

Reviews for Chiral Boronates Synthesis

5694

COMMUNICATIONS TO THE EDITOR

Vol. 78

der) and 1245 cm^{-1} ; $[\alpha]^{25\text{D}} +70^\circ$ (CHCl_3); (*Anal.* Calcd. for $\text{C}_{25}\text{H}_{33}\text{FO}_8$: C, 62.49; H, 6.92; F, 3.95. Found: C, 62.71; H, 7.06; F, 3.63). Saponification of VIIb with sodium methoxide in methanol gave 9 α -fluoro-11 β ,16 α ,17 α ,21-tetrahydroxy-4-pregnene-3,20-dione (VIIa), m.p. 257–260° d. (previous softening and browning); λ_{max} 238.5 $m\mu$ (ϵ 16,300; ν_{max} 3635, 3440, 1720, 1674 and 1630 cm^{-1} ; $[\alpha]^{25\text{D}} +91^\circ$ (pyridine); *Anal.* Calcd. for $\text{C}_{21}\text{H}_{29}\text{FO}_8$: C, 63.62; H, 7.37; F, 4.79. Found: C, 63.47; H, 7.51; F, 4.49).

Microbiological dehydrogenation of VIIb with *Corynebacterium simplex*^{2a} gave after acetylation of the crude fermentation mixture 16 α ,21-diacetoxy-9 α -fluoro-11 β ,17 α -dihydroxy-1,4-pregnadiene-3,20-dione (VIIIb), m.p. 158–235°^{5b}; λ_{max} 239 $m\mu$ (ϵ 15,200); ν_{max} 3390, 1740 (shoulder), 1730, 1660, 1610, 1608 (inflection) and 1235 cm^{-1} ; $[\alpha]^{25\text{D}} +22^\circ$ (CHCl_3); (*Anal.* Calcd. for $\text{C}_{25}\text{H}_{31}\text{FO}_8$: C, 62.75; H, 6.53; F, 3.97. Found: C, 63.45; H, 7.44; F, 4.39). Saponification afforded the free steroid VIIIa,

A NEW TECHNIQUE FOR THE CONVERSION OF OLEFINS INTO ORGANOBORANES AND RELATED ALCOHOLS

Sir:

In the presence of aluminum chloride the reducing powers of sodium borohydride are greatly enhanced.¹ We now wish to report that this reagent readily reacts with simple olefins, such as ethylene, 1- and 2-pentene, cyclohexene, and styrene, at temperatures of 25°, to form the corresponding trialkylboranes in yields of 90%.

Trialkylboranes are readily oxidized to the borate esters² which can be hydrolyzed to the corresponding alcohols. The reaction can be carried out without isolation of any of the intermediates. In this way cyclohexene has been converted into cyclohexanol, 1-hexene into 1-hexanol, styrene into 2-phenylethanol and 1,1-diphenylethylene into 2,2-diphenylethanol. The yields based on olefin are good, in the range of 70–90%. The following procedures are representative.

Reporter: Ran-Ning Guo

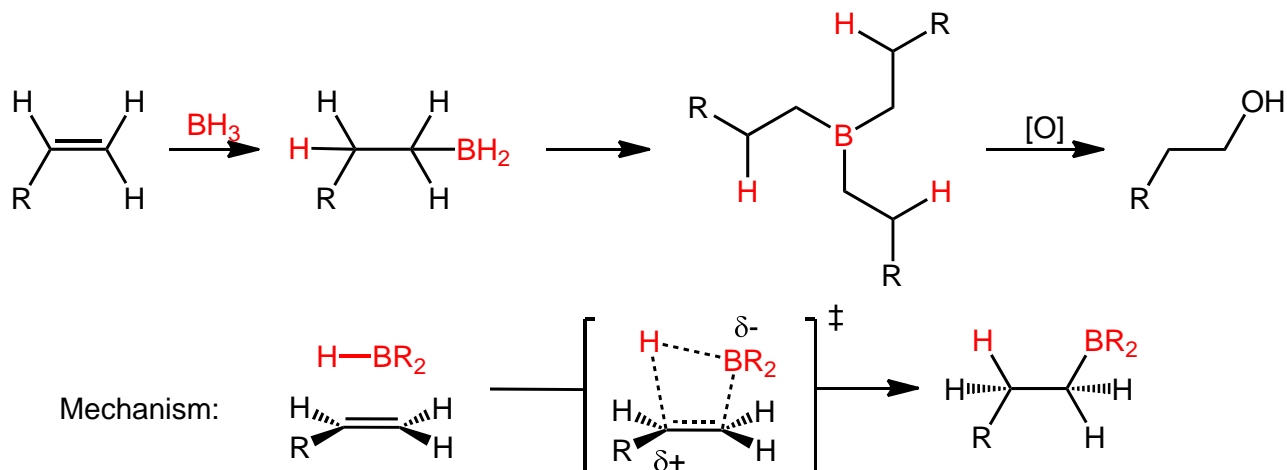
Checker: Zhi-Shi Ye

Date: 2012/05/22

Contents

- 1 Hydroboration
- 2 Enantioselective Hydroboration
- 3 Homologation
- 4 Enantioselective Hydrogenation
- 5 Conclusion

Introduction to Hydroboration



Major characteristics of hydroboration:

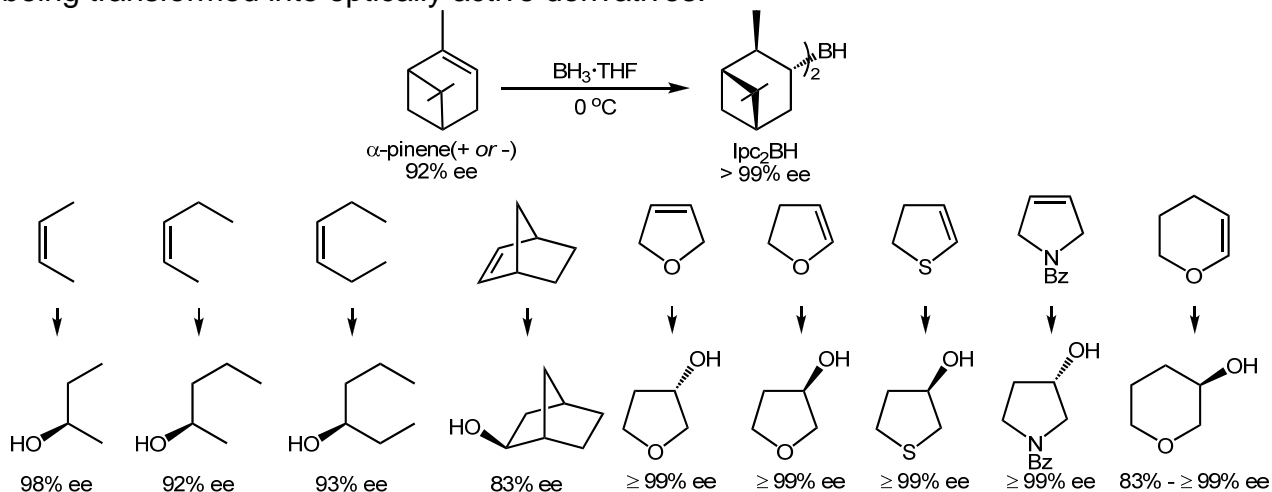
- Essentially instantaneous and quantitative
- Addition proceeds in an anti-Markovnikov manner
- Involves a cis addition of the H-B bonds
- Take place preferentially from the less hindered side
- No rearrangements of the carbon skeleton
- Most functional groups can tolerate hydroboration

Yield
dr.
er.
Chemoselectivity
Regioselectivity

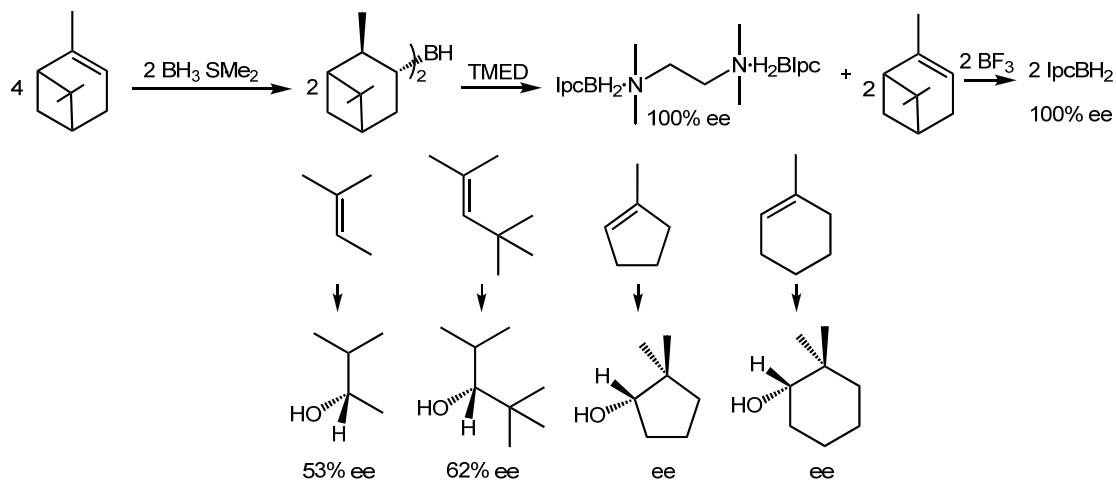
First Publication: H. C. Brown, *J. Am. Chem. Soc.* **1956**, 78, 5694;
Review: H. C. Brown, *Org. React.* **1963**, 13, 1.

Enantioselective Hydroboration

Dialkylboranes derived from optically active terpenes or steroids might convert olefins into organoborane moieties capable of being transformed into optically active derivatives.

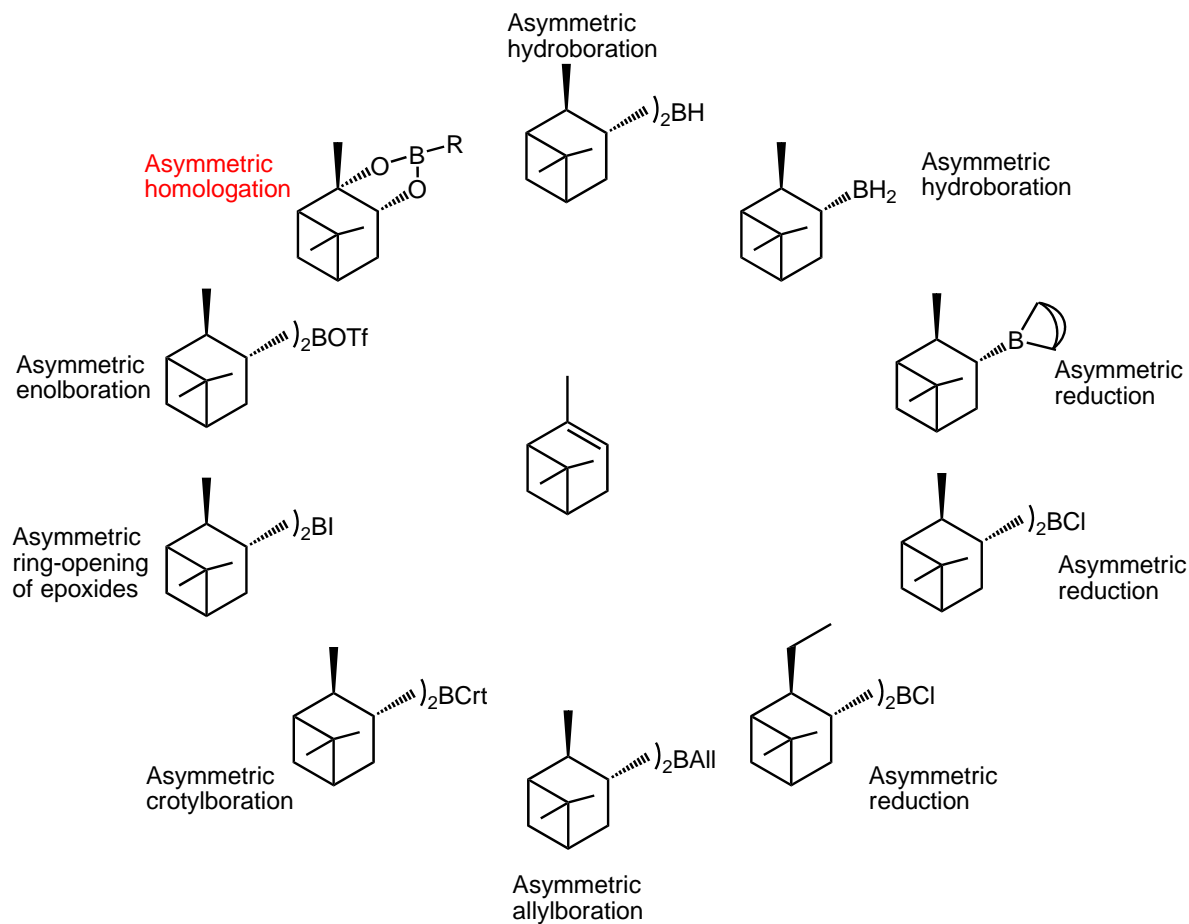


"The first truly successful, nonenzymatic, asymmetric synthesis" - Brown



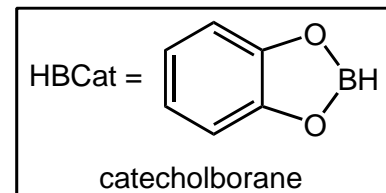
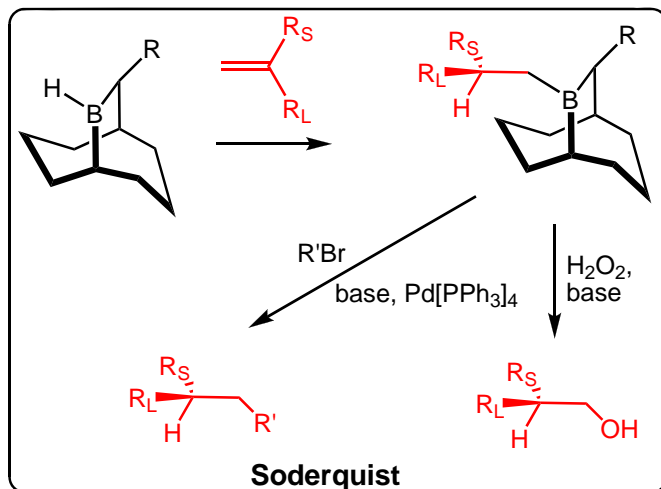
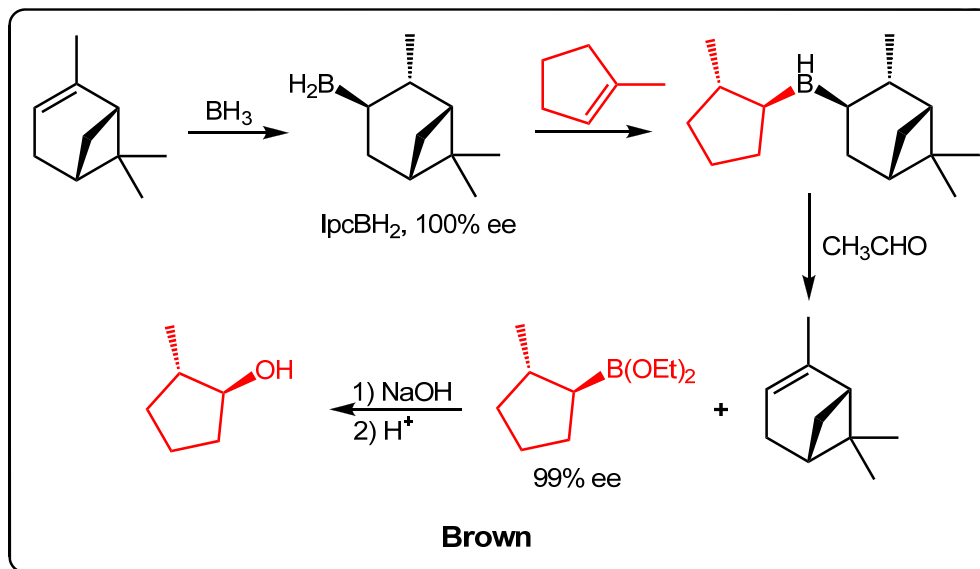
First Publication: H. C. Brown, *J. Am. Chem. Soc.* **1961**, 83, 486;
Review: H. C. Brown, *Acc. Chem. Res.* **1988**, 21, 287.

Enantioselective Hydroboration



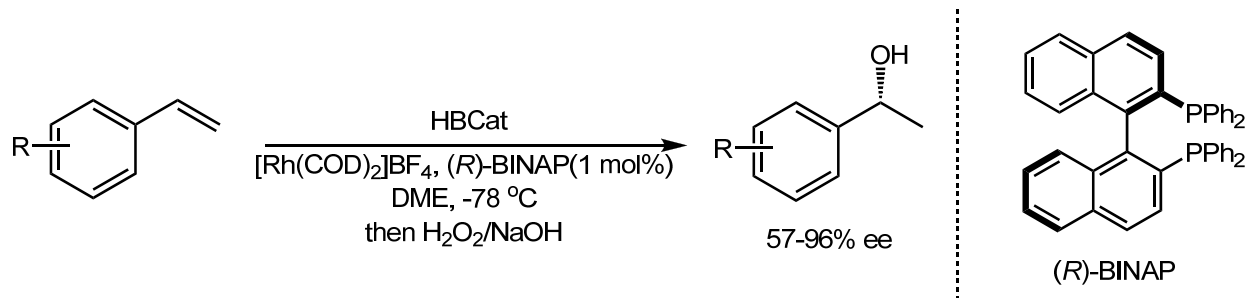
H. C. Brown, *Pure & Appl. Chem.* **1991**, 63, 307;
H. C. Brown, *J. Org. Chem.* **1995**, 500, 1.

Enantioselective Hydroboration



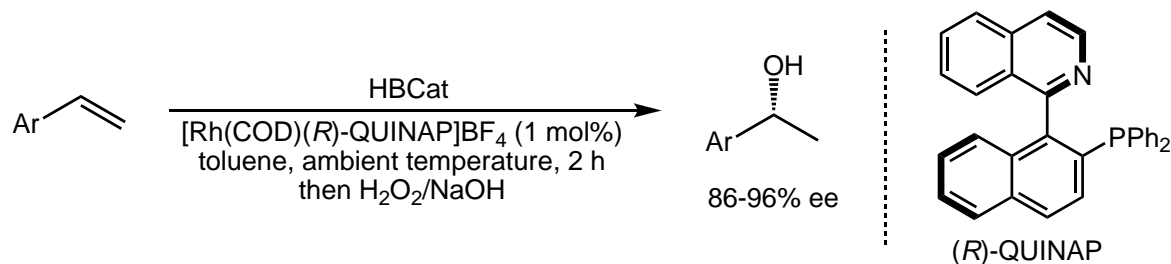
Catecholborane: H. C. Brown, *J. Am. Chem. Soc.* **1971**, 93, 1816;
Catalyzed: H. Nöth, *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 878.

Enantioselective Hydroboration



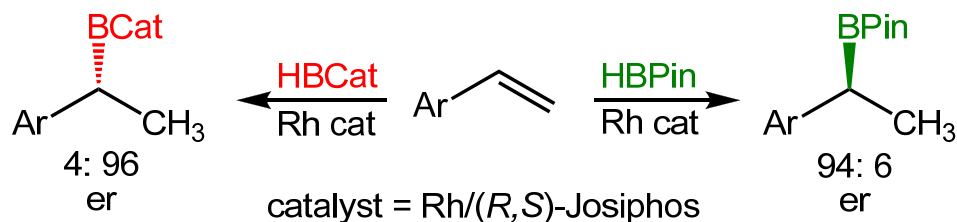
High regioselectivity observed for electron donating and withdrawing groups
Limitations: Steric bulk requires higher temperatures but lead to lower ee value.

T. Hayashi, *J. Am. Chem. Soc.* **1989**, *111*, 3426;
T. Hayashi, *Tetrahedron Asymm.* **1991**, *2*, 601.



J. M. Brown, *Chem. Eur. J.* **1999**, *5*, 1320.

Enantioselective Hydroboration



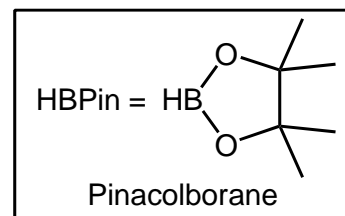
Opposite enantiomers obtained from catechol and pinacol borane in the hydroboration of styrene

C. M. Crudden, *Chem. Commun.* **2009**, 6704.

HBPin vs. HBCat

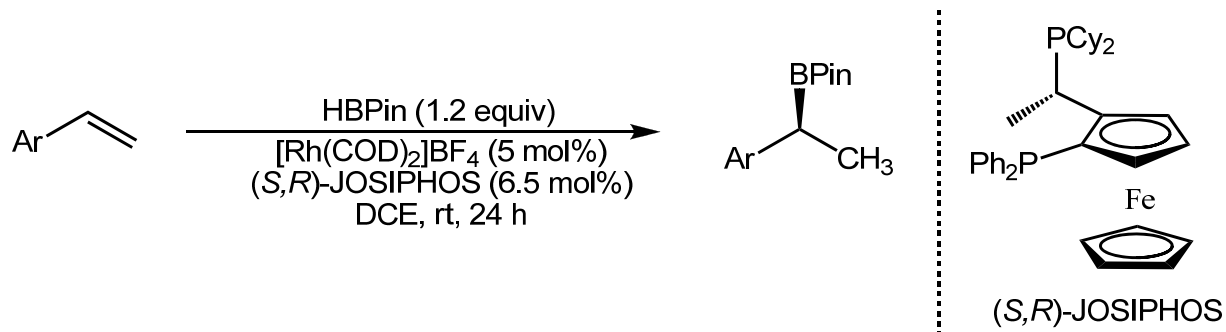
HBCat: lack of steric hindrance, relatively sensitive to hydrolysis and decomposition reactions.

HBPin: greater steric demand, greater stability but low acidity and reactivity. (Binap-modified catalysts-----Josiphos and Quinap-modified catalysts)

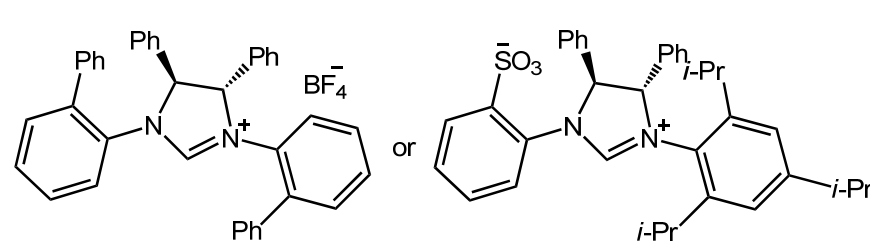
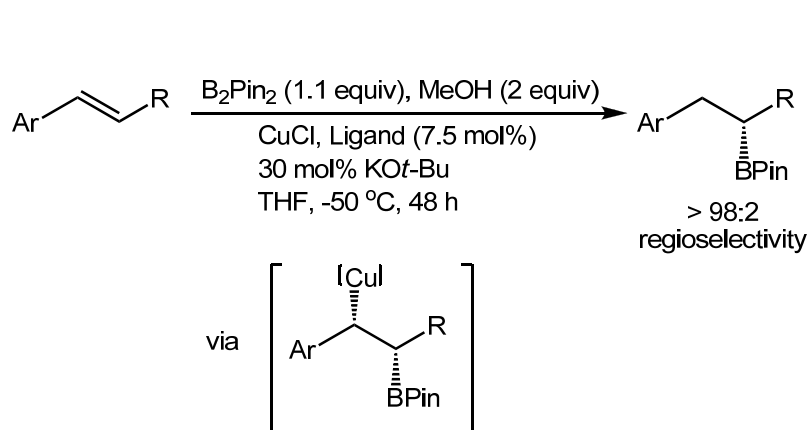


P. Knochel, *J. Org. Chem.* **1992**, 57, 3482.

Enantioselective Hydroboration

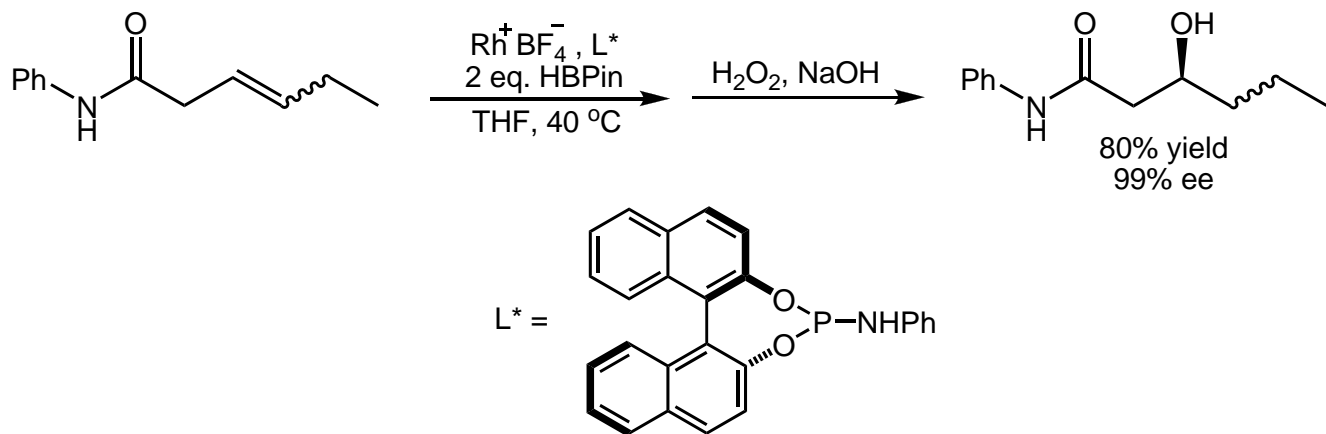


C. M. Crudden, *J. Am. Chem. Soc.* **2004**, 126, 9200.



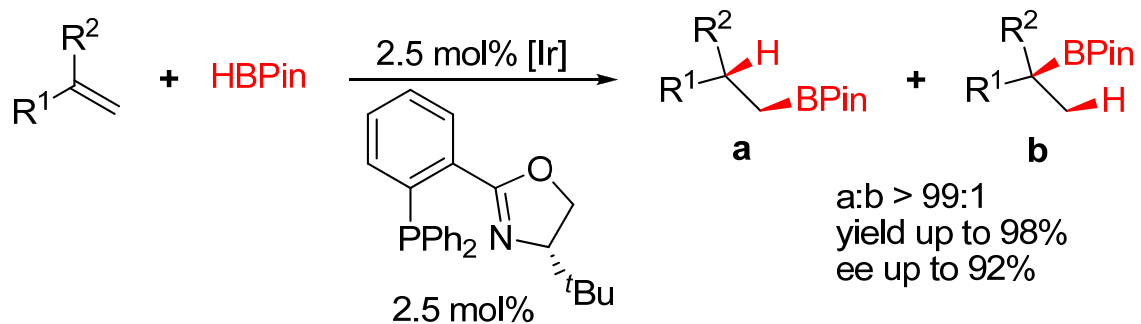
A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, 131, 3160.

Enantioselective Hydroboration



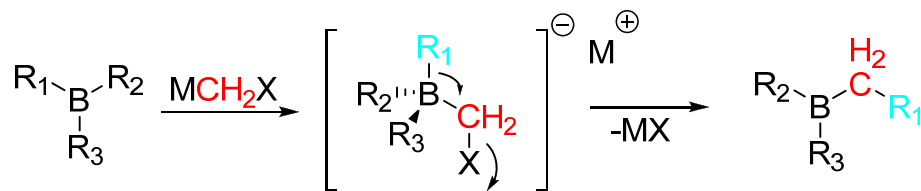
Amide-Directed Catalytic Asymmetric Hydroboration

J. M. Takacs. *J. Am. Chem. Soc.* **2008**, 130, 3734.

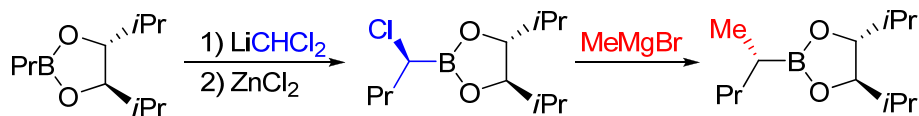
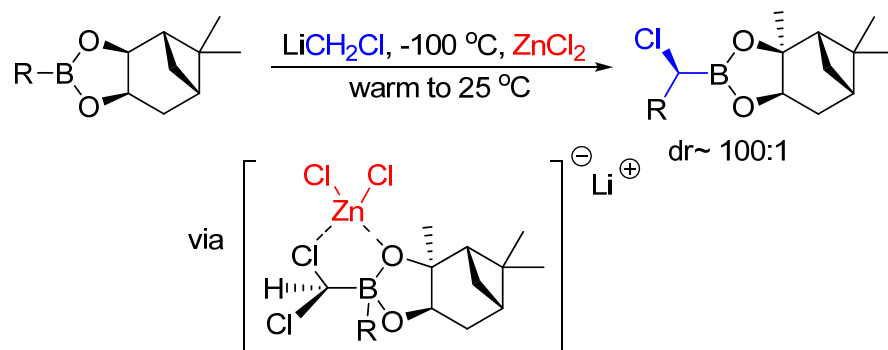


C. Mazet, *Chem. Commun.* **2011**, 47, 298.

Homologation

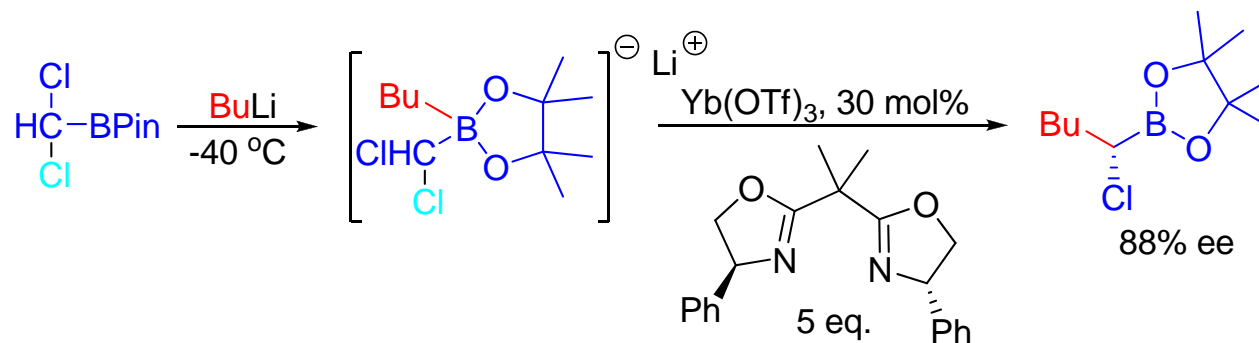


The empty orbital on boron, which is attacked by a nucleophilic reagent, increasing the reactivity of the B–C bonds in the resulting borate species. Migration of one of the boron–carbon bonds then occurs with loss of the X group, resulting in homologation of the migrating group.



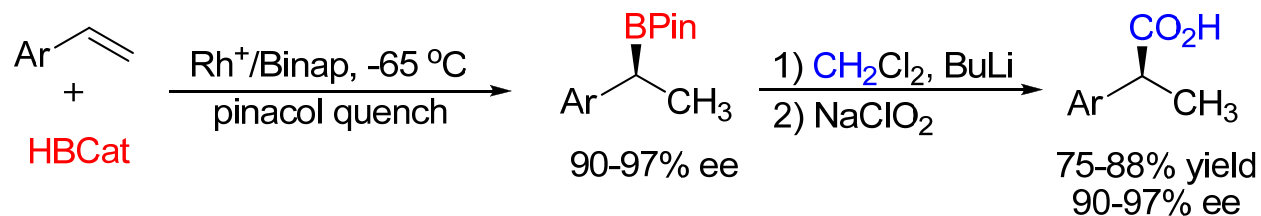
First Publication: D. S. Matteson, *J. Am. Chem. Soc.* **1980**, *102*, 7588.
Reviews: D. S. Matteson, *Chem. Rev.* **1989**, *89*, 1535.

Homologation



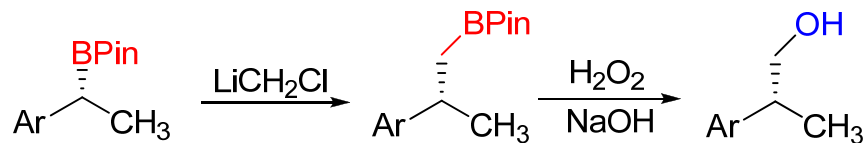
Achiral dichloromethylborane, bisoxazolines and metal triflates including Yb(OTf)₃ as Lewis acids.

P. K. Jadhav, *J. Am. Chem. Soc.* **1997**, 119, 846.

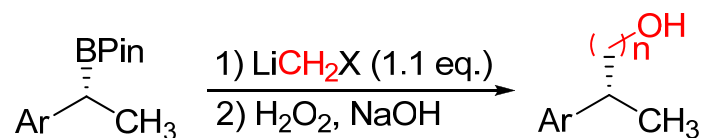


Two step hydroboration–homologation procedure

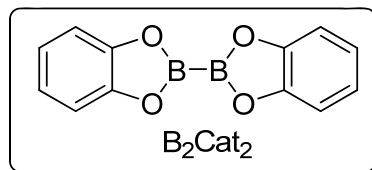
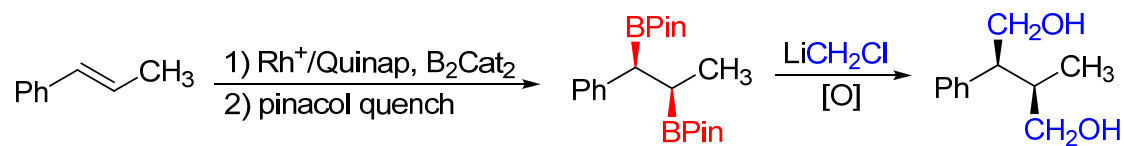
C. M. Crudden, *Chem. Commun.* **1999**, 611.



C. M. Crudden, *J. Org. Chem.* **1999**, 64,9704.



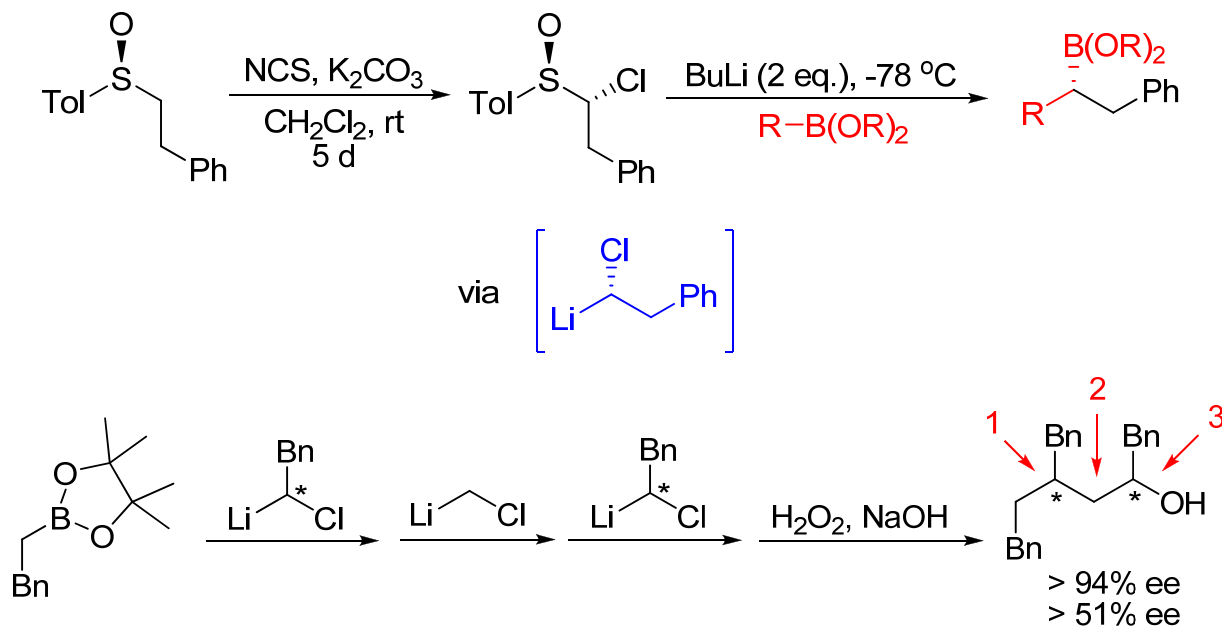
C. M. Crudden, *Chem. Commun.* **2000**, 721.



J. B. Morgan, J. P. Morken, *J. Am. Chem. Soc.* **2003**, 125, 8702.

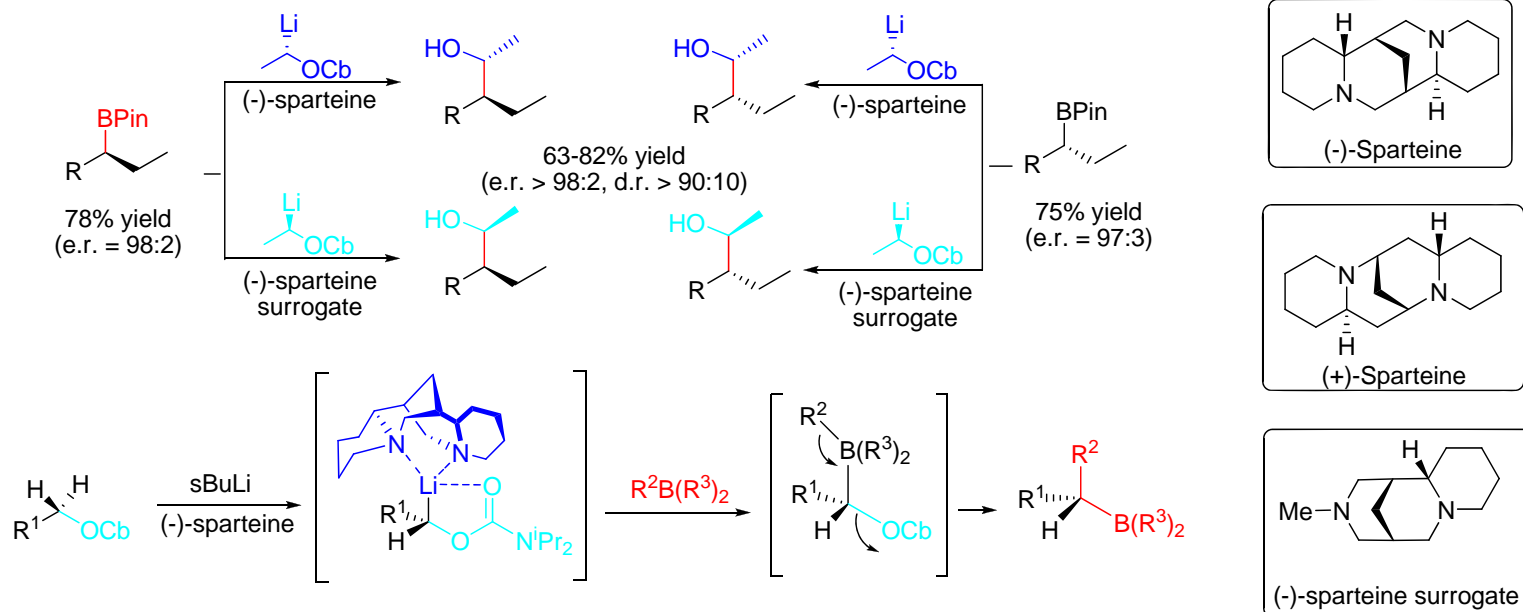
Homologation

In addition to the homologation of organoboron species with existing chirality, there have been several advances in the use of chiral homologating agents with achiral boranes. carbenoid that shows high configurational and chemical stability but sufficient reactivity to effect homologation of boronic esters



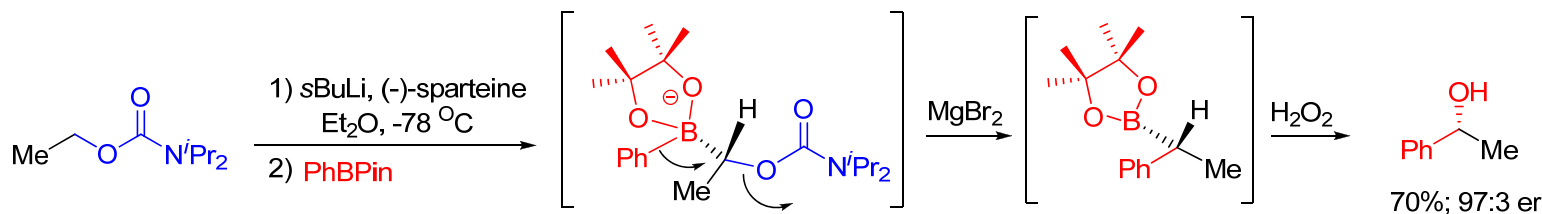
P. R. Blakemore, *Org. Lett.* **2006**, *8*, 773.

Homologation



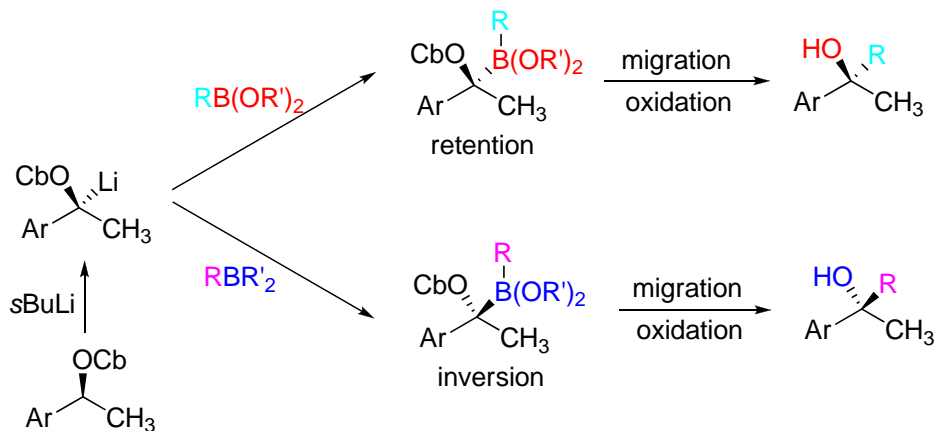
The only difficulty with this method is its reliance on synthetic surrogates for (+)-sparteine, which is not naturally available, if the other enantiomer of the product is desired.

V. K. Aggarwal. *Angew. Chem. Int. Ed.* **2007**, 46, 7491.

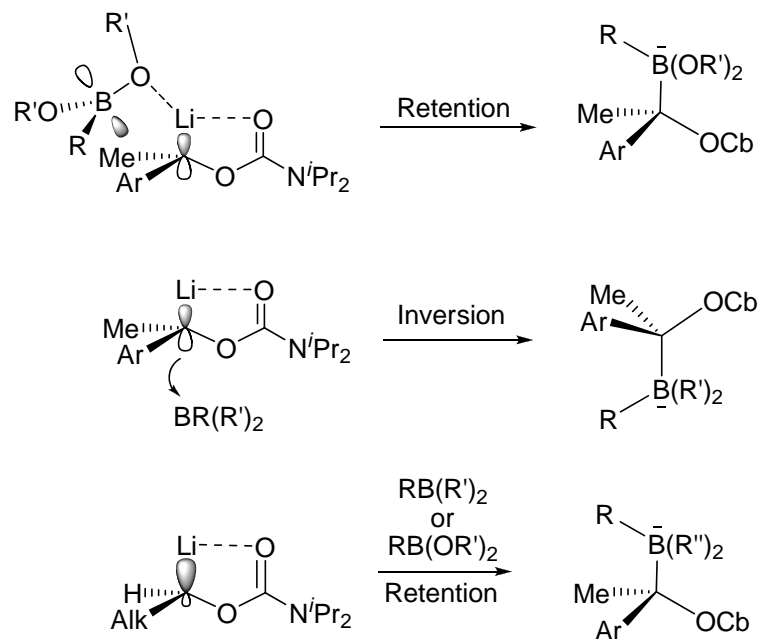


P. O'Brien, *Angew. Chem. Int. Ed.* **2008**, 47, 2734.

Homologation

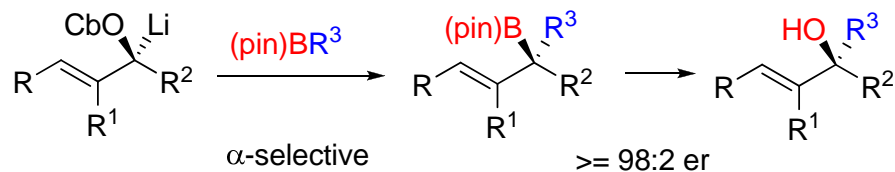


In the case of boronic esters, the oxygen of the ester complexes with the lithium of the metallated carbamate and so is delivered on the same face as the metal. In the absence of such complexation, as in the case of the boranes, reaction occurs on the face opposite to the metal where there is significant electron density owing to the partially flattened nature of the carbanion. However, it should be noted that reactions of lithiated alkylcarbamates derived from non-benzylic primary alcohols occur with complete retention of stereochemistry with both boranes and boronic esters, presumably because in this case the non-mesomerically stabilized carbanion is essentially sp^3 hybridized and has very little electron density opposite the metal.

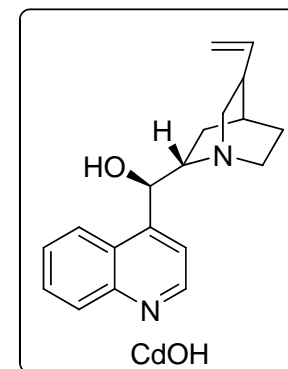
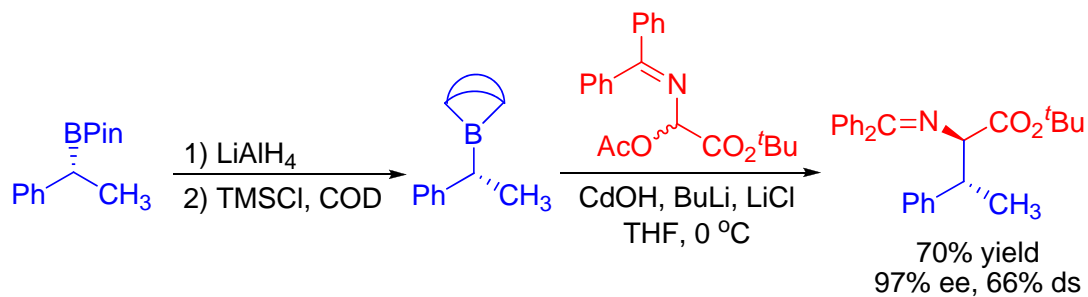


V. K. Aggarwal, *Nature*, **2008**, 456, 778.

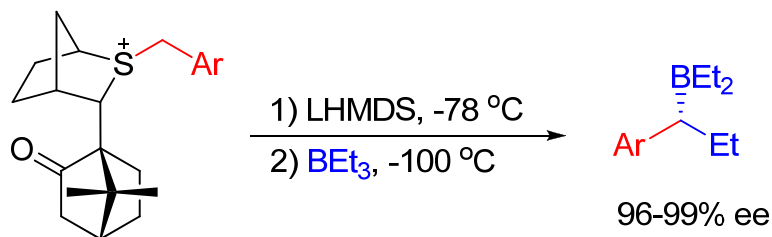
Homologation



V. K. Aggarwal, *J. Am. Chem. Soc.* **2012**, 134 7570.



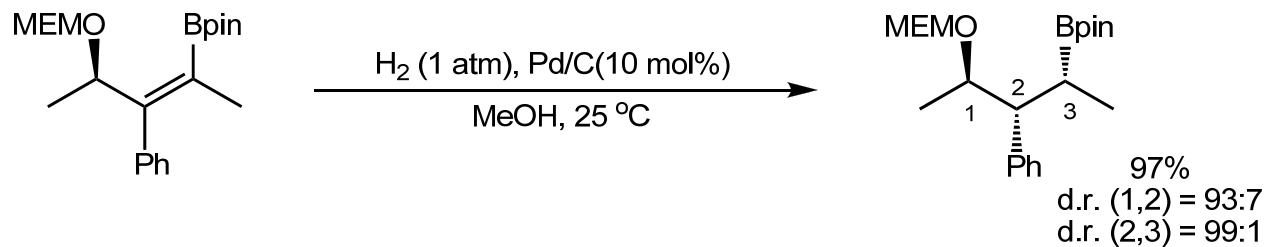
M. J. O'Donnell, *J. Am. Chem. Soc.* **2003**, 125, 2370.



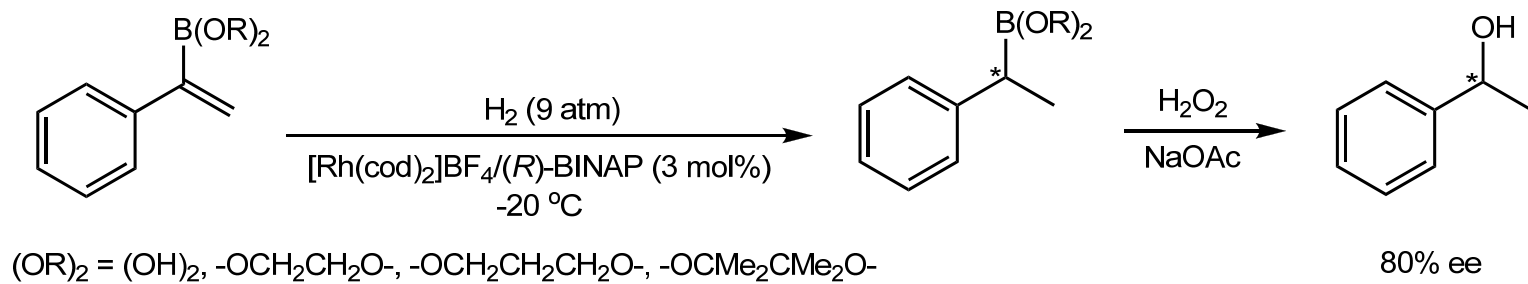
V. K. Aggarwal, *J. Am. Chem. Soc.* **2005**, 127, 1642.

V. K. Aggarwal, *J. Am. Chem. Soc.* **2007**, 129, 14632.

Enantioselective Hydrogenation

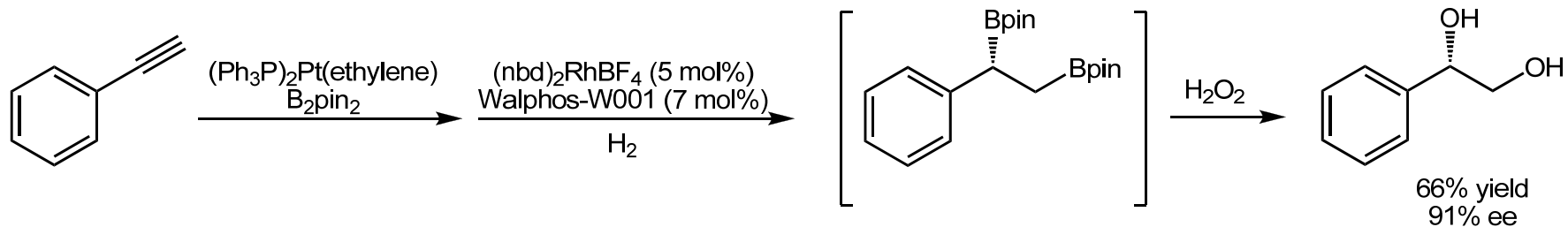


P. Knochel, *Org. Lett.* **2002**, 4, 2861.

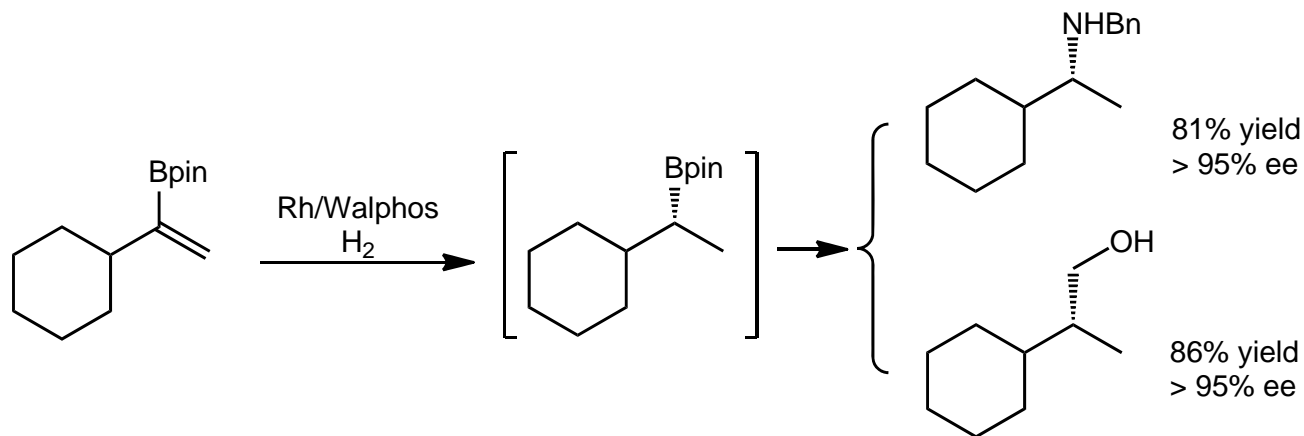


N. Miyaura, *J. Organomet. Chem.* **2002**, 642, 145.

Enantioselective Hydrogenation

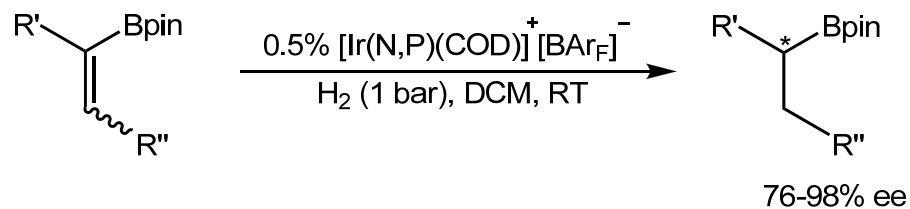


J. P. Morken, *J. Am. Chem. Soc.* **2004**, 126, 15338.

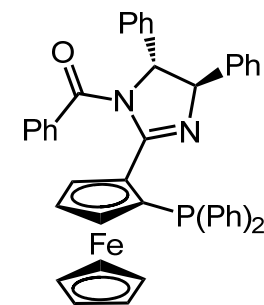
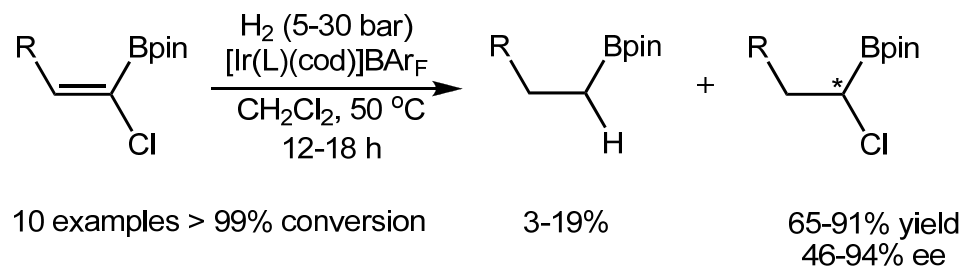


J. P. Morken, *Org. Lett.* **2006**, 8, 2413.

Enantioselective Hydrogenation

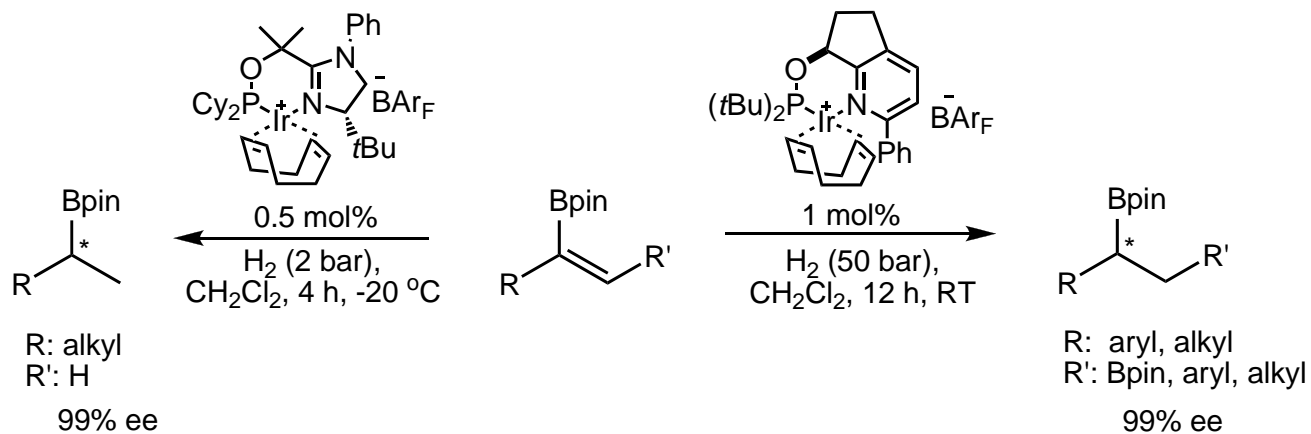


P. G. Andersson, *Chem. Commun.* **2009**, 5996.



Z. Časar, *Angew. Chem. Int. Ed.* **2011**, 51, 1014.

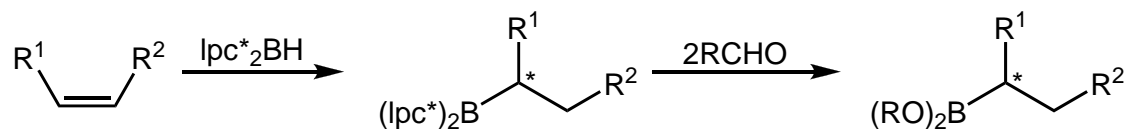
Enantioselective Hydrogenation



A. Pfaltz, *Chem. Eur. J.* **2012**, ASAP.
DOI: 10.1002/chem.201200246.

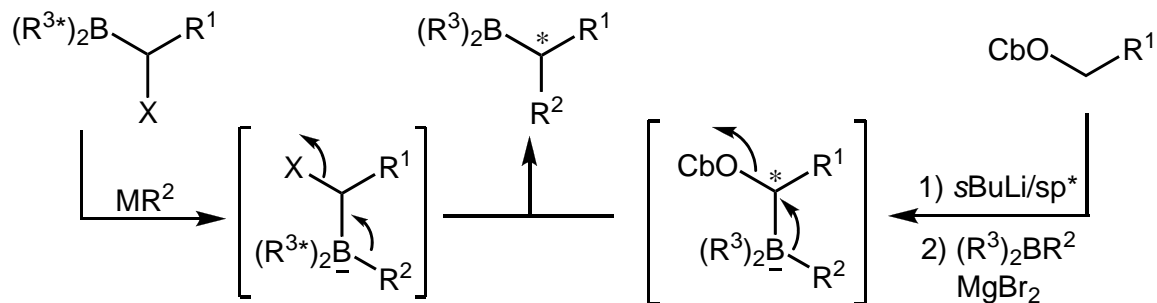
Conclusion

a) Hydroboration



Ipc^{*}₂BH: diisopinocampheylborane

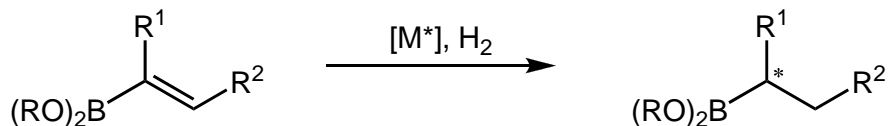
b) Homologation



R¹ and R²: alkyl or aryl;
M: Li or MgX;
X: Cl, Br or I;

R³: diol;
Cb: C(O)N(iPr)₂;
sp^{*}: (-)-spartein

c) Hydrogenation



R¹ and R²: alkyl and aryl; [M^{*}]: [Rh] or [Ir]

Conclusion

Method	Representatives	Chirality	Loading	Catalyst/Reagent
Enantioselective Hydroboration	H.C. Brown, H. Nöth, C.M. Crudden, etc.	Substrate control & reagent control	Stoichiometric or catalytic	[Rh] or [Ir] [Cu]
Homologation	D.S. Matterson, V.K. Aggarwal, etc.	Substrate control & reagent control	Stoichiometric	MRX, MR*X
Enantioselective Hydrogenation	J. P. Morken, P.G. Andersson, A. Pfaltz, etc.	Chiral ligand	catalytic	[Rh] or [Ir]

Enantioselective Hydrogenation : Avoid regioselectivity problems often encountered in catalytic and stoichiometric hydroborations, and a wide range of potential catalysts available.

Thanks!