibashi, N. Nakamura, T. Sato, M. Takeuchi, and M. Ikeda, Tetrahedron Lett., **32**, 1725 (1991).

714. T. Sato, N. Nakamura, K. Ikeda, M. Okada, H. Ishibashi, and M. Ikeda, J. Chem. Soc., Perkin Trans. 1, **1992**, 2399.

715. C. Lampard, J. A. Murphy, and N. Lewis, J. Chem. Soc., Chem. Commun., **1993**, 295.

716. Y. Watanabe, Y. Ueno, L. Tanaka, M. Okawara, and T. Endo, Tetrahedron Lett., **28**, 3953 (1987).

717. K. Shankaran, C. P. Sloan, and V. Snieckus, Tetrahedron Lett., **26**, 6001 (1985).

718. K. Jones, M. Thompson, and C. Wright, J. Chem. Soc., Chem. Commun., **1986**, 115.

719. K. Kobayashi, M. Itoh, and H. Suginone, Tetrahedron Lett., **28**, 3369 (1987).

720. C. P. A. Kunka and J. Warkentin, Can. J. Chem., **68**, 575 (1990).

721. K. R. Biggs, P. J. Parsons, D. J. Tapolzcay, and J. M. Underwood, Tetrahedron Lett., **30**, 7115 (1989).

722. A. L. J. Beckwith and S. W. Westwood, Tetrahedron, **45**, 5269 (1989).

723. A. Srikrishna and K. C. Pullaiah, Tetrahedron Lett., **28**, 5203 (1987).

724. B. Roudot, T. Durand, J. P. Girard, J. C. Rossi, L. Schio, S. P. Khanapure, and J. Rokach, Tetrahedron Lett., **34**, 8245 (1993).

725. S. Fukuzawa, A. Nakanishi. T. Fujinami, and S. Sakai, J. Chem. Soc., Perkin Trans. 1, **1988**, 1669.

726. R. Kiesewetter and P. Margaretha, Helv. Chim. Acta, **70**, 121 (1987).

727. C. Wright, M. Shulkind, K. Jones, and M. Thompson, Tetrahedron Lett., **28**, 6389 (1987).

728. J. P. Dittani and H. Ramanathan, Tetrahedron Lett., **29**, 45 (1988).

729. M. Tsukazaki and V. Snieckus, Can. J. Chem., **70**, 1486 (1992).

730. U. Albrecht, R. Wartchow, and H. M. R. Hoffmann, Angew. Chem., Int. Ed. Engl., **31**, 910 (1992).

731. A. Srikishina and K. Kroshnan, Tetrahedron Lett., **29**, 4995 (1988).

732. E. R. Lee, I. Lakomy, P. Bigler, and R. Scheffold, Helv. Chim. Acta, **74**, 146 (1991).

733. H. Togo and O. Kikuchi, Hetereocycles, **28**, 373 (1989).

734. J. C. Lopez, A. M. Gomez, and B. Fraser-Reid, J. Chem. Soc., Chem. Commun., **1993**, 762.

735. W. Xu and P. S. Mariano, J. Am. Chem. Soc., **113**, 1431 (1991).

736. K. Jones and J. M. D. Storey, J. Chem. Soc., Chem. Commun., **1992**, 1766.

737. Y. Chapleur and N. Moufid, J. Chem. Soc., Chem. Commun., **1989**, 39.

738. R. J. Ferrier and P. M. Petersen, Tetrahedron, **46**, 1 (1990).

739. A. DeMesmaeker, P. Hoffmann, and B. Ernst, Tetrahedron Lett., **29**, 6585 (1988).

740. A. J. Clark and K. Jones, Tetrahedron Lett., **30**, 5485 (1989).

741. A. J. Clark and K. Jones, Tetrahedron, **48**, 6875 (1992).

742. M. J. Begley, M. Ladlow, and G. Pattenden, J. Chem. Soc., Perkin Trans. 1, **1988**, 1095.

743. M. Koreeda and D. C. Visger, Tetrahedron Lett., **33**, 6603 (1992).

744. A. N. Abeywickrema, A. L. J. Beckwith, and S. Gerba, J. Org. Chem., **52**, 4072 (1987).

745. L. K. Dyall, Aust. J. Chem., **32**, 643 (1979).

746. J. Yoshida, S. Nakatani, K. Sakaguchi, and S. Isoe, J. Org. Chem., **54**, 3383 (1989).

747. A. Srikrishna and G. Veera Raghava Sharma, Tetrahedron Lett., **29**, 6487 (1988).

748. R. J. Ferrier, P. M. Petersen, and M. A. Taylor, J. Chem. Soc., Chem. Commun., **1989**, 1247.

749. N. Moufid and Y. Chapleur, Tetrahedron Lett., **32**, 1799 (1991).

750. R. Nouguier, C. Lesueur, E. DeRiggi, M. P. Bertrand, and A. Virgili, Tetrahedron Lett., **31**, 3541 (1990).

751. J. Cossy and D. Belotti, Tetrahedron Lett., **29**, 6113 (1988).

752. K. Tamao, K. Maeda, T. Yamaguchi, and Y. Ito, J. Am. Chem. Soc., **111**, 4984 (1989).

753. S. Knapp and F. S. Gibson, J. Org. Chem., **57**, 4802 (1992).

754. J. Ardisson, J. P. Ferezou, M. Julia, Y. Li, L. W. Liu, and A. Pancrazi, Bull. Soc. Chim. Fr., **129**, 387 (1992).

755. J. Arolisson, J. P. Frzou, and M. Julia, Tetrahedron Lett., **28**, 2001 (1987).

756. A. L. J. Beckwith, S. P. Joseph, and R. T. A. Mayadunne, J. Org. Chem. **58**, 4198 (1993).

757. D. L. Boger and R. S. Coleman, J. Am. Chem. Soc., **110**, 4796 (1988).

758. J. E. Lyons, C. H. Schiesser, and K. Sutej, J. Org. Chem., **58**, 5632 (1993).

759. D. S. Middleton, N. S. Simpkins, and N. K. Terret, Tetrahedron, **46**, 545 (1990).

760. A. DeMesmaeker, P. Hoffmann, and B. Ernst, Tetrahedron Lett., **30**, 57 (1989).

761. K. S. Grkninger, K. F. Jger, and B. Giese, Liebigs Ann. Chem., **1987**, 731.

762. Y. Ueno, K. Chino, and M. Okawara, Tetrahedron Lett., **23**, 2575 (1982).

763. J. C. Lopez, A. M. Gomez, and S. Valverde, J. Chem. Soc., Chem. Commun., **1992**, 613.

764. D. Batty and D. Crich, Tetrahedron Lett., **33**, 875 (1992).

765. D. Batty and D. Crich, J. Chem. Soc., Perkin Trans. 1, **1992**, 3193.

766. S. Hanessian, P. Beaulieu, and D. Dub, Tetrahedron Lett., **27**, 5071 (1986).

767. D. L. J. Clive and A. Y. Mohammed, Heterocycles, **28**, 1157 (1989).

768. K. Jones and C. McCarthy, Tetrahedron Lett., **30**, 2657 (1989).

769. H. McNab, J. Chem. Soc., Perkin Trans. 1, **1984**, 377.

770. H. McNab and G. S. Smith, J. Chem. Soc., Chem. Commun., **1982**, 996.

771. T. A. K. Smith and G. H. Whitham, J. Chem. Soc., Chem. Commun., **1989**, 313.

772. T. Honda, M. Satoh, and Y. Kobayashi, J. Chem. Soc., Perkin Trans. 1, **1992**, 1557.

773. M. Carda and J. A. Alberto, Tetrahedron, **48**, 9789 (1992).

774. E. J. Enholm and A. Trivellas, J. Am. Chem. Soc., **111**, 6463 (1989).

775. R. Leardini, D. Nanni, M. Santori, and G. Zanardi, Tetrahedron, **48**, 3961 (1992).

776. D. Batty and D. Crich, J. Chem. Soc., Perkin Trans. 1, **1992**, 3205.

777. M. J. Begley, H. Bhandal, J. H. Hutchinson, and G. Pattenden, Tetrahedron Lett., **28**, 1317 (1987).

778. M. J. Begley, D. R. Cheshire, T. Harrison, J. H. Hutchinson, P. L. Myers, and G. Pattenden, Tetrahedron, **45**, 5215 (1989).

779. M. Carda and J. A. Marco, Tetrahedron Lett., **32**, 5191 (1991).

780. E. J. Enholm, H. Satici, and A. Trivellas, J. Org. Chem. **54**, 5841 (1989).

781. V. Pedretti, J.-M. Mallet, and P. Sina, Carbohydr. Res., **244**, 247 (1993).

782. P. J. Parsons, P. Willis, and S. C. Eyley, Tetrahedron, **48**, 9461 (1992).

783. D. L. J. Clive and J. R. Bergstra, J. Org. Chem., **56**, 4976 (1991).

784. A. DeMaesmaeker, P. Hoffmann, T. Winkler, and A. Waldner, Synlett, **1990**, 201.

785. T. Honda, M. Hoshi, and M. Tsubuki, Heterocycles, **34**, 1515 (1992).

786. H. Nagano, Y. Seko, and K. Nakai, J. Chem. Soc., Perkin Trans. 1, **1990**, 2153.

787. S. Kano, Y. Yuasa, T. Yokomatsu, K. Asami, and S. Shibuya, J. Chem. Soc., Chem. Commun., **1986**, 1717.

788. M. C. Fong and C. H. Schiesser, Tetrahedron Lett., **34**, 4347 (1993).

789. S. Kano, Y. Yuasa, K. Asami, and S. Shibuya, Heterocycles, **27**, 1437 (1988).

790. W. R. Bowman, H. Heaney, and B. M. Jordan, Tetrahedron Lett., **29**, 6657 (1988).

791. A. DeMesmaeker, A. Waldner, P. Hoffmann, T. Mindt, P. Hug, and T. Winkler, Synlett, **1990**, 687.

792. H. Ishibashi, H. Nakatani, S. Iwaml, T. Sato, N. Nakamura, and M. Ikeda, J. Chem. Soc., Chem. Commun., **1989**, 1767.

793. J. M. Dener, D. J. Hart, and S. Ramesh, J. Org. Chem., **53**, 6022 (1988).

794. R. A. Alonso, G. D. Vite, R. E. McDevitt, and B. Fraser-Reid, J. Org. Chem., **57**, 573 (1992).

795. G. D. Vite, R. A. Alonso, and B. Fraser-Reid, J. Org. Chem., **54**, 2268 (1989).

796. P. J. Parsons, P. A. Willis, and S. C. Eyley, J. Chem. Soc., Chem. Commun., **1988**, 283.

797. H. Hashimoto, K. Furuichi, and T. Miwa, J. Chem. Soc., Chem. Commun., **1987**, 1002.

798. T. V. RajanBabu, J. Org. Chem., **53**, 4522 (1988).

799. D. L. Boger, R. J. Wysocki, Jr., and T. Ishizaki, J. Am. Chem. Soc., **112**,

5230 (1990).

800. D. L. Boger and R. J. Wysocki, Jr., J. Org. Chem., **54**, 1239 (1989).

801. A. DeMesmaeker, P. Hoffmann, B. Ernst, P. Hug, and T. Winkler, Tetrahedron Lett., **30**, 6307 (1989).

802a. A. DeMesmaeker, P. Hoffmann, B. Ernst, P. Hug, and T. Winkler, Tetrahedron Lett., **30**, 6311 (1989).

802. A. Haudrechy and P. Sina, Carbohydr. Res., **216**, 375 (1991).

803. A. J. Bloodworth and M. D. Spencer, Tetrahedron Lett., **31**, 5513 (1990).

804. E. Lee, C. H. Yoon, and T. H. Lee, J. Am. Chem. Soc., **114**, 10981 (1992).

805. K. S. Feldman, H. M. Berven, and A. L. Romanelli, J. Org. Chem., **58**, 6851 (1993).

806. A. Gossen, C. W. McCleland, and F. C. Rinaldi, J. Chem. Soc., Perkin Trans. 2, **1993**, 279.

807. T. Sato, S. Ishida, H. Ishibashi, and M. Ikeda, J. Chem. Soc., Perkin Trans. 1, **1991**, 353.

808. A. J. Clark, K. Jones, C. McCarthy, and J. M. D. Storey, Tetrahedron Lett., **23**, 2829 (1991).

809. M. J. Tomaszewski and J. Warkentin, Tetrahedron Lett., **33**, 2123 (1992).

810. R. Leardini, D. Nanni, A. Tundo, G. Zanardi, and F. Ruggieri, J. Org. Chem., **57**, 1842 (1992).

811. K. Kobayashi, A. Kinishi, Y. Kanno, and H. Suginome, J. Chem. Soc., Perkin Trans. 1, **1993**, 111.

812. T. Hamada, M. Ohmori, and O. Yoremitsu, Tetrahedron Lett., **1977**, 1519.

813. D. Crich, K. A. Eustace, and T. J. Ritchie, Heterocycles, **28**, 67 (1989).

814. C. Chen and D. Crich, Tetrahedron Lett., **34**, 1545 (1993).

815. R. Leardini, D. Nanni, A. Tundo, and G. Zanardi, Gazz. Chim. Ital., **119**, 637 (1989).

816. R. Leardini, G. F. Pedulli, A. Tundo, and G. Zanardi, J. Chem. Soc., Chem. Commun., **1984**, 1320.

817. A. R. Forrester, M. Gill, and R. H. Thomson, J. Chem. Soc., Chem. Commun., **1976**, 677.

818. F. D. Lewis and G. D. Reddy, Tetrahedron Lett., **33**, 4249 (1992).

819. R. Leardini, D. Nanni, A. Tundo, and G. Zanardi, J. Chem. Soc., Chem. Commun., **1989**, 757.

820. S. Takano, M. Suzuki, A. Kijiwa, and K. Ogasawara, Chem. Lett., **1990**, 315.

821. F. A. Neugebauer and I. Umminger, Chem. Ber., **113**, 1205 (1980).

822. S. A. Hitchcock and G. Pattenden, Tetrahedron Lett., **31**, 3641 (1990).

823. D. J. Hart and J. A. McKinney, Tetrahedron Lett., **30**, 2611 (1989).

824. E. C. Ashby and N. P. Tung, Tetrahedron Lett., **1984**, 4333.

825. W. Zhang and P. Dowd, Tetrahedron Lett., **33**, 7307 (1992).

826. T. Rajamannar and K. K. Balasubramanian, Tetrahedron Lett., **29**, 5789 (1988).

827. D. P. Curran and S. C. Kuo, Tetrahedron, **43**, 5653 (1987).

828. D. Hobbs-Mallyou and D. A. Whiting, J. Chem. Soc., Chem. Commun., **1991**, 1324.

829. J. S. Yadav, T. K. Praveen Kumar, and V. R. Gadgil, Tetrahedron Lett., **33**, 3687 (1992).

830. P. Bakuzis, O. O. S. Campos, and M. L. F. Bakuzis, J. Org. Chem., **41**, 3261 (1976).

831. S. Pal, M. Mukherjee, D. Podder, A. U. Mukherjee, and U. R. Ghahk, J. Chem. Soc., Chem. Commun., **1991**, 1591.

832. A. P. Neary and P. J. Parsons, J. Chem. Soc., Chem. Commun., **1989**, 1090.

833. D. P. Curran and D. M. Rakiewicz, J. Am. Chem. Soc., **107**, 1448 (1985).

834. J. Cossy, D. Belotti, and J. P. Pete, Tetrahedron Lett., **28**, 4547 (1987).

835. J. Cossy, D. Belotti, and J. P. Pete, Tetrahedron, **46**, 1859 (1990).

836. C. E. Mowbray and G. Pattenden, Tetrahedron Lett., **34**, 127 (1993).

837. Y.-J. Chen and W.-Y. Lin, Tetrahedron Lett., **33**, 1749 (1992).

838. J. M. Fang and M. Y. Chen, Tetrahedron Lett., **28**, 2853 (1987).

839. A. K. Ghosh, K. Ghosh, P. Sitaram, and U. R. Chatak, J. Chem. Soc., Chem. Commun., **1993**, 809.

840. D. P. Curran and M. H. Chen, Tetrahedron Lett., **26**, 4991 (1985).

841. G. Pattenden and S. J. Teague, J. Chem. Soc., Perkin Trans. 1, **1988**, 1077.

842. L. M. Van der Linde and A. J. A. Van der Weerdt, Tetrahedron Lett., **25**, 1201 (1984).

843. J. W. Grissom and T. L. Calkins, J. Org. Chem., **58**, 5422 (1993).

844. G. A. Kraus and Y. S. Hon, J. Org. Chem., **50**, 4605 (1985).

845. A. Srikrishna, G. V. R. Sharma, and P. Hemamalini, J. Chem. Soc., Chem. Commun., **1990**, 1681.

846. J. W. Grissom and T. L. Calkins, Tetrahedron Lett., **33**, 2315 (1992).

847. K. Vijaya Bhaskar and G. S. R. Subba Rao, Tetrahedron Lett., **30**, 225 (1989).

848. T. L. Fevig, R. L. Elliott, and D. P. Curran, J. Am. Chem. Soc., **110**, 5064

(1988).

849. J. C. Chottard and M. Julia, Bull. Soc. Chim. Fr., **1968**, 3700.

850. Y. S. Kulkarni, M. Niwa, E. Ron, and B. B. Snider, J. Org. Chem., **52**, 1568 (1987).

851. D. P. Curran and W. Shen, Tetrahedron, **49**, 755 (1993).

852. M. J. Begley, G. Pattenden, and G. M. Robertson, J. Chem. Soc., Perkin Trans. 1, **1988**, 1085

853. G. Pattenden and G. M. Robertson, Tetrahedron Lett., **27**, 399 (1986).

854. Y.-J. Chen, C.-M. Chen, and W.-Y. Lin, Tetrahedron Lett., **34**, 2962 (1993).

855. A. Srikrishna, P. Hemamalini, and G. Veera Raghava Sharma, Tetrahedron Lett., **32**, 6609 (1991).

856. A. Srikrishna, P. Hemamalini, and G. Veera Raghava Sharma, J. Org. Chem., **58**, 2509 (1993).

857. Y. K. Rao and M. Nagarajan, J. Org. Chem., **54**, 5678 (1989).

858. Y. Koteswar Rao and M. Nagarajan, Tetrahedron Lett., **29**, 107 (1988).

859. K. Shishido, G. Kiyoto, A. Tsuda, Y. Takaishi, and M. Shibuya, J. Chem. Soc., Chem. Commun., **1993**, 793.

860. E. Wenkert, B. C. Bookser, and T. S. Arrhenius, J. Am. Chem. Soc., **114**, 644 (1992).

861. R. P. Quirk and F. H. Murphy, Tetrahedron Lett., **1979**, 301.

862. A. G. Myers and K. R. Condroski, J. Am. Chem. Soc., **115**, 7926 (1993).

863. L. A. Paquette, C. S. Ra, and T. W. Silvestri, Tetrahedron, **45**, 3099 (1989).

864. A. Osuka, H. Shimizu, H. M. Chiba, H. Suzuki, and K. Maruyama, J. Chem. Soc., Perkin Trans. 1, **1983**, 2073.

865. E. Hobloth and H. Lund, Acta Chem. Scand., Ser. B, **B31**, 395 (1977).

866. A. S. Kende, F. H. Ebetino, and T. Ohta, Tetrahedron Lett., **26**, 3063 (1985).

867. A. S. Kende, K. Koch, and C. A. Smith, J. Am. Chem. Soc., **110**, 2210 (1988).

868. L. A. Paquette, I. A. Colapret, and D. R. Andrews, J. Org. Chem., **50**, 201 (1985).

869. S. K. Pradhan, T. V. Radhakrishnan, and R. Subramanian, J. Org. Chem., **41**, 1943 (1976).

870. B. Arreguy San Miguel, B. Maillard, and B. Delmond, Tetrahedron Lett., **28**, 2127 (1987).

871. P. A. Zoretic, X. Weng, and M. L. Caspar, Tetrahedron Lett., **32**, 4819 (1991).

872. A. V. R. Rao, B. V. Rao, D. R. Reddy, and A. K. Singh, J. Chem. Soc., Chem. Commun., **1989**, 400.

873. D. L. J. Clive, A. G. Angoh, and S. M. Bennet, J. Org. Chem., **52**, 1339 (1987).

874. S. Wolff and H. M. R. Hoffmann, Synthesis, **1988**, 760.

875. L. Benati and P. C. Montevecchi, J. Org. Chem., **46**, 4570 (1981).

876. K. Last and H. M. R. Hoffmann, Synthesis, **1989**, 901.

877. C. P. Chuang, J. C. Gallucci, D. J. Hart, and C. Hoffman, J. Org. Chem., **53**, 3218 (1988).

878. C. P. Chuang, J. C. Gallucci, and D. J. Hart, J. Org. Chem., **53**, 3210 (1988).

879. B. W. A. Yenng, J. L. M. Contelles, and B. Fraser-Reid, J. Chem. Soc., Chem. Commun., **1989**, 1160.

880. W. B. Motherwell and A. M. K. Pennell, J. Chem. Soc., Chem. Commun., **1991**, 877.

881. P. Bhattacharyya, S. S. Jash, and A. K. Dey, J. Chem. Soc., Chem. Commun., **1984**, 1668.

882. G. Ariamala and U. U. Balasubramanian, Tetrahedron Lett., **29**, 3335 (1988).

883. R. Yamaguchi, T. Hamasaki, and K. Utimoto, Chem. Lett., **1988**, 913.

884. C. P. Sloan, J. C. Cuevas, C. Quesnelle, and V. Snieckus, Tetrahedron Lett., **29**, 4685 (1988).

885. T. Sugawara, B. A. Otter, and T. Ueda, Tetrahedron Lett., **29**, 75 (1988).

886. T. Ghosh and H. Hart, J. Org. Chem., **54**, 5073 (1989).

887. C. P. Chuang and D. J. Hart, J. Org. Chem., **48**, 1782 (1983).

888. J. Marco-Contelles, A. Martinez-Grau, M. Bernabe, N. Martin, and C. Seoane, Synlett, **1991**, 165.

889. M. P. Crozet and W. Kassar, C. R. Acad. Sci. Ser. 2, **300**, 99 (1985).

890. K. S. Kim, J. H. Kim, Y. K. Kim, Y. S. Park, and C. S. Hahn, Carbohydr. Res., **194**, C1 (1989).

891. R. Kiesewetter, A. Grott, and P. Margharetha, Helv. Chim. Acta, **71**, 502 (1988).

892. S. Danishefsky and E. Taniyama, Tetrahedron Lett., **24**, 15 (1983).

893. R. Leardini, A. Tundo, and G. Zanardi, J. Chem. Soc., Perkin Trans. 1, **1981**, 3164.

894. D. P. Curran and H. Liu, J. Am. Chem. Soc., **113**, 2127 (1991).

895. H. M. R. Hoffmann, B. Schmidt, and S. Wolff, Tetrahedron, **45**, 6113 (1989).

896. Y. D. Vankar and N. C. Chaudhuri, Synth. Commun., **21**, 885 (1991).

897. J. J. Koehler and W. N. Speckamp, Tetrahedron Lett., **1977**, 631.

898. S. Hanessian, Y. L. Bennani, and R. di Fabio, Acta Cryst., **C46**, 934 (1990).

899. A. V. Rama Rao, J. S. Yadav, C. S. Rao, and S. Chandrasekhar, J. Chem. Soc., Perkin Trans. 1, **1990**, 1211.

900. M. E. Jung and G. L. Hatfield, Tetrahedron Lett., **24**, 3175 (1983).

901. A. Alonso, C. S. Burgey, B. V. Rao, G. D. Vite, R. Vollerthun, M. A. Zotolla, and B. Fraser-Reid, J. Am. Chem. Soc., **115**, 6666 (1993).

902. K. C. Nicolaou, D. G. McGarry, P. K. Somers, C. A. Veale, and G. T. Furst, J. Am. Chem. Soc., **109**, 2504 (1987).

903. J. Lejeune and J. Y. Lallemand, Tetrahedron Lett., **33**, 2977 (1992).

904. J. C. Lopez and B. Fraser-Reid, J. Am. Chem. Soc., **111**, 3450 (1989).

905. S. A. Gloves, S. L. Golding, A. Goosen, and C. W. McCleland, J. Chem. Soc., Perkin Trans. 1, **1981**, 842.

906. C. C. Yang, H. T. Chang, and J. M. Fang, J. Org. Chem., **58**, 3100 (1993).

907. A. L. Beck, M. Mascal, C. J. Moody, A. M. Z. Slawin, D. J. Williams, and W. J. Coates, J. Chem. Soc., Perkin Trans. I, 1992, 797.

908. A. L. J. Beckwith and D. R. Boate, J. Org. Chem., **53**, 4339 (1988).

909. S. A. Glover and J. Warkentin, J. Org. Chem., **58**, 2115 (1993).

910. P. Renaud, J.-P. Vionnet, and P. Vogel, Tetrahedron Lett., **32**, 3491 (1991).

911. D. J. Hart, H. C. Huang, R. Krishnamurthy, and T. Schwartz, J. Am. Chem. Soc., **111**, 7507 (1989).

912. J. Marco-Contelles, P. Ruiz-Fernández, and B. Sánchez, J. Org. Chem., **58**, 2894 (1993).

913. M. Ladlow and G. Pattenden, J. Chem. Soc., Perkin Trans. 1, **1988**, 1107.

914. H. E. Bode, C. G. Sowell, and R. D. Little, Tetrahedron Lett., **31**, 2525 (1990).

915. A. R. Forrester, M. Gill, J. S. Sadd, and R. H. Thomson, J. Chem. Soc., Chem. Commun., **1975**, 291

916. D. J. Hart and W. C. Wu, Tetrahedron Lett., **32**, 4099 (1991).

917. M. P. Bertrand, J.-M. Surzur, H. Oumar-Mahamat, and C. Moustrou, J. Org. Chem., **56**, 3089 (1991).

918. B. Chenera, C.-P. Chuang, D. J. Hart, and C.-S. Lai, J. Org. Chem., **57**, 2018 (1992).

919. D. L. J. Clive and S. Daigneault, J. Org. Chem., **56**, 5285 (1991).

920. B. Vacher, A. Samat, A. Allouche, A. Laknifly, A. Baldy, and M. Chanon, Tetrahedron, **44**, 2925 (1988).

921. M. Ladlow and G. Pattenden, Tetrahedron Lett., **26**, 4413 (1985).

922. M. Ishizaki, K. Ozaki, A. Kaematsu, T. Isoda, and O. Hoshino, J. Org. Chem., **58**, 3877 (1993).

923. T. Ueda and S. Shuto, Nucleosides Nucleotides, **3**, 295 (1984).

924. C. Lamas, C. Saa, L. Castedo, and D. Dominguez, Tetrahedron Lett., **33**, 5663 (1992).

925. F. E. Ziegler and P. G. Harran, Tetrahedron Lett., **34**, 4505 (1993).

926. L. A. Paquette, A. G. Schaefer, and J. P. Springer, Tetrahedron, **43**, 5567 (1987).

927. T. Yamamoto, S. Ishibuchi, T. Ishizuka, M. Haratake, and T. Kunieda, J. Org. Chem, **58**, 1997 (1993).

928. L. Benati, P. Spagnolo, A. Tundo, and G. Zanardi, J. Chem. Soc., Perkin Trans. 1, **1979**, 1536.

929. L. Benati, G. Placucci, P. Spangnolo, A. Tundo, and G. Zanardi, J. Chem. Soc., Perkin Trans. 1, **1977**, 1694.

930. S. Caddick, K. Aboutayab, and R. West, Synlett, **1993**, 231.

931. R. Ahmed-Schofield and P. S. Mariano, J. Org. Chem., **50**, 5667 (1985).

932. R. Leardini, A. Tundo, G. Zanardi, and G. F. Pedulli, Synthesis, **1985**, 107.

933. A. R. Forrester, A. S. Ingram, and R. H. Thomson, J. Chem. Soc., Perkin Trans. 1, **1972**, 2847.

934. Y. Hirai, A. Hagiwara, T. Terada, and T. Yamazaki, Chem. Lett., **1987**, 2417.

935. L. Belvisi, C. Gennari, G. Poli, C. Scolastico, and B. Salom, Tetrahedron: Asymmetry, **4**, 273 (1993).

936. D. C. Lathbury, P. J. Parsons, and I. Pinto, J. Chem. Soc., Chem. Commun., **1988**, 81.

937. R. Leardini, M. Lucarini, A. Nanni, D. Nanni, G. F. Pedulli, A. Tundo, and G. Zanardi, J. Org. Chem., **58**, 2419 (1993).

938. R. Ahmed-Schofield and P. S. Mariano, J. Org. Chem., **52**, 1478 (1987).

939. A. J. Walkington and D. A. Whiting, Tetrahedron Lett., **30**, 4731 (1989).

940. K. S. Feldman and C. J. Burns, J. Org. Chem., **56**, 4601 (1991).

941. J. K. Choi, D. C. Ha, D. J. Hart, C. S. Lee, S. Ramesh, and S. Wu, J. Org. Chem., **54**, 279 (1989).

942. J. K. Dickson, Jr., R. Tsang, J. M. Llera, and B. Fraser-Reid, J. Org. Chem., **54**, 5350 (1989).

943. S. Kano, Y. Ynasa, T. Yokomatsu, K. Asami, and S. Shibuya, Chem. Pharm. Bull., **36**, 2934 (1988).

944. D. L. J. Clive and A. C. Joussef, J. Chem. Soc., Perkin Trans. 1, **1991**, 2797.

945. D. L. Boger, T. Ishizaki, R. J. Wysocki, Jr., S. A. Munk, P. A. Kitos, and O. Suntornwat, J. Am. Chem. Soc., **111**, 6461 (1989).

946. K. Jones and J. Wilkinson, J. Chem. Soc., Chem. Commun., **1992**, 1767.

947. G. Just and G. Sacripante, Can. J. Chem., **65**, 104 (1987).

948. R. C. Larock and N. H. Lee, J. Org. Chem., **56**, 6253 (1991).

949. V. I. Minkin, E. P. Ivakhnenko, A. I. Shif, L. P. Olekhnovich, O. E. Kompan, A. I. Yanovskii, and Y. T. Struchkov, J. Chem. Soc., Chem. Commun. **1988**, 990.

950. Y. C. Xin, J.-M. Mallet, and P. Sinaÿ, J. Chem. Soc., Chem. Commun., **1993**, 864.

951. B. Vauzeilles, D. Cravo, J.-M. Mallet, and P. Sinaÿ, Synlett, **1993**, 522.

952. A. G. Myers, D. Y. Gin, and D. H. Rogers, J. Am. Chem. Soc., **115**, 2036 (1993).

953. T. Sano, H. Inoue, and T. Ueda, Chem. Pharm. Bull., **33**, 1856 (1985).

954. A. M. Rosa, S. Prabhahav, and A. M. Lobo, Tetrahedron Lett., **31**, 1881 (1990).

955. G. Stork, R. K. Boeckmann, Jr., D. F. Taber, W. C. Still, and J. Singh, J. Am. Chem. Soc., **101**, 7107 (1979).

956. D. P. Curran and H. Liu, J. Am. Chem. Soc., **114**, 5863 (1992).

957. A. Gopalsamy and K. K. Balasubramanian, J. Chem. Soc., Chem. Commun., **1988**, 28.

958. G. A. Kraus and H. Kim, Synth. Commun., **23**, 55 (1993).

959. J. J. Koehler and W. N. Speckamp, Tetrahedron Lett., **1977**, 635.

960. K. A. Parker, D. M. Spero, and J. van Epp, J. Org. Chem., **53**, 4628 (1988).

961. T. Ghosh and H. Hart, J. Org. Chem., **53**, 2396 (1988).

962. G. Stork and R. Mah, Tetrahedron Lett., **30**, 3609 (1989).

963. S. Karady, E. G. Corley, N. L. Abrahamson, and L. M. Weinstock, Tetrahedron Lett., **30**, 2191, (1989).

964. A. I. Meyers and B. A. Lefka, Tetrahedron, **43**, 5663 (1987).

965. S. A. Ahmad-Junan and D. A. Whiting, J. Chem. Soc., Chem. Commun., **1988**, 1160.

966. N. S. Narasimhan and I. S. Aidhen, Tetrahedron Lett., **29**, 2987 (1988).

967. S. Takauo, M. Suzuki, A. Kijima, and K. Ogosawara, Tetrahedron Lett., **31**, 2315 (1990).

968. Y. Ozlu, D. E. Cladingboel, and P. J. Parsons, Synlett, **1993**, 357.

969. R. Tsang and B. Fraser-Reid, J. Am. Chem. Soc., **108**, 2116 (1986).

970. J. C. Estevez, M. C. Villaverde, R. J. Estevez, and L. Castedo,

Tetrahedron, **49**, 2783 (1993).

971. J. C. Estevez, M. C. Villaverde, R. J. Estevez, and L. Castedo, Tetrahedron Lett., **32**, 529 (1991).

972. H. Pak, J. K. Dickson, Jr., and B. Fraser-Reid, J. Org. Chem., **54**, 5337 (1989).

973. J. Grimshaw and A. Prasanna de Silva, Can. J. Chem., **58**, 1880 (1980).

974. J. Grimshaw and A. Prasanna de Silva, J. Chem. Soc., Chem. Commun., **1979**, 193.

975. Y. Kubo, N. Asai, and T. Araki, J. Org. Chem., **50**, 5484 (1985).

976. H. Pak, I. I. Canalda, and B. Fraser-Reid, J. Org. Chem., **55**, 3009 (1990).

977. R. V. Bonnert, M. J. Davies, J. Howarth, and P. R. Jenkis, J. Chem. Soc., Chem. Commun., **1990**, 148.

978. G. Majetich, J. S. Song, C. Ringold, and G. A. Nemeth, Tetrahedron Lett., **31**, 2239 (1990).

979. T. Ueda, S. Shuto, M. Satoh, and H. Iuone, Nucleosides Nucleotides, **4**, 401 (1985).

980. M. D. Bachi and D. Denenmark, J. Am. Chem. Soc., **111**, 1886 (1989).

981. J. J. Jenkinson, J. P. Parsons, and S. C. Eyley, Synlett, **1992**, 679.

982. S. Takano, M. Suzuki, and K. Ogasawara, Heterocycles, **31**, 1151 (1990).

983. D. E. Cladingboel and P. J. Parsons, J. Chem. Soc., Chem. Commun. **1990**, 1543.

984. R. A. Holton and A. D. Williams, J. Org. Chem., **53**, 5983 (1988).

985. K. A. Parker and D. Fokas, J. Am. Chem. Soc., **114**, 9688 (1992).

986. M. Kim, K. Kawada, R. S. Gross, and D. S. Watt, J. Org. Chem., **55**, 504 (1990).

987. K. Kawada, M. Kim, and D. S. Watt, Tetrahedron Lett., **30**, 5989 (1989).

988. H. Finch, L. M. Harwood, G. M. Robertson, and R. C. Sewell, Tetrahedron Lett., **30**, 2585 (1989).

989. M. Ishizaki, K. Kurihara, E. Tanazawa, and O. Hoshino, J. Chem. Soc., Perkin Trans. 1, **1993**, 101.

990. A. Kurek-Tyrlik, J. Wicha, A. Zarecki, and G. Snatzke, J. Org. Chem., **55**, 3484 (1990).

991. S. Kim and P. L. Fuchs, J. Am. Chem. Soc., **113**, 9864 (1991).

992. K. N. V. Duong, A. Gaudemer, M. O. Johnson, R. Quilivic, and J. Zylber, Tetrahedron Lett., **34**, 2997 (1975).

993. S. A. Ahmad-Junan, A. J. Walkington, and D. A. Whiting, J. Chem. Soc., Chem. Commun., **1989**, 1613.

994. E. Ottow, G. Neef, and R. Wiechert, Angew. Chem., **101**, 776 (1989).

995. A. K. Singh, R. K. Bakshi, and E. J. Corey, J. Am. Chem. Soc., **109**, 6187 (1987).

996. M. Koreeda and I. A. George, Chem. Lett., **1990**, 83.