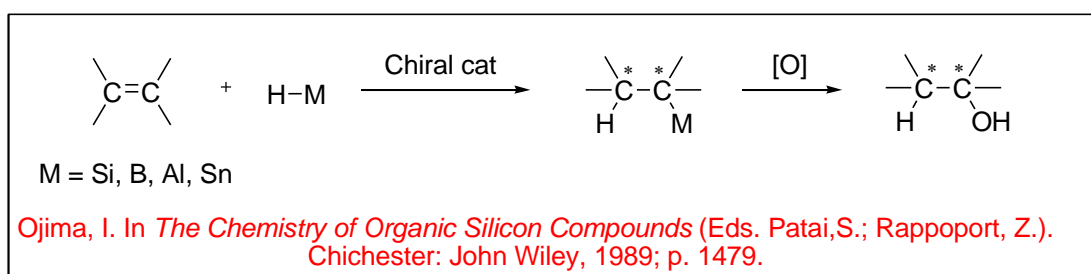# Module 8 Asymmetric Hydrosilylation and Related Reactions

Lecture 28

8.1 Hydrosilylation of Alkenes I

Asymmetric hydrosilylation and hydroboration of carbon-carbon double bonds followed by oxidative cleavage of the C-Si and C-B bonds give effective methods for the construction of optically active alcohols (Scheme 1).
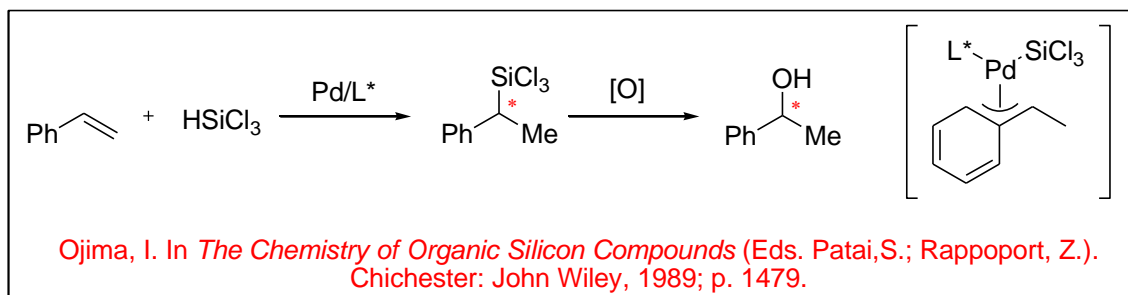

M = Si, B, Al, Sn

Ojima, I. In *The Chemistry of Organic Silicon Compounds* (Eds. Patai,S.; Rappoport, Z.). Chichester: John Wiley, 1989; p. 1479.

Scheme 1

Asymmetric hydrosilylation of carbon-carbon unsaturated substrates provides effective methods for the synthesis of optically active organosilanes, which are versatile intermediates in organic synthesis. Chiral alkyl and aryl silanes can be converted into optically active alcohols with retention configuration by oxidative cleavage of a carbon-silicon bond into carbon-oxygen bond, while the diastereoselective reaction of chiral allyl- and allenyl silanes with C=O bond can give homoallylic and homopropargylic alcohols.

8.1.1 Reactions of Styrene and its Derivatives

Chiral Palladium-catalyzed asymmetric hydrosilylation of styrene with trichlorosilane has been extensively studied. The reaction proceeds with excellent regioselectivity to give 1-phenyl-1-silylethane *via* a stable □-benzyl palladium intermediate (Scheme 2).


Ojima, I. In *The Chemistry of Organic Silicon Compounds* (Eds. Patai,S.; Rappoport, Z.). Chichester: John Wiley, 1989; p. 1479.

Scheme 2

Scheme 3 illustrates the possible mechanism. Deuterium-labeling studies suggest that the β-hydrogen elimination is found to be much faster compared to the reductive elimination from the intermediate **II**. The involvement hydropalladation in the catalytic cycle has been revealed by the side product analysis from the reaction of *o*-allylstyrene.


Uozumi, Y. *et al. J. Org. Chem.* **1998**, *63*, 6137
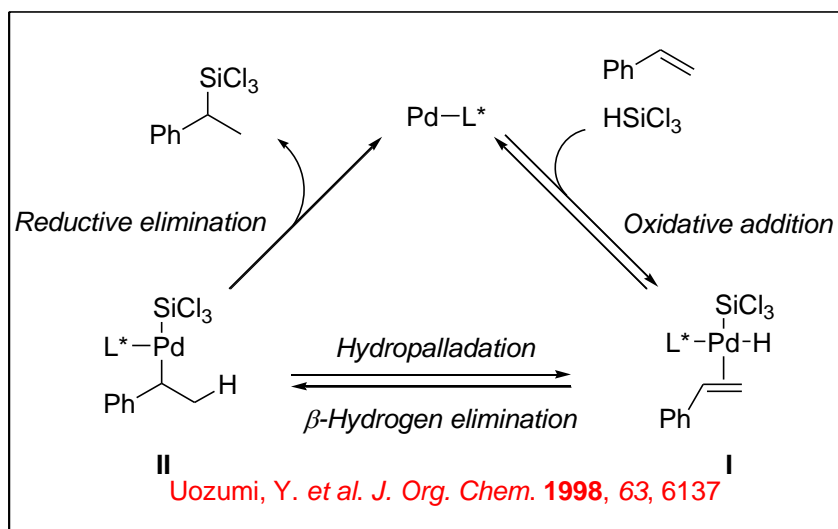
Scheme 3

The reaction has been utilized in the synthesis of 1-aryl-1,2-diols from arylacetylenes (Scheme 4). Platinum-catalyzed hydrosilylation of arylacetylene gives (*E*)-1-aryl-2-(trichlorosilyl)ethanes that could be further reacted with trichlorosilane in the presence of chiral palladium complex to afford optically active 1-aryl-1,2-bis(trichlorosilyl)ethanes. The latter could be transformed into optically active 1,2-diol via oxidative cleavage of the carbon-silicon bond into carbon oxygen bond.


Shimada, T. *et al.*, *J. Am. Chem. Soc.* **2002**, *124*, 1584
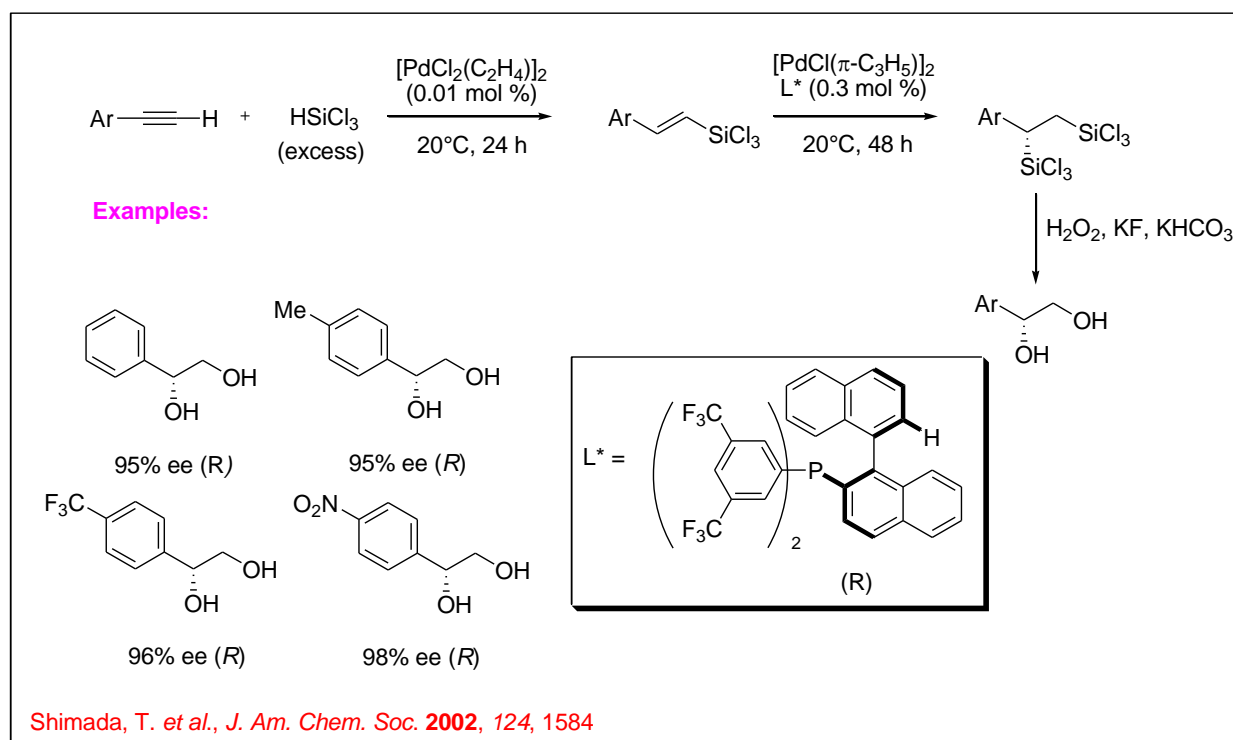
Scheme 4

Other chiral catalysts have also been employed for the asymmetric hydrosilylation of alkenes. The chiral *bis*(oxazolinyl)phenylrhodium complex catalyzes the asymmetric hydrosilylation of styrenes with hydro(alkoxy)silanes in high enantioselectivity, although the regioselectivity is found to be somewhat moderate (Scheme 5).

Tsuchiya, Y. *et al.*, *Synlett* **2004**, 2099.
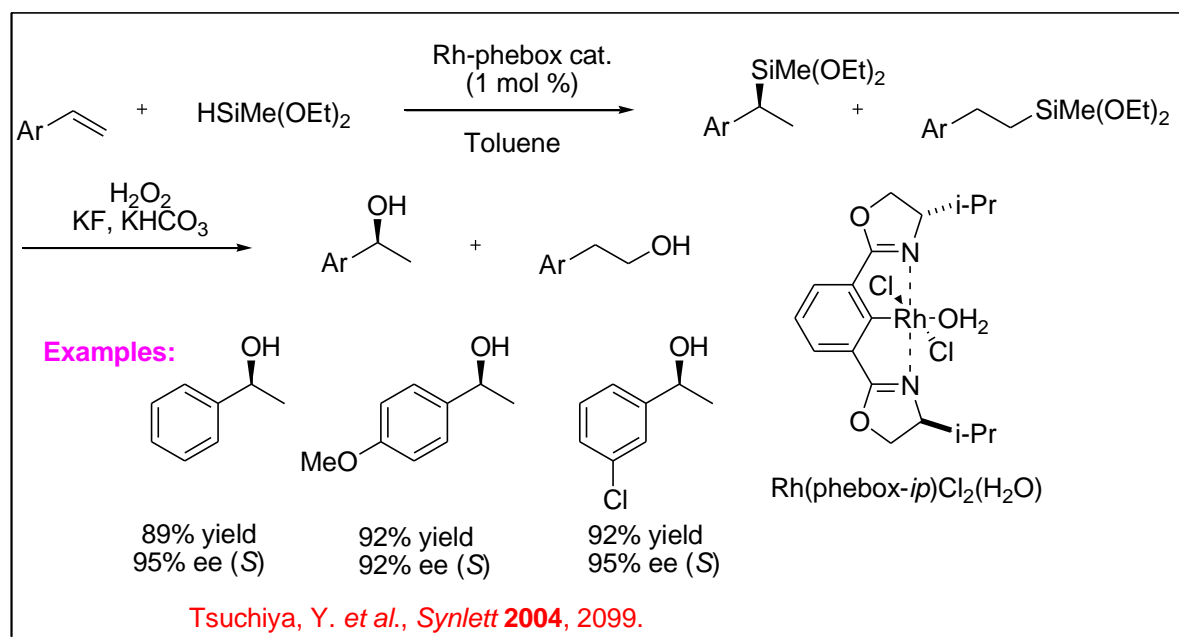
Scheme 5

α-Substituted styrenes proceed reaction with phenylsilane to afford benzylic *tert*-alkylsilanes in the presence chiral organolanthanide as catalyst in moderate enantioselectivity (Scheme 6).

Molander, G. A. *et al.*, *Organometallics* **1998**, *17*, 3754.
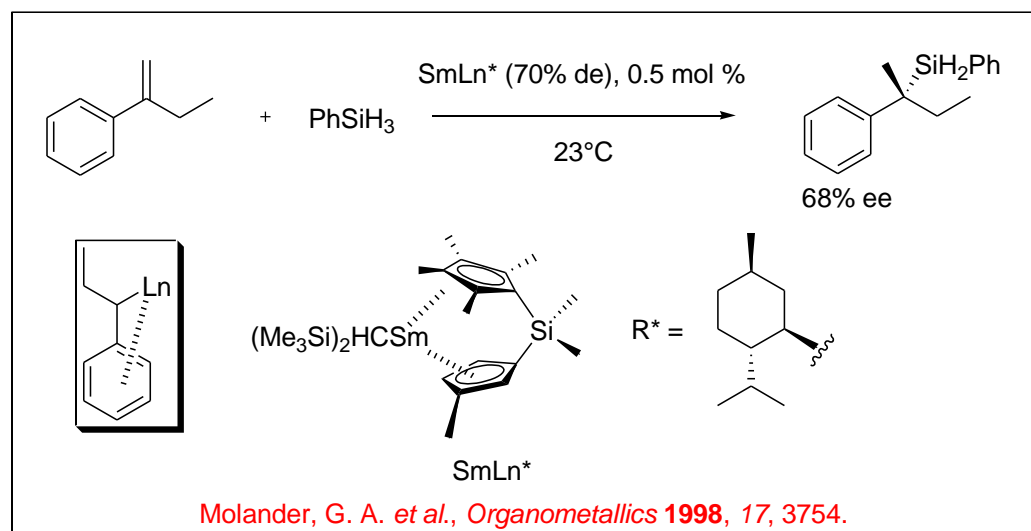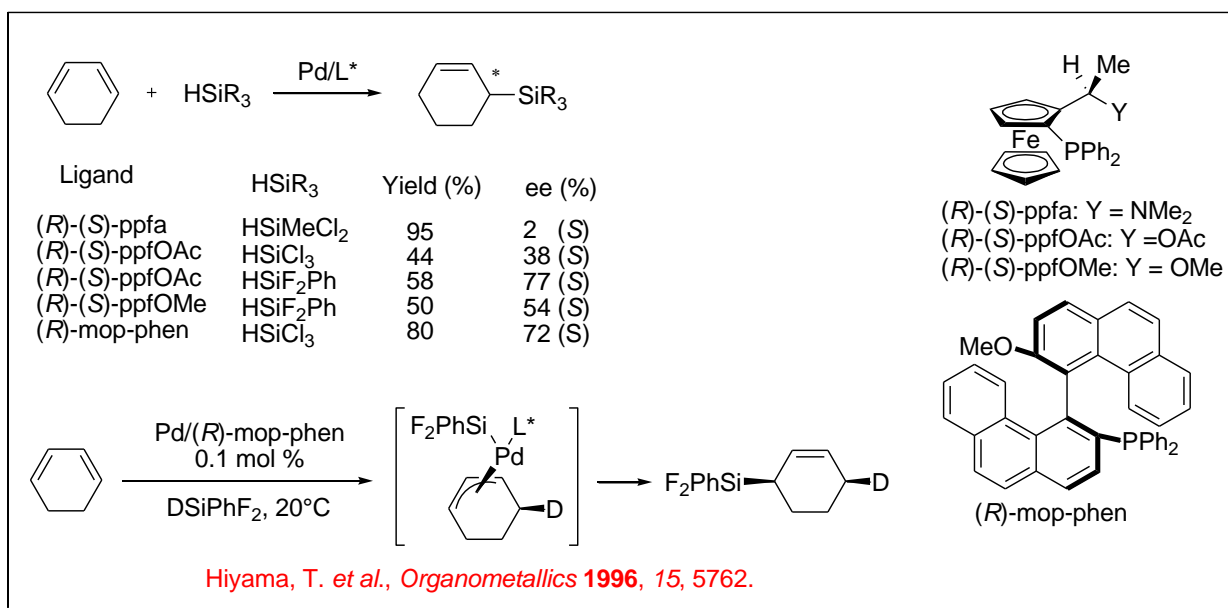
Scheme 6

8.1.2 Reactions of 1,3-Dienes

The reaction of 1,3-dienes with hydrosilanes having electron-withdrawing groups on silicon affords synthetically useful optically active silanes in the presence of chiral palladium complex (Scheme 7). The reaction proceeds in a 1,4-fashion providing chiral allylsilanes that could be converted into homoallylic alcohols on the reaction with aldehydes.
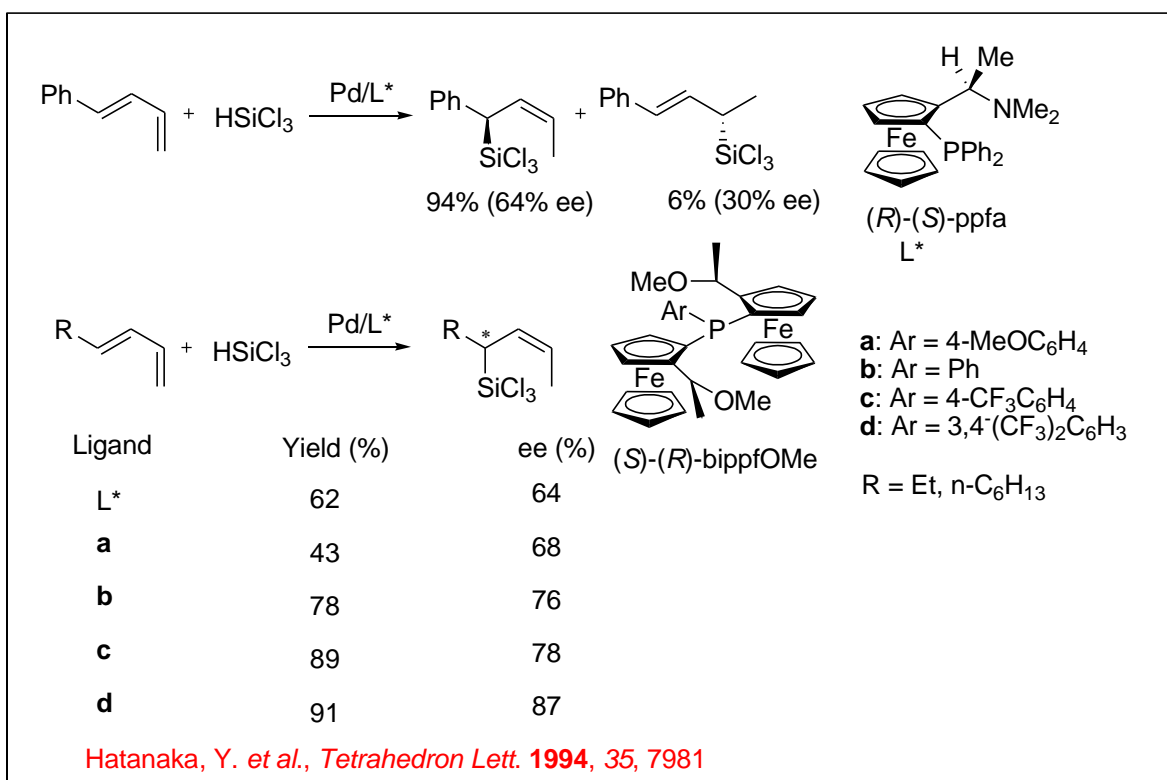

Masse, C. E. *et al.*, *Chem. Rev.* **1995**, *95*, 1293.
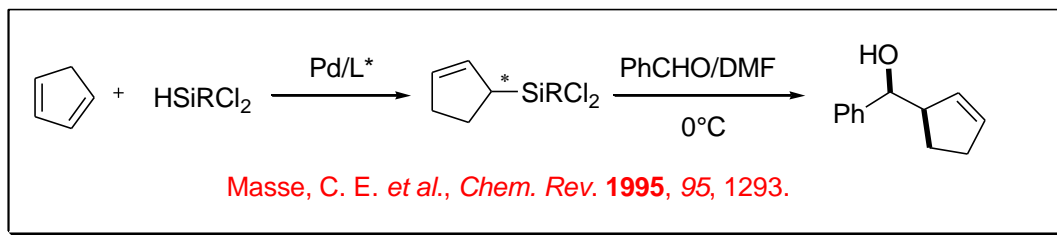
Scheme 7

The use of ferrocenylphosphine and mop-phen ligands has been demonstrated for the hydrosilylation of cyclo-1,3-hexadiene in the presence of palladium salts (Scheme 8). The reaction with phenyldifluorosilane afforded the highest enantioselectivity compared to that with trichlorsilane or methyldichlorosilane. Based on the reaction of with deuterium-labeled silane the involvement of □-allylpalladium intermediate and 1,4-*cis*-addition has been proposed.

Ligand	$HSiR_3$	Yield (%)	ee (%)
(*R*)-(*S*)-ppfa	$HSiMeCl_2$	95	2 (*S*)
(*R*)-(*S*)-ppfOAc	$HSiCl_3$	44	38 (*S*)
(*R*)-(*S*)-ppfOAc	$HSiF_2Ph$	58	77 (*S*)
(*R*)-(*S*)-ppfOMe	$HSiF_2Ph$	50	54 (*S*)
(*R*)-mop-phen	$HSiCl_3$	80	72 (*S*)

(*R*)-(*S*)-ppfa: Y = NMe₂
(*R*)-(*S*)-ppfOAc: Y =OAc
(*R*)-(*S*)-ppfOMe: Y = OMe

(*R*)-mop-phen

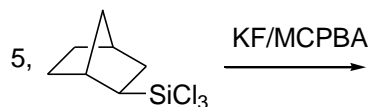Hiyama, T. *et al.*, *Organometallics* **1996**, *15*, 5762.
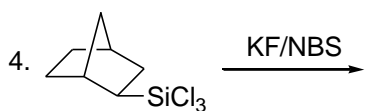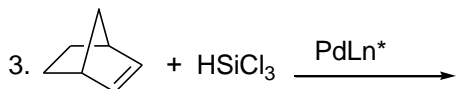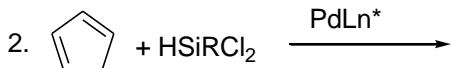
Scheme 8

In case of linear 1,3-dienes, the regioselectivity has become an issue. In the reaction of 1-phenyl-1,3-butadiene using ferrocenyl ligand, (*R*)-(*S*)-ppfa, the formation of a mixture of regioisomeric allylsilanes is observed (Scheme 9). However, in the reaction of alkyl substituted 1,3-dienes, 1,3-hexadiene and 1,3-decadiene, a single regioisomer is obtained with moderate enantioselectivity. Improvement in the enantioselectivity is observed employing the *bis*(ferrocenyl)monophophine ligands **a-d** having two planar chiral ferrocenyl moieties on phosphorus atom.

Ligand	Yield (%)	ee (%)
L*	62	64
a	43	68
b	78	76
c	89	78
d	91	87

Hatanaka, Y. *et al.*, *Tetrahedron Lett.* **1994**, *35*, 7981

Scheme 9

Problems

Write the major products for the following reactions.

1.   Ph——≡   + HSiCl₃ $\xrightarrow{[PtCl_2(C_2H_4)_2]_2}$

2.   ⬠ + HSiRCl₂ $\xrightarrow{PdLn^*}$

3.   (norbornene) + HSiCl₃ $\xrightarrow{PdLn^*}$

4.   (norbornane)–SiCl₃ $\xrightarrow{KF/NBS}$

5,   (norbornane)–SiCl₃ $\xrightarrow{KF/MCPBA}$

Reference/Text Book

- I. Ojima, *Catalytic Asymmetric Synthesis*, 3rd ed., Wiley, New Jersey, 2010.

- M. B. Smith, *Organic Synthesis*, 2nd edition, McGraw Hill, New Delhi, 2004.

Lecture 29

8.1 Hydrosilylation of Alkenes II

8.1.2 Reactions of 1,3-Dienes

The reaction of 1-buten-3-ynes substituted with bulky groups at the alkyne terminus affords enantiomerically enriched allenylsilanes in the presence of palladium complex (Scheme 1). For example, the reaction of 5,5-dimethyl-1-hexen-3-yne using (S)-(R)-bisppfOMe**a** proceeds in a 1,4-fashion to give allenyl(trichloro)silanes in high regio- and enantioselectivity. Further enhancement in the enantioselectivity is shown employing chiral phosphametallocene **b** having a sterically demanding η^5-C$_5$Me$_5$ moiety.
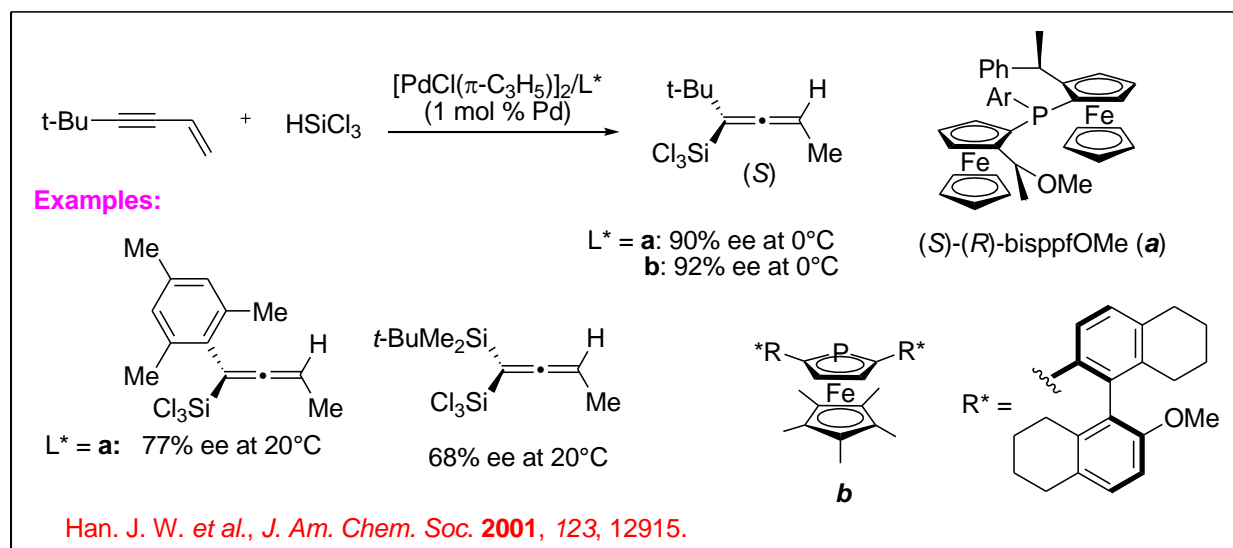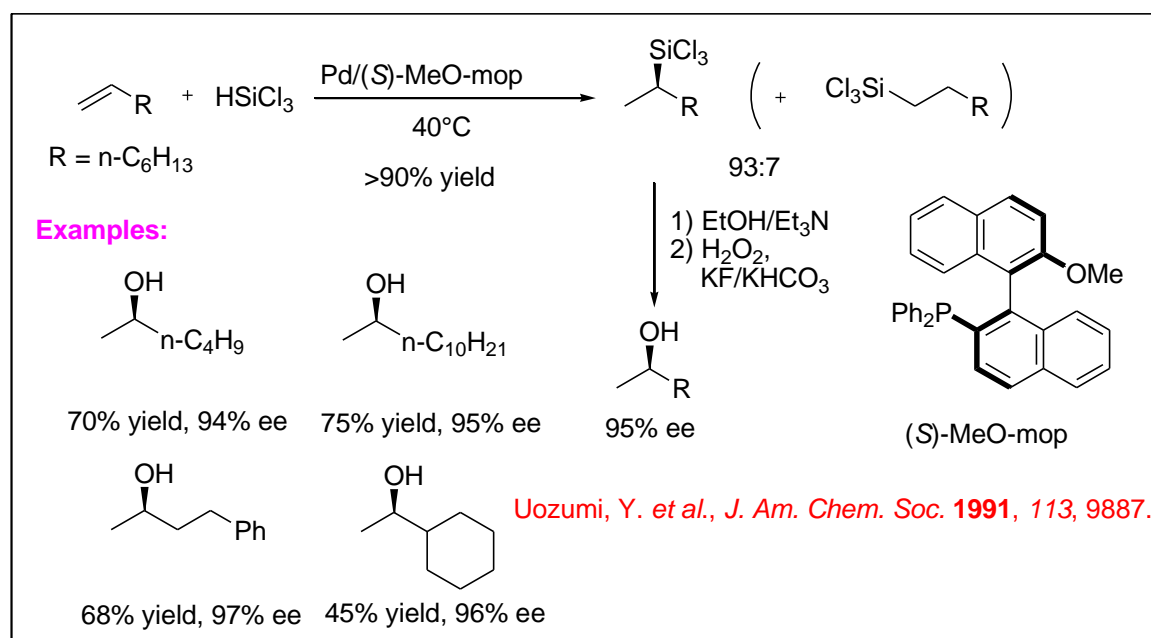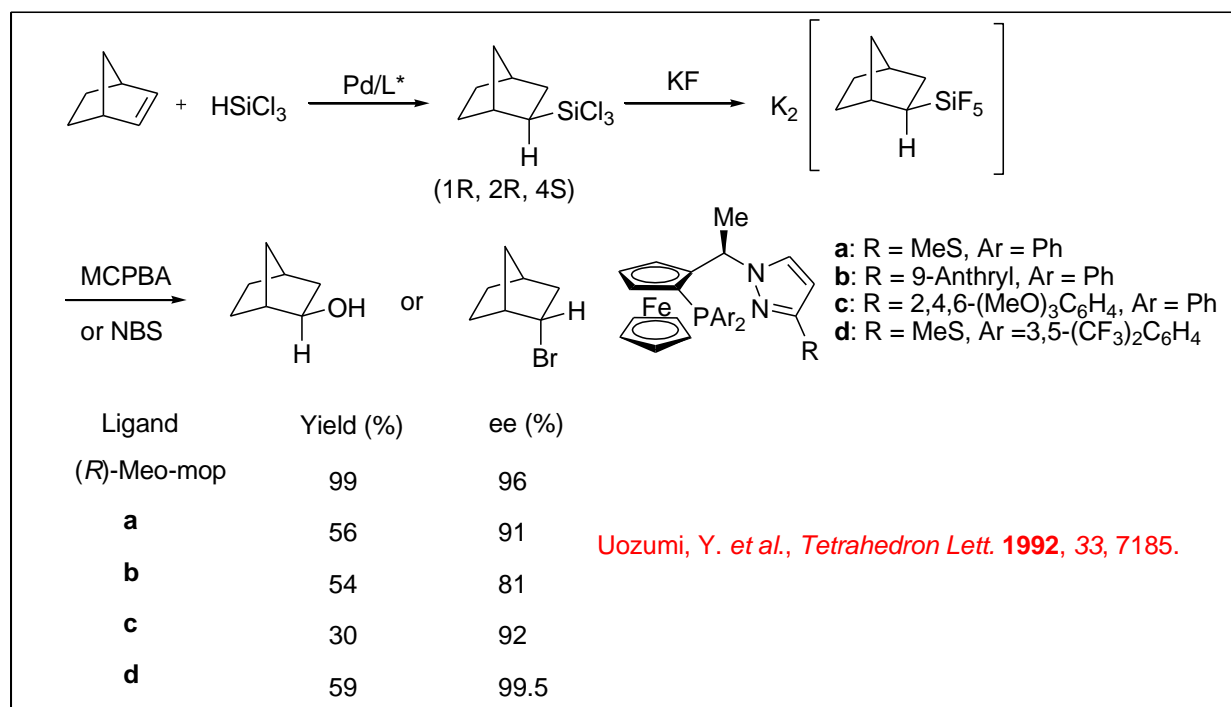

Scheme 1

8.1.3 Reactions of Alkyl Substituted Alkenes

Hydrosilylation of simple terminal alkenes give branched products with high regioselectivity. The palladium systems show exceptional catalytic system compared to Pt, Ni and Rh based systems. For example, the hydrosilylation of 1-octene with trichlorosilane using palladium-(S)—MeO-mop gives a 93:7 mixture of 1-octylsilane and 2-octylsilane with 95% ee (Scheme 2).

The above catalytic system is also effective for the hydrosilylation of cyclic alkenes, such as norbornene and bicyclo[2.2.2]octane, 2,5-dihydrofuran and norbornadiene. For example, the reaction of norbornene gives *exo* adduct exclusively (Scheme 3). The hydrosilylated product can be transformed into *exo*-2-norbornanol or *endo*-2-bromonorbornane via the corresponding pentafluorosilicate. In addition, chiral ferrocenylmonophosphines **a-d** are too found to be effective for this process with excellent enantioselectivity.
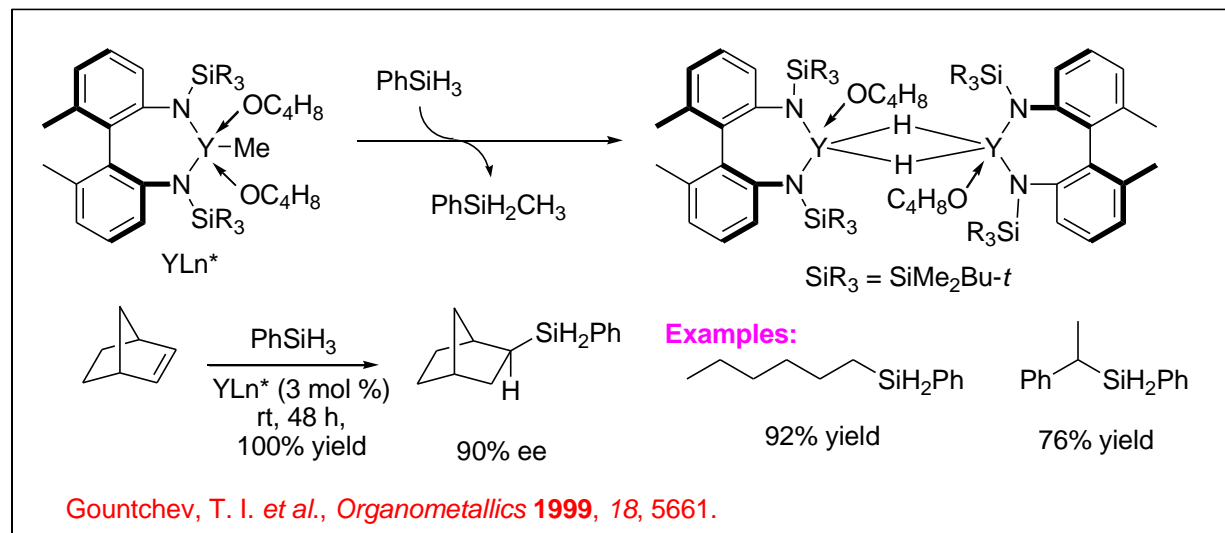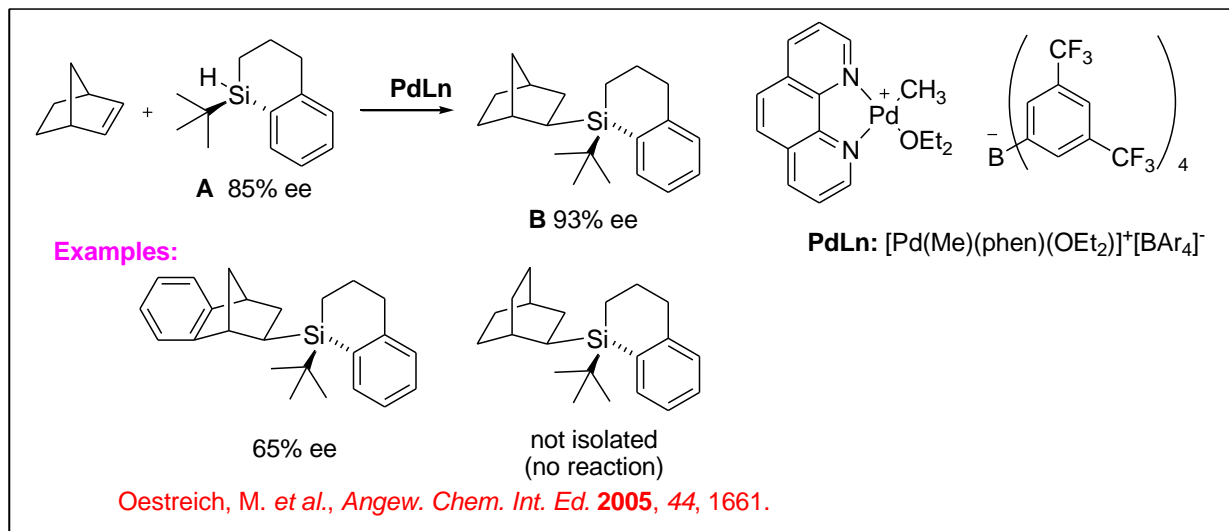

Scheme 2

a: R = MeS, Ar = Ph
b: R = 9-Anthryl, Ar = Ph
c: R = 2,4,6-(MeO)$_3$C$_6$H$_4$, Ar = Ph
d: R = MeS, Ar =3,5-(CF$_3$)$_2$C$_6$H$_4$

Ligand	Yield (%)	ee (%)
(*R*)-Meo-mop	99	96
a	56	91
b	54	81
c	30	92
d	59	99.5

Uozumi, Y. *et al.*, *Tetrahedron Lett.* **1992**, *33*, 7185.

Scheme 3

Chiral yttrium hydride complex (d^0 metal complex) bearing non-Cp ligand catalyzes the hydrosilylation of norbornene with phenylsilane to produce *exo*-adduct with 90% ee (Scheme 4). More recently, the first chirality transfer from silicon to carbon in a reagent-controlled reaction of norbornene is reported in the presence of achiral palladium complex. The hydrosilylation of norbornene with chiral silane A having 85% ee is found to form the hydrosilylated product B with 93% ee exhibiting asymmetric amplification (Scheme 5).
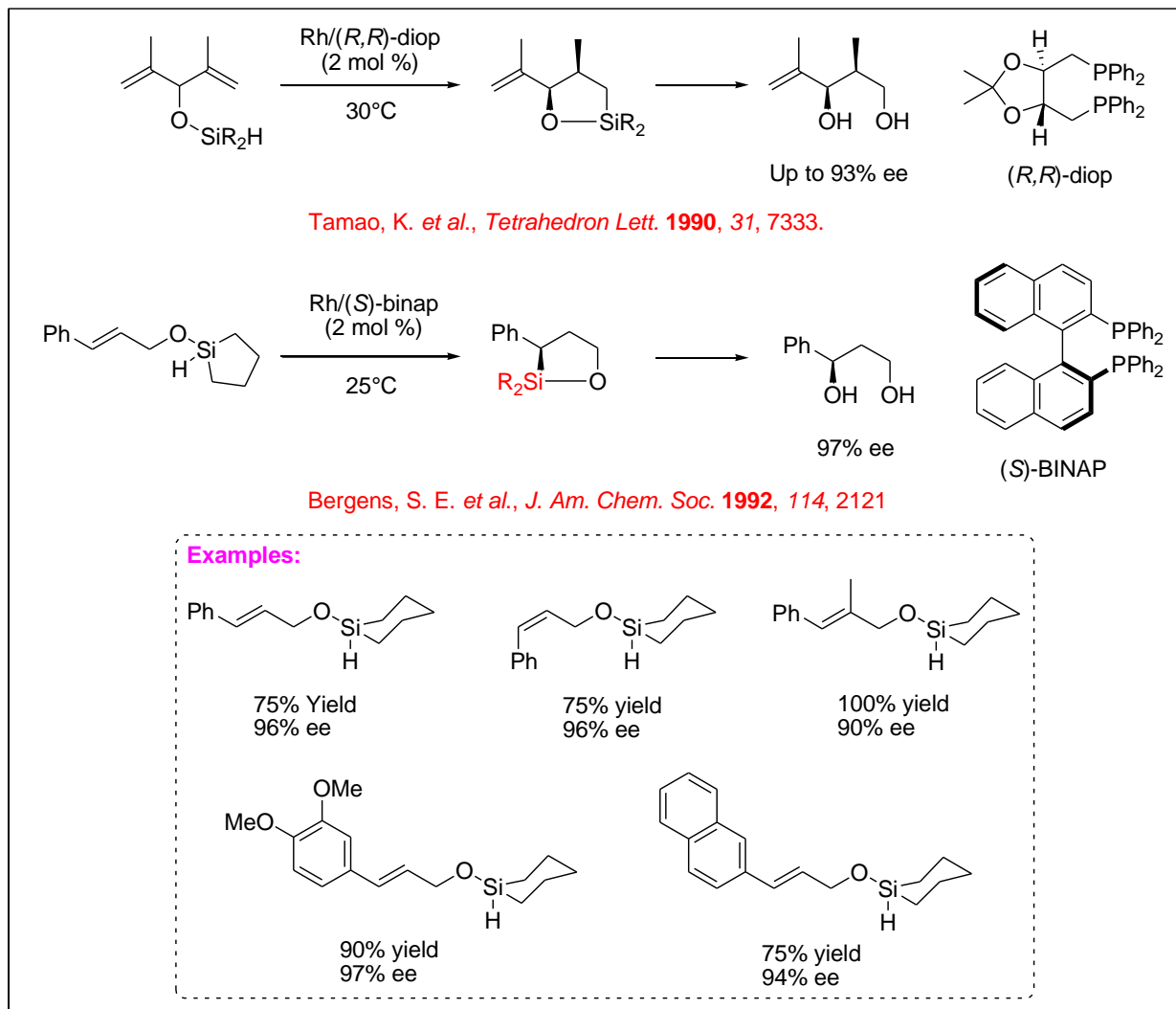

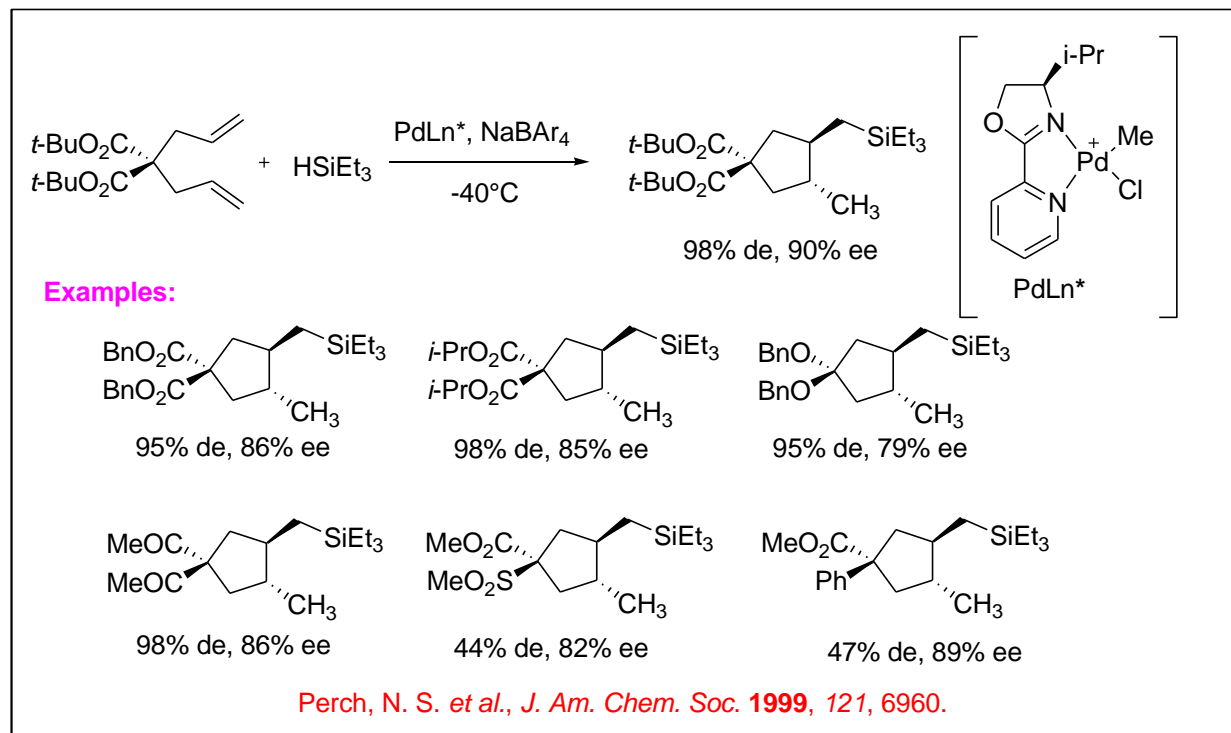Gountchev, T. I. *et al.*, *Organometallics* **1999**, *18*, 5661.

Scheme 4

Scheme 5

8.1.4 Intramolecular Hydrosilylation

Synthesis of optically active polyols from allylic alcohols can be achieved using chiral Rh-catalyzed intramolecular hydrosilylation followed by oxidation ofallyloxy hydrosilanes (Scheme 6). For example, hydrosilyl ether of di(2-propenyl)methanol can be converted into optically active 1,3-diol using intramolecular hydrosilylation in the presence of chiral rhodium-(R,R)-diop followed by oxidation. Rh-BINAP is also found to be effective catalyst for the intramolecular hydrosilylation of hydrosilyl ethers of allyl alcohols.

Tamao, K. *et al.*, *Tetrahedron Lett.* **1990**, *31*, 7333.

Bergens, S. E. *et al.*, *J. Am. Chem. Soc.* **1992**, *114*, 2121

Examples:

75% Yield
96% ee

75% yield
96% ee

100% yield
90% ee

90% yield
97% ee

75% yield
94% ee

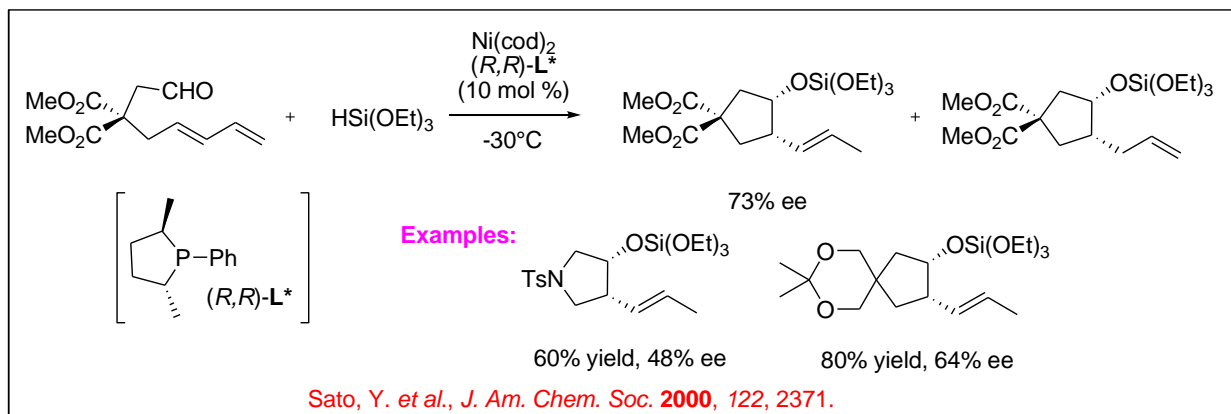**Scheme 6**

Scheme 7

8.1.5 Cyclization/Hydrosilylation

Asymmetric cyclization and hydrosilylation of α,ω-diunsaturated compounds such as 1,6-dienes and 1,6-enynes affords powerful tool for the construction of optically active functionalized carbocycles. For example, the tandem reaction of diallylmalonate in the presence of cationic Pd complex bearing a chiral pyridine-oxazoline proceeds with high diastereoselectivity to yield the corresponding trans-substituted cyclopentane with 90% ee (Scheme 7).

The reactions of 1,6-diynes using cationic Rh complexes bearing chiral bisphosphine gives the hydrosilylated alkylidenecyclopentanes with high enantioselectivity. For example, the 1,6-enyne proceeds reaction with triethylsilane in the presence of cationic Rh and (R)-biphemp to give hydrosilylated alkylidene cyclopentane in 92% ee (Scheme 8). Subsequently, chiral Rh complex containing spiro diphosphine (R)-sdp is found to be effective for this process.

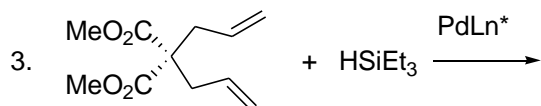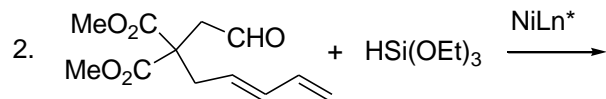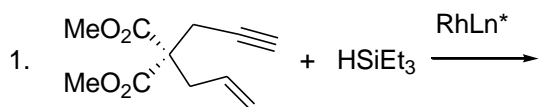Fan, B-M. *et al.*, *Angew. Chem. Int. Ed.* **2007**, *46*, 1275.
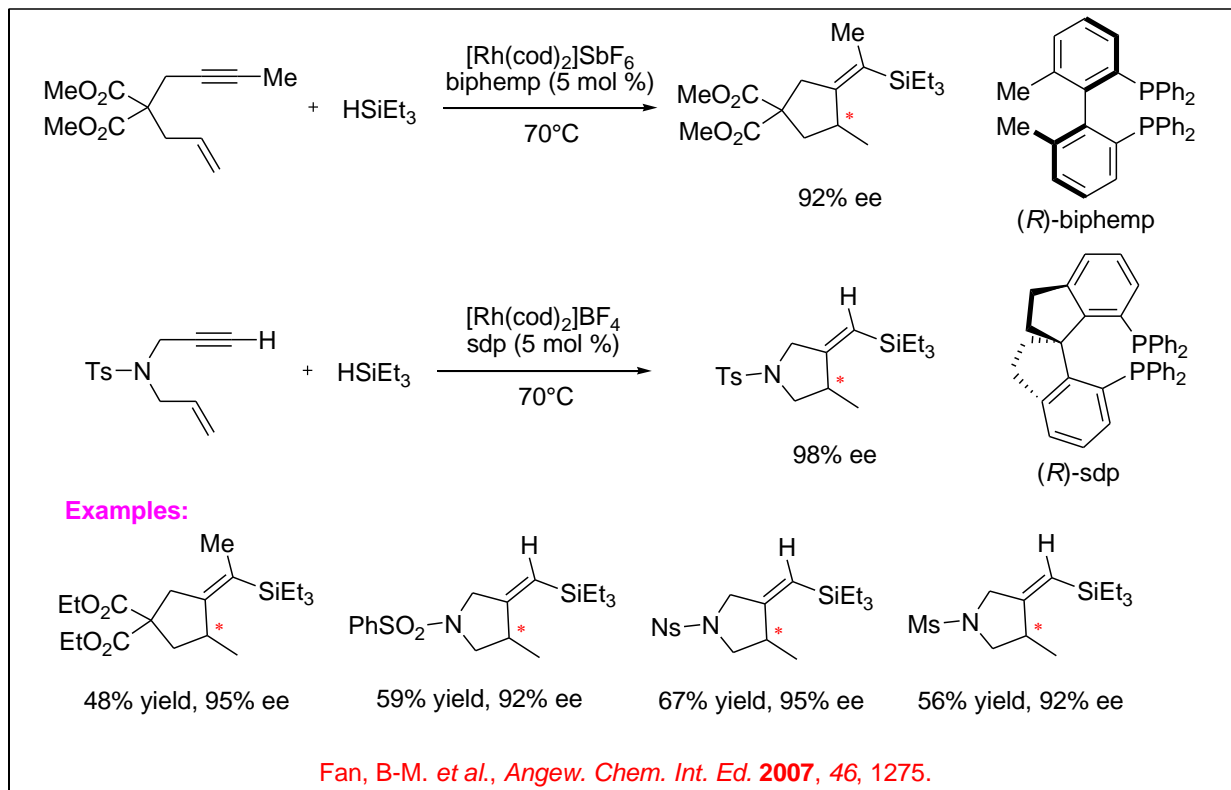
Scheme 8

The synthesis of carbocycles can also be accomplished by the cyclization of ω-formyl-1,3-dienes in the presence of hydrosilanes and chiral nickel complex (Scheme 9). For example, zerovalent nickel complex of (2R,5R)-2,5-dimethyl-1-phenylphospholane catalyzes the cyclization of 1,3-dienes with a tethered formyl group in the presence of triethoxysilane to give five-membered carbocycle with 73% ee.

Sato, Y. *et al.*, *J. Am. Chem. Soc.* **2000**, *122*, 2371.

Scheme 9

Problems

Complete the following reactions.

1.
MeO_2C ... MeO_2C (enyne) + HSiEt$_3$ $\xrightarrow{RhLn^*}$

2.
MeO_2C MeO_2C CHO (diene) + HSi(OEt)$_3$ $\xrightarrow{NiLn^*}$

3.
MeO_2C ... MeO_2C (diene) + HSiEt$_3$ $\xrightarrow{PdLn^*}$

Reference/Text Book

- I. Ojima, *Catalytic Asymmetric Synthesis*, 3rd ed., Wiley, New Jersey, 2010.

- M. B. Smith, *Organic Synthesis*, 2nd edition, McGraw Hill, New Delhi, 2004.

Lecture 30

8.3 Hydroboration, Hydroalumination and Hydrostannation of Alkenes

8.3.1 Hydroboration of Alkenes

Chiral Rh catalyzed hydroboration of alkenes provides effective method for the synthesis of optically active organoboranes, which are versatile intermediates in organic synthesis. The carbon-boron bond can be converted into several functional group by subsequent carbon-carbon, carbon-oxygen, boron-carbon or carbon-nitrogen bond-forming reactions with retention of stereochemistry (Scheme 1).
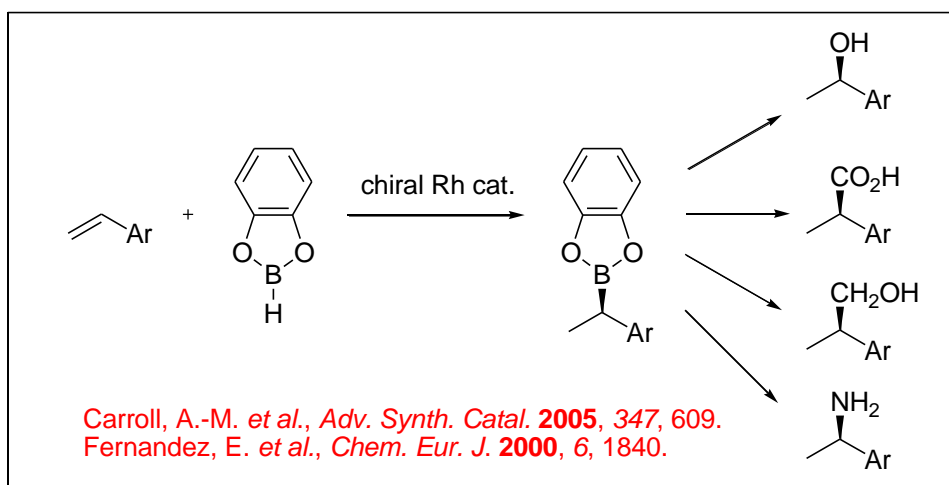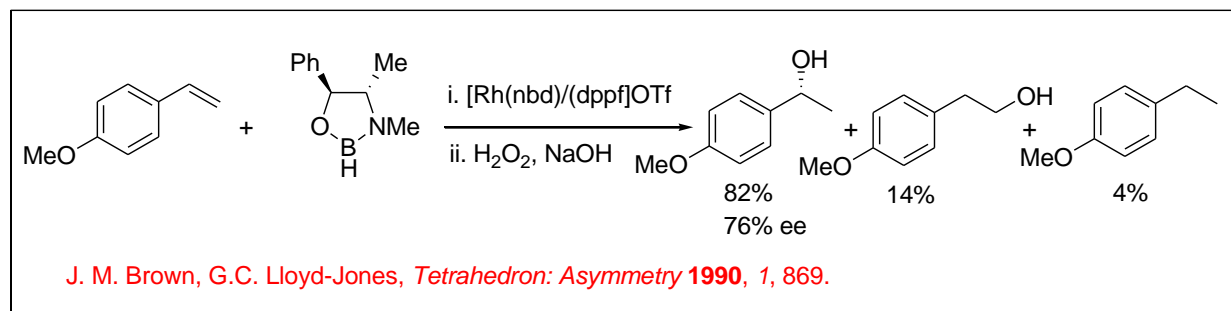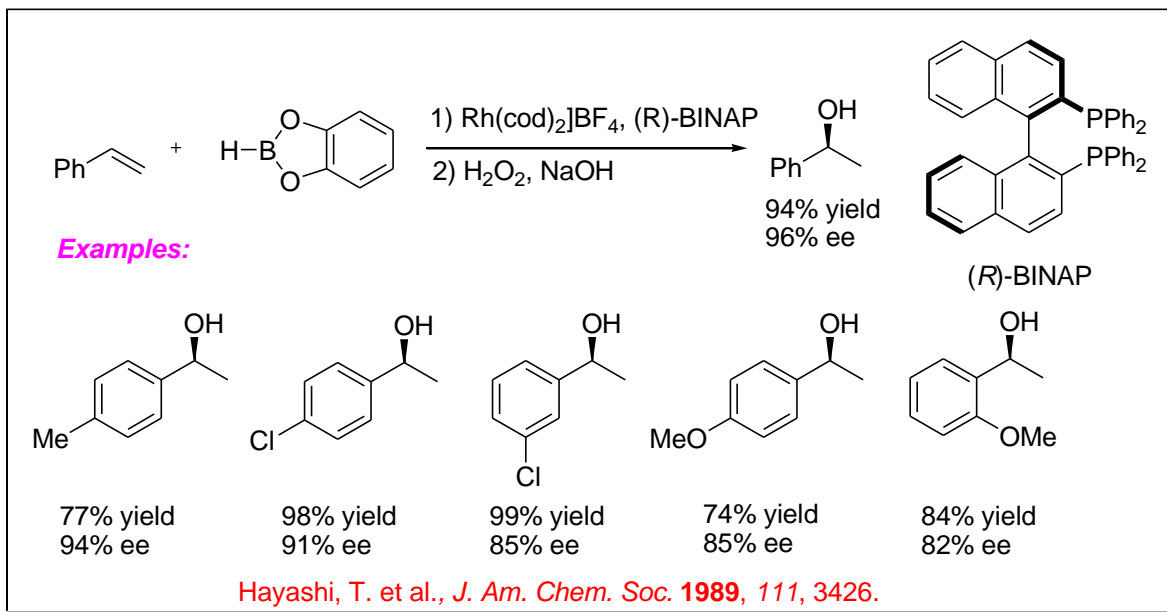

Scheme 1
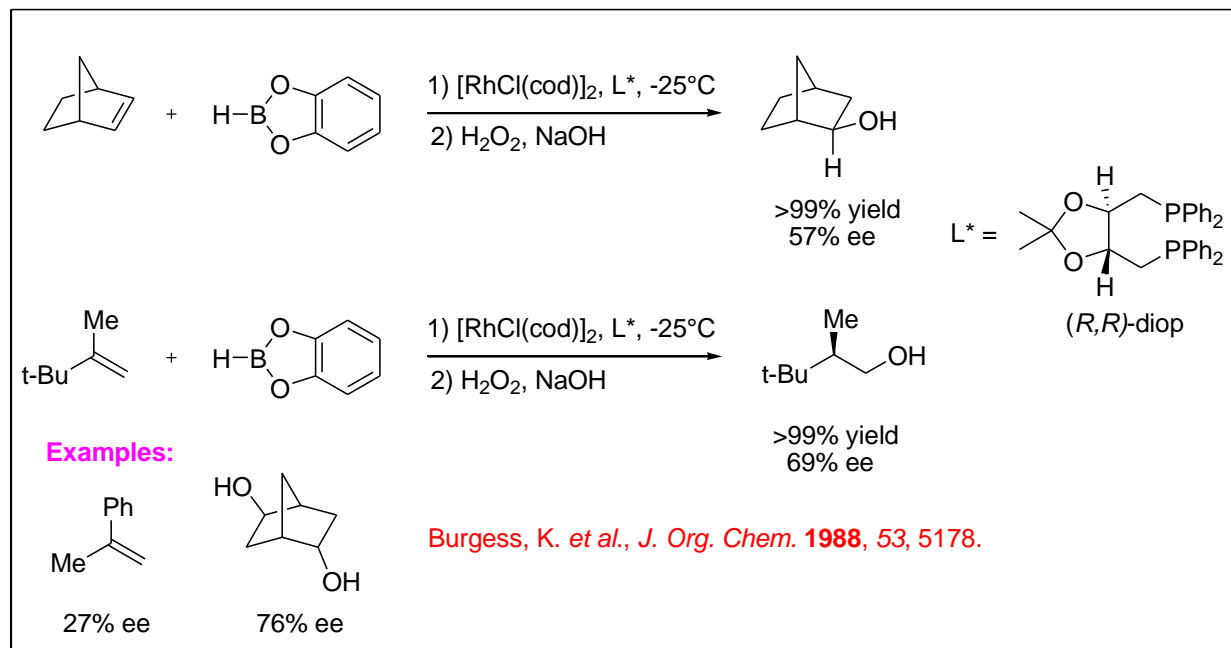
Scheme 2

The first catalytic asymmetric hydroboration of norbornene and 2-*tert*-butylpropene with catecholborane appeared in the presence of Rh-(*R*,*R*)-diop complex (Scheme 2). The products, 2-hydroxynorbornane and 2,3,3-trimethylbutanol are obtained after the treatment with alkaline hydrogen peroxide solution.

The use of the combination of chiral borane and achiral catalyst has been demonstrated for the asymmetric hydroboration. For example, the hydroboration of 4-methoxystyrene proceeds with chiral borane derived from pseudoephedrine in the presence of achiral rhodium complex to the corresponding secondary alcohol with 76% ee after the oxidation (Scheme 3).
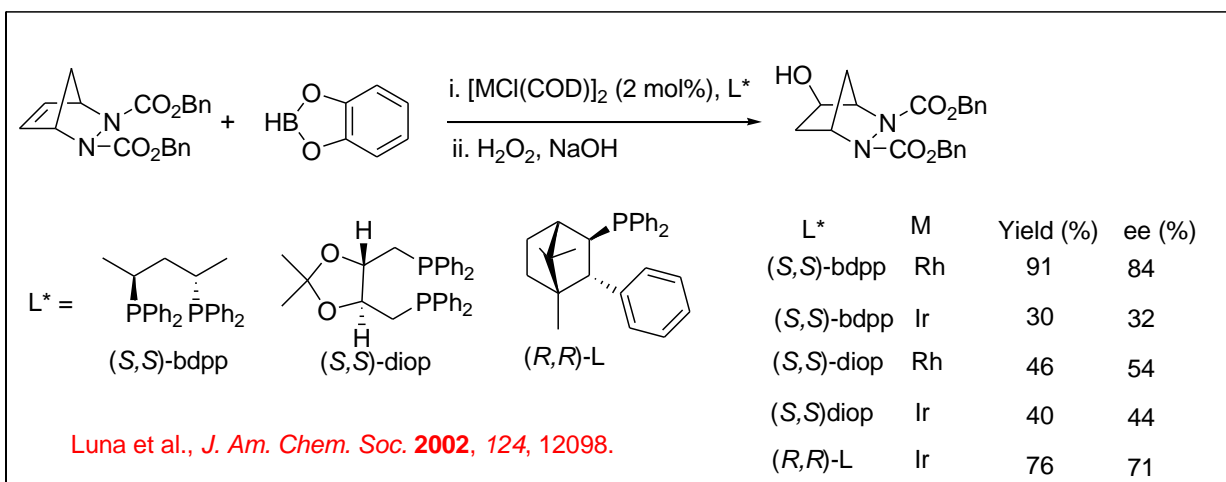

Scheme 3

The reaction of vinylarenes with catecholborane has been extensively studied using chiral Rh complex. For example, the cationic Rh-(*R*)-BIANP catalyzes the hydroboration of styrene with complete branch selectivity to afford 1-phenylethanol with 96% ee after oxidation. The regioselectivity is opposite to that observed with uncatalyzed reactions (Scheme 4).
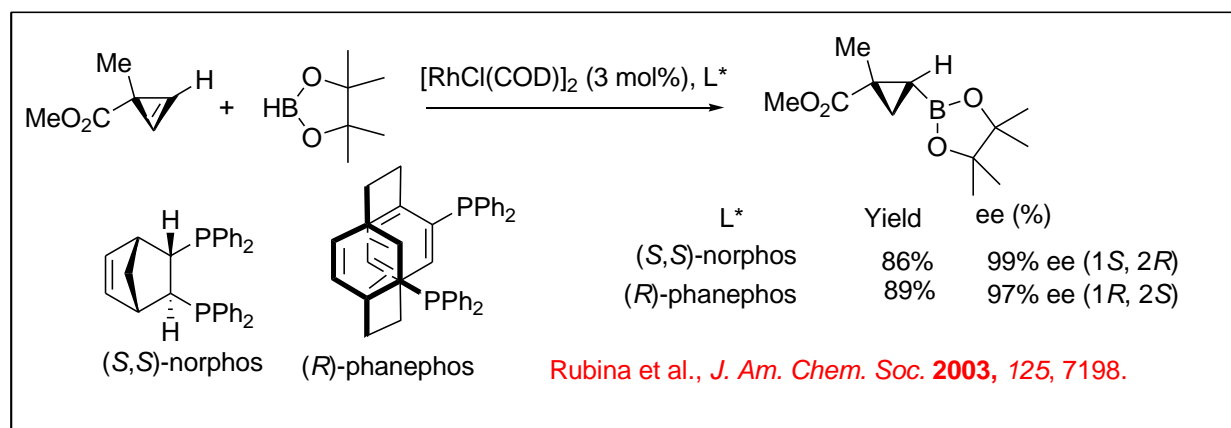

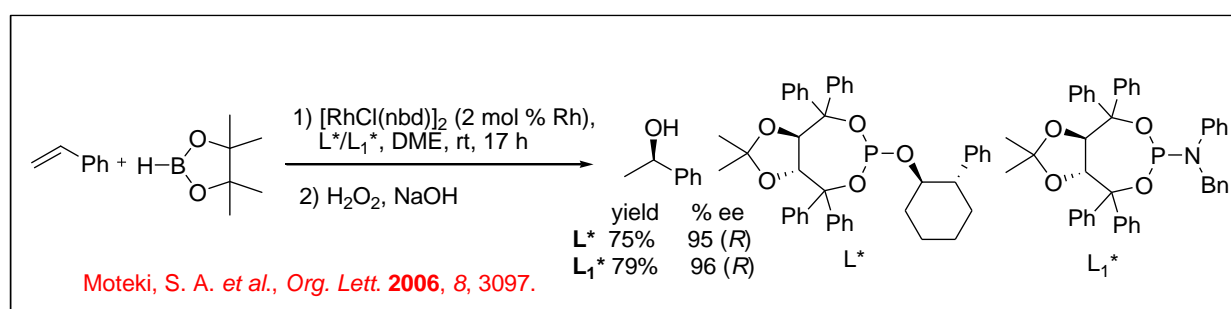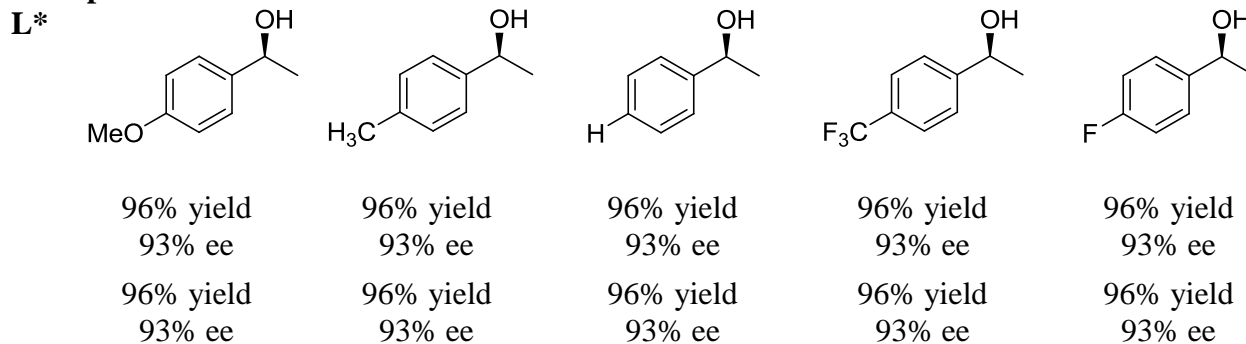Hayashi, T. et al*., J. Am. Chem. Soc.* **1989**, *111*, 3426.

Scheme 4

Asymmetric desymmetrization of *meso*-bicyclic hydrazines has been shown with catecholborane using chiral Rh and Ir-based complexes (Scheme 5). A reversal of enantioselectivity is observed between the Rh and Ir catalysts.

L*	M	Yield (%)	ee (%)
(*S*,*S*)-bdpp	Rh	91	84
(*S*,*S*)-bdpp	Ir	30	32
(*S*,*S*)-diop	Rh	46	54
(*S*,*S*)diop	Ir	40	44
(*R*,*R*)-L	Ir	76	71

Luna et al., *J. Am. Chem. Soc.* **2002**, *124*, 12098.

Scheme 5
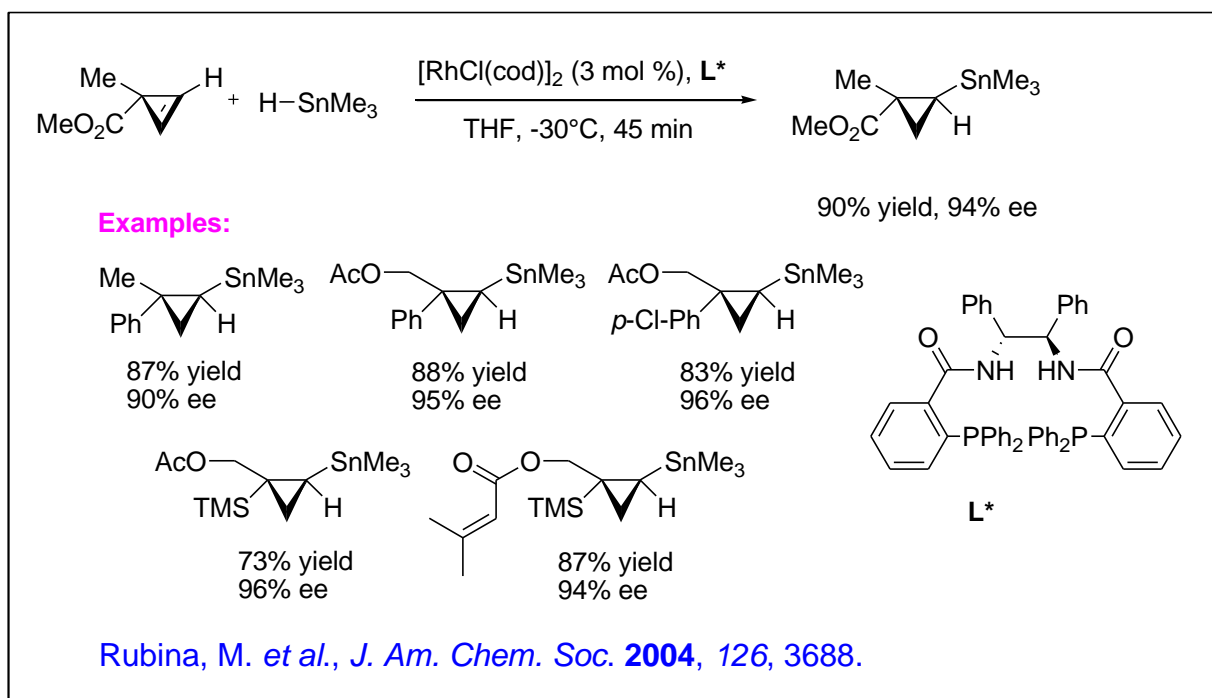
Scheme 6

Scheme 7

The reaction of cyclopropene is studied with pinacolborane as a new hydroborating agent in the presence of a series of chiral Rh phosphine complexes (Scheme 6). The reaction using pinacolborane showed enhanced selectivity compared to that with catecholborane due to steric control between the substrates and the hydroborating agent.

Rh complexes with chiral monodentate phosphate and phosphoramidite derived from taddol are studied for the hydroboration of vinylarenes with pinacolborane (Scheme 7). The reactions of a series of vinylarenes having electron withdrawing- and donating substituted proceed with high enantioselectivity

8.3.2 Hydroalumination and Hydrostannation of Alkenes

Lautens, M. *et al.*, *J. Am. Chem. Soc.* **1995**, *117*, 532.

Scheme 8
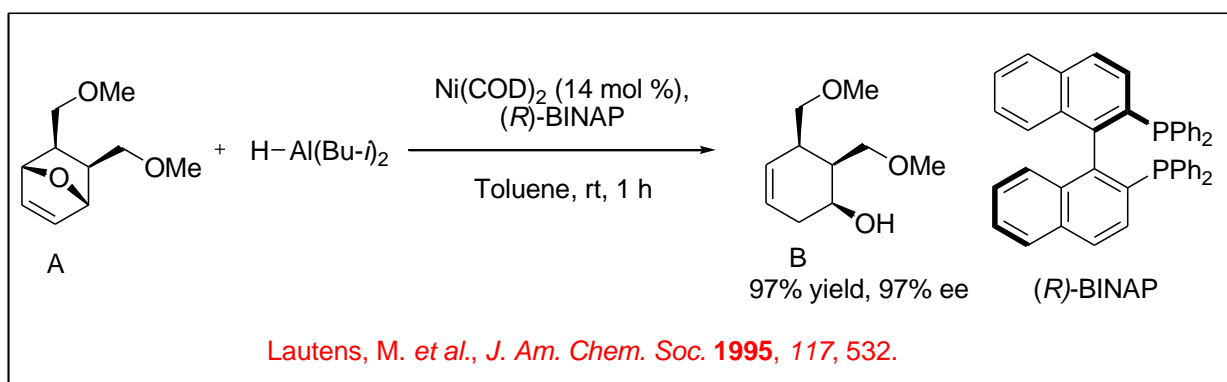
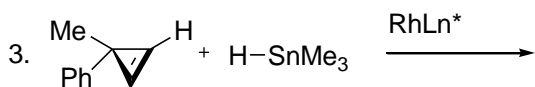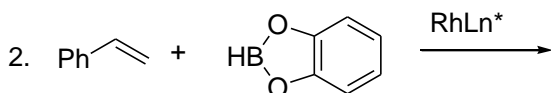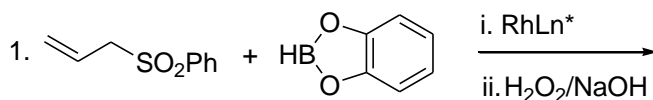Rubina, M. *et al.*, *J. Am. Chem. Soc.* **2004**, *126*, 3688.

Scheme 9

While the catalytic asymmetric hydrosilylation and hydroboration reactions are well known, the catalytic hydroalumination and hydrostannation of alkenes are rare. Chiral nickel complex is used for the asymmetric hydroalumination of oxabicyclic alkenes. For example, Ni-(R)-BINAP catalyzes the reaction of A with iso-Bu$_2$AlH to give B with 97% ee (Scheme 8).
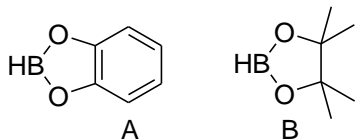
The first example for the asymmetric hydrostannation of cyclopropenes is appeared using Rh-complex bearing chiral diphenylphosphinobenzoic acid-derived L* (Scheme 9). The product trans-cyclopropylstannane is obtained with 94% ee. The procedure is general and the reaction a series of substituted cyclopropenes is demonstrated.

Problems

A. Predict the major product for the following reactions.

1. (allyl-SO$_2$Ph) + HB(catechol) → i. RhLn* → ii. H$_2$O$_2$/NaOH

2. Ph-CH=CH$_2$ + HB(catechol) → RhLn*

3. Me,Ph-cyclopropene-H + H–SnMe$_3$ → RhLn*

B. How will you prepare the following hydroborating agents?

A   B

Reference/Text Book

- I. Ojima, *Catalytic Asymmetric Synthesis*, 3rd ed., Wiley, New Jersey, 2010.

- M. B. Smith, *Organic Synthesis*, 2nd edition, McGraw Hill, New Delhi, 2004.