

Massachusetts Institute of Technology
Organic Chemistry 5.512

April 19, 2006
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Unit 4
Stereocontrolled 1,2-Addition to Carbonyl Groups

★ General Principles

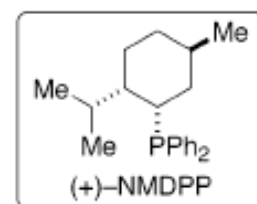
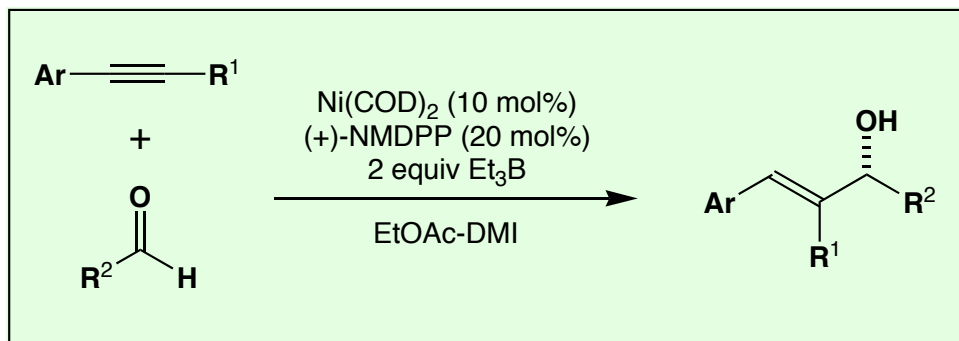
- ★ Substrate Control: 1,2-Induction by Molecular Framework
- ★ Substrate Control: 1,3-Induction by Molecular Framework
- ★ Reagent Control: Organozinc and Related Addition Reactions
Addition of Alkyl, Aryl, Alkenyl, and Alkynyl Metal Compounds

Asymmetric Addition of Alkenylmetal Compounds to Aldehydes

★ Alkenylzinc Additions

★ Jamison Vinylation

Miller, K. M.; Huang, W.-S.; Jamison, T. F. *J. Am. Chem. Soc.* **2003**, 125, 3442



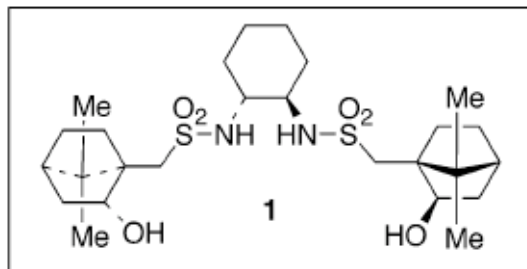
J. D. Morrison ligand

★ Asymmetric Addition of Alkenylmetal Compounds to Aldehydes

★ Frontier: Asymmetric Vinylation of Ketones

P. J. Walsh *J. Am. Chem. Soc.* **2004**, *126*, 6538, *J. Org. Chem.* **2005**, *70*, 448,
J. Am. Chem. Soc. **2005**, *127*, 8355

modified Yoshioka ligand



★ Frontier: Enantioselective NHK (Nozaki-Hiyama-Kishi) Reactions

Y. Kishi et al. *J. Am. Chem. Soc.* **2004**, *126*, 12248, *Org. Lett.* **2004**, *6*, 5031

★ Asymmetric Addition of Alkynylzinc Compounds to Aldehydes

Reviews:

- (1) "Asymmetric Alkynylzinc Additions to Aldehydes and Ketones", Pu, L. *Tetrahedron* **2003**, *59*, 9873
- (2) "Acetylenes in Catalysis: Enantioselective Additions to Carbonyl Groups and Imines and Applications Beyond", Cozzi, P. G.; Hilgraf, R.; Zimmermann, N. *Eur. J. Org. Chem.* **2004**, 4095



Erick M. Carreira

