

Massachusetts Institute of Technology
Organic Chemistry 5.512

March 16, 2007
Prof. Rick L. Danheiser

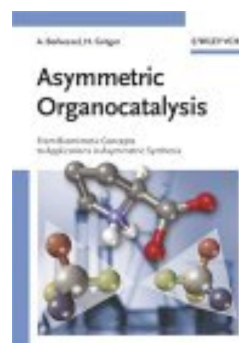
Unit 2
Stereocontrolled Alkylation
and Related Electrophilic Substitution Strategies

V. Catalytic Methods

- ★ α -Oxidation of Aldehydes and Ketones (*H. Yamamoto, MacMillan, Zhong, Y. Hayashi*)
- ★ Alkylation of Imine Derivatives of α -Amino Esters (*O'Donnell, Corey, Maruoka*)
- ★ Tsuji Allylation of Ketones (*Stoltz, Trost*)
- ★ Enantioselective Protonation Strategies (*Fu*)



Special Issue on
Asymmetric Organocatalysis
Accts. Chem. Res. **2004**, 37, 487-631

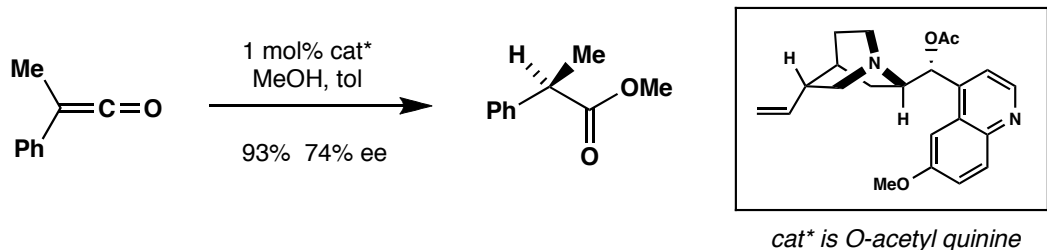


"Asymmetric Organocatalysis"
A. Berkessel and H. Gröger
Wiley-VCH, **2005**

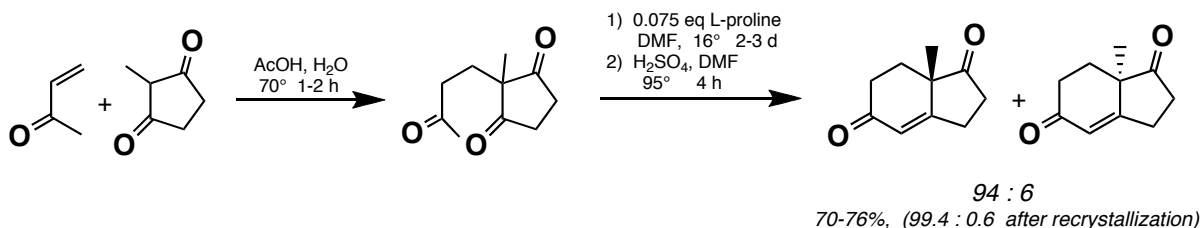
- ★ Catalysis by Enzymes
- ★ Transition Metal Organometallic Catalysis
- ★ "Organocatalysts"

Asymmetric Organocatalysis: Early Milestones

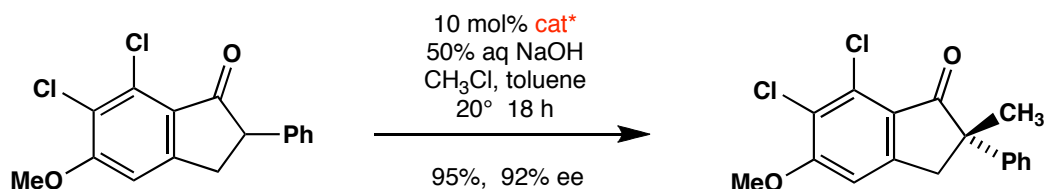
★ H. Pracejus *Liebigs Ann. Chem.* **1960**, 634, 9; *J. Prakt. Chem.* **1964**, 24, 195



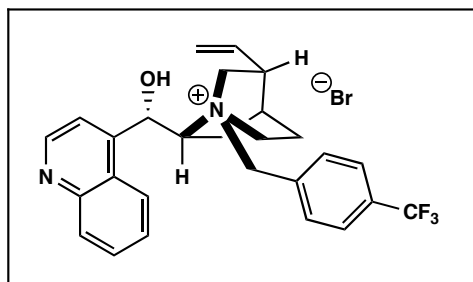
★ Z. G. Hajos, D. R. Parrish *J. Org. Chem.* **1974**, 39, 1615; also U. Eder, G. Sauer, and R. Wiechert . . . see *Org. Synth. Coll. Vol.* 7, 363 and 368



★ E. J. J. Grabowski et al. *J. Am. Chem. Soc.* **1984**, 106, 446;
J. Org. Chem. **1987**, 52, 4745



cat^*
cinchoninium bromide
derivative



Enantioselective Organocatalytic Oxidation of Aldehydes with Nitrosobenzene



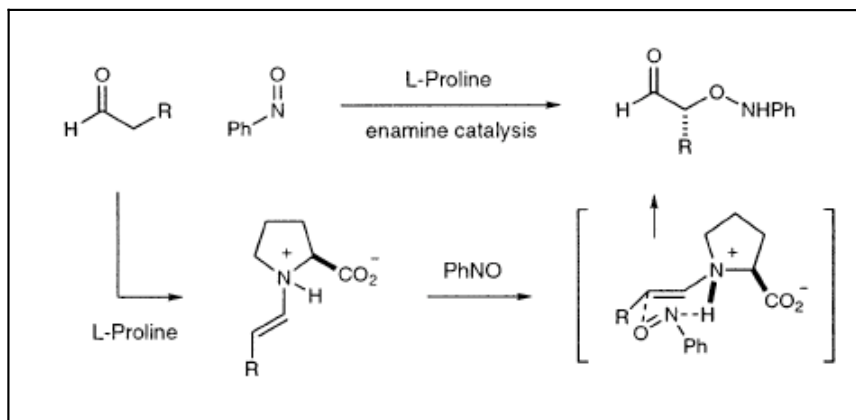
Hisashi Yamamoto
University of Chicago

Review

Yamamoto, H.; Momiyama N.
Chem. Commun. **2005**, 3514



David MacMillan
Princeton University



Reviews on Catalytic, Enantioselective "Heterofunctionalization" of Carbonyl Compounds

Janey, J. M. *Angew. Chem. Int. Ed.* **2005**, 44, 4292

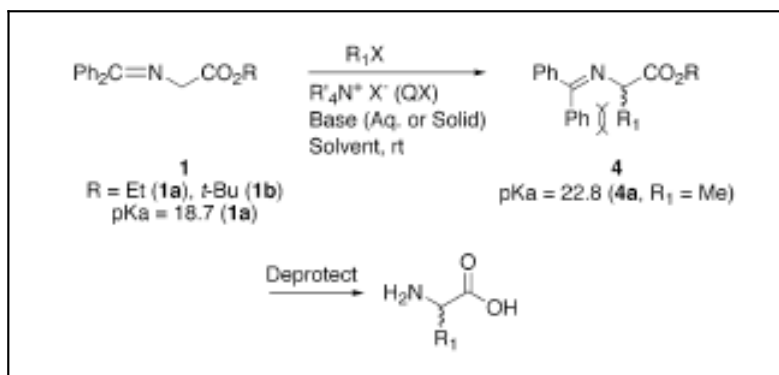
Guillena, G.; Ramon, D. J. *Tetrahedron: Asymmetry* **2006**, 17, 1465

Marigo, M; Jorgensen, K. A. *Chem. Commun.* **2006**, 2001

Alkylation of Imine Derivatives of α -Amino Esters



Martin J. O'Donnell
IUIPUI



Enantioselective Tsuji Allylation

Minireview

You, S.-L.; Dai, L.-X. . *Angew. Chem. Int. Ed.* **2006**, 45, 5246

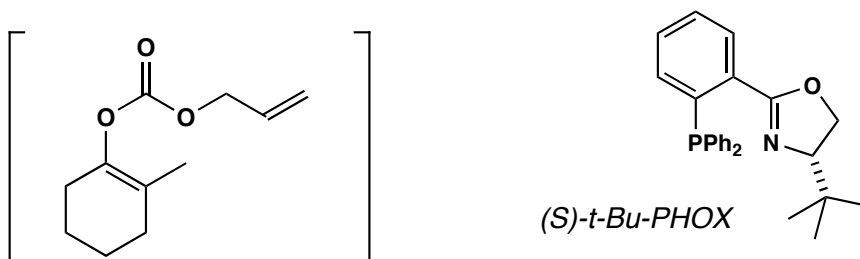
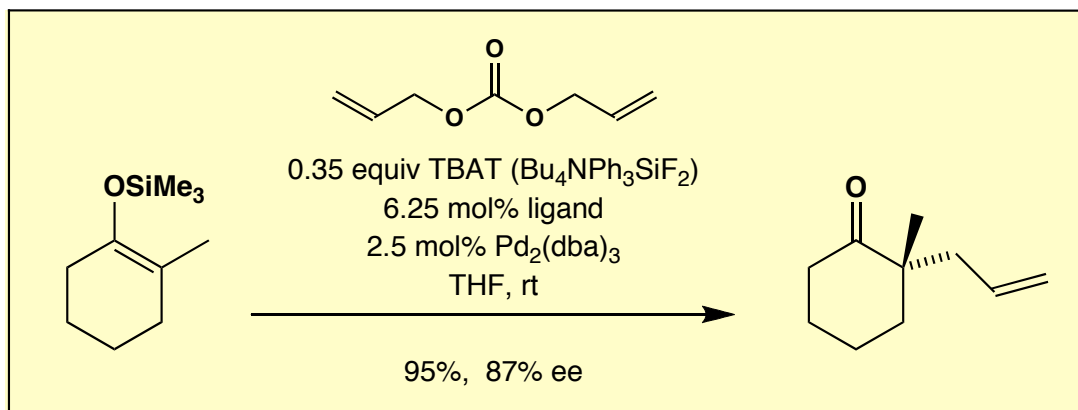
Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, 126, 15,044

Trost, B. M.; Xu, J. *J. Am. Chem. Soc.* **2005**, 127, 2846

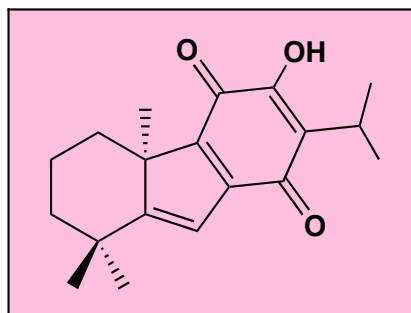
Trost, B. M.; Xu, J. *J. Am. Chem. Soc.* **2005**, 127, 17180

Trost, B. M. Bream, R. N.; Xu, J. *Angew. Chem. Int. Ed.* **2006**, 45, 3109

Braun, M.; Meier, T. *Angew. Chem. Int. Ed.* **2006**, 45, 6952

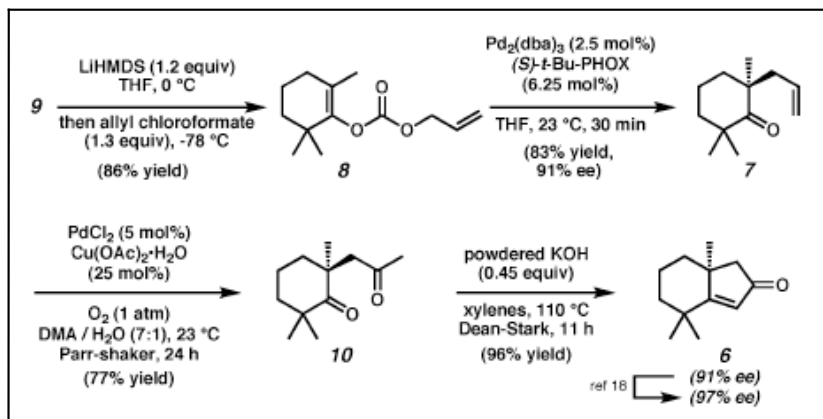


Case Study



$(+)$ -Dichroanone

McFadden, R. M.; Stoltz, B. M.
J. Am. Chem. Soc. **2006**, 128, 7738



Enantioselective Protonation Strategies

Review: J.-C. Plaquevent *Tetrahedron Asymmetry* **2004**, 15, 3653

Enantioselective Addition of Amines to Ketenes Catalyzed by a Planar-Chiral Derivative

B. L. Hodous; G. C. Fu *J. Am. Chem. Soc.* **2002**, 124, 10,006

