

Massachusetts Institute of Technology
Organic Chemistry 5.512

April 24, 2006
Prof. Rick L. Danheiser

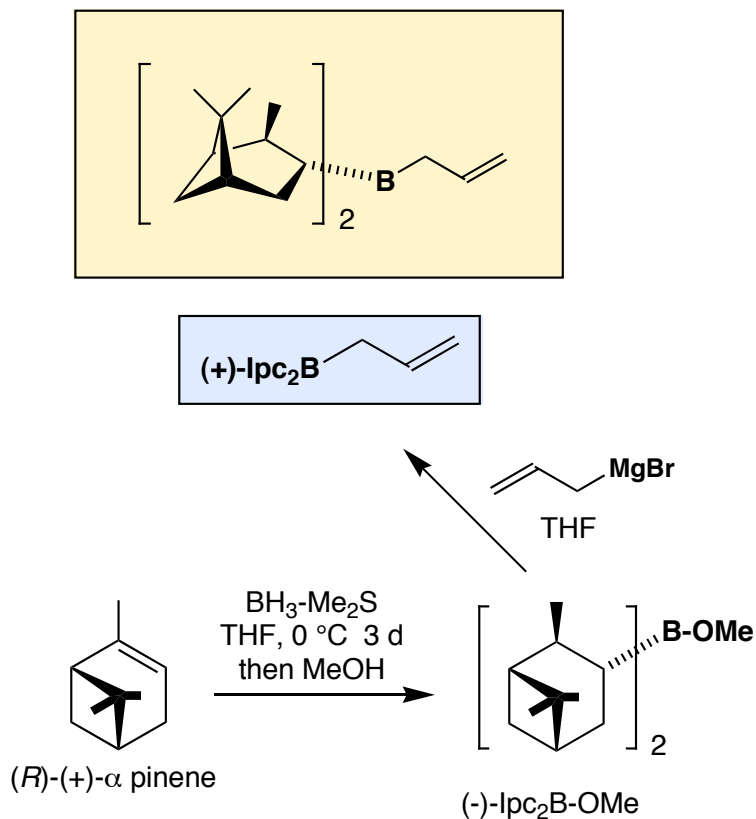
Unit 5
Stereocontrolled 1,2-Addition of Allylmetal Compounds
to Carbonyl Groups

- ★ Introduction: Mechanism and Transition States
- ★ Substrate Control: Addition of Achiral Allylmetals to α -Chiral Aldehydes
- ★ Reagent Control: Addition of Chiral Allylmetals to Achiral Aldehydes
- ★ Reagent Control: Addition of Allylmetals to Achiral Aldehydes (w/ Chiral Lewis Acids)

Allylboron Compounds



H. C. Brown
1912-2004



Allyltitanium Compounds

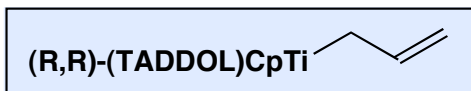
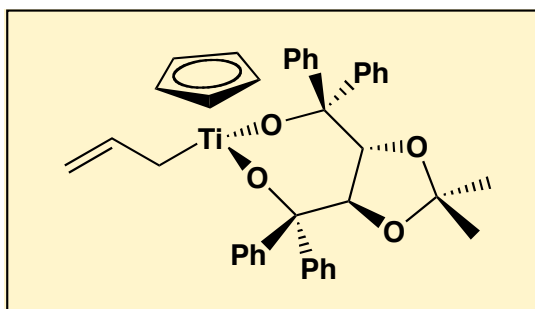
Reviews:

"Synthesis and Reactivity of Allyltitanium Derivatives" Szymoniak and Moise, C.

In *Titanium and Zirconium in Organic Synthesis*, Marek, I., Ed.; Wiley-VCH, 2002, pp 451-474.

"Chiral Titanium Complexes for Enantioselective Addition of Nucleophiles to Carbonyl Groups"

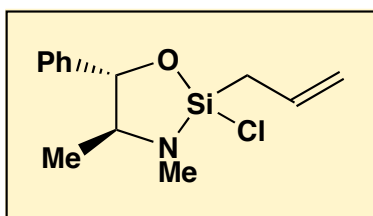
Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, 92, 807



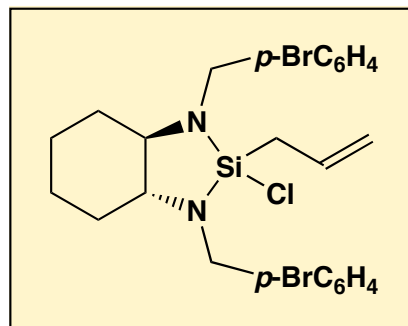
Dieter Seebach

TADDOL Ligands

Allylsilicon Compounds



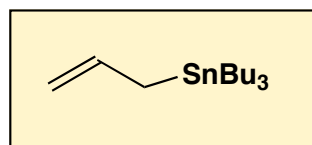
J. L. Leighton



See "Highly Diastereo- and Enantioselective Reagents for Aldehyde Crotylation" Hackman, B. M.; Lombardi, P. J.; Leighton, J. L. *Org. Lett.* **2004**, 6, 4375 and references cited therein

"Origins of Stereoselectivity in Strain-Release Allylations" Zhang, X.; Houk, K. N.; Leighton, J. L. *Angew. Chem. Int. Ed.* **2005**, 44, 938

Allylstannanes



Keck, G. E.; Krishnamurthy *Org. Synth.* **1998**, 75, 12

Review: J. A. Marshall *Chem. Rev.* **1991**, 91, 31

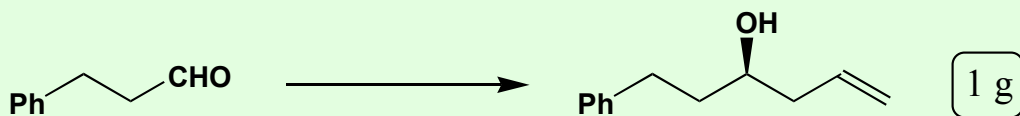
Useful recent **review:** "BINOL: A Versatile Chiral Reagent"

Brunel, J. M. *Chem. Rev.* **2005**, 105, 857



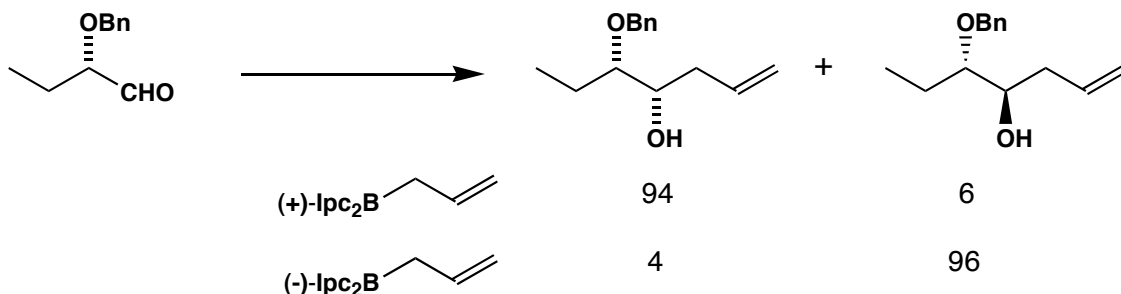
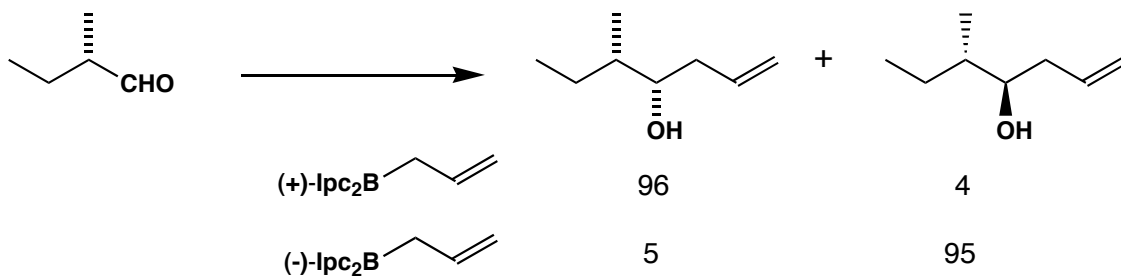
Gary E. Keck

Allylmetal Showdown



Method	Cost	Selectivity	Preparation (steps)
Roush	\$5	80:20	2 (Storable)
Carriera (only non-enolizable)	\$14	80:20	0
Brown	\$14	98:2	1 (<i>in situ</i>)
Leighton (pseudoephedrine)	\$20	94:6	1 (Storable)
Keck	\$19	98:2	0
Duthaler	\$414	97:3	2 (Storable)

Double Asymmetric Synthesis: Addition of Chiral Allylmetals to Chiral Aldehydes



Double Asymmetric Synthesis: Addition of Chiral Allylmetals to Chiral Aldehydes

