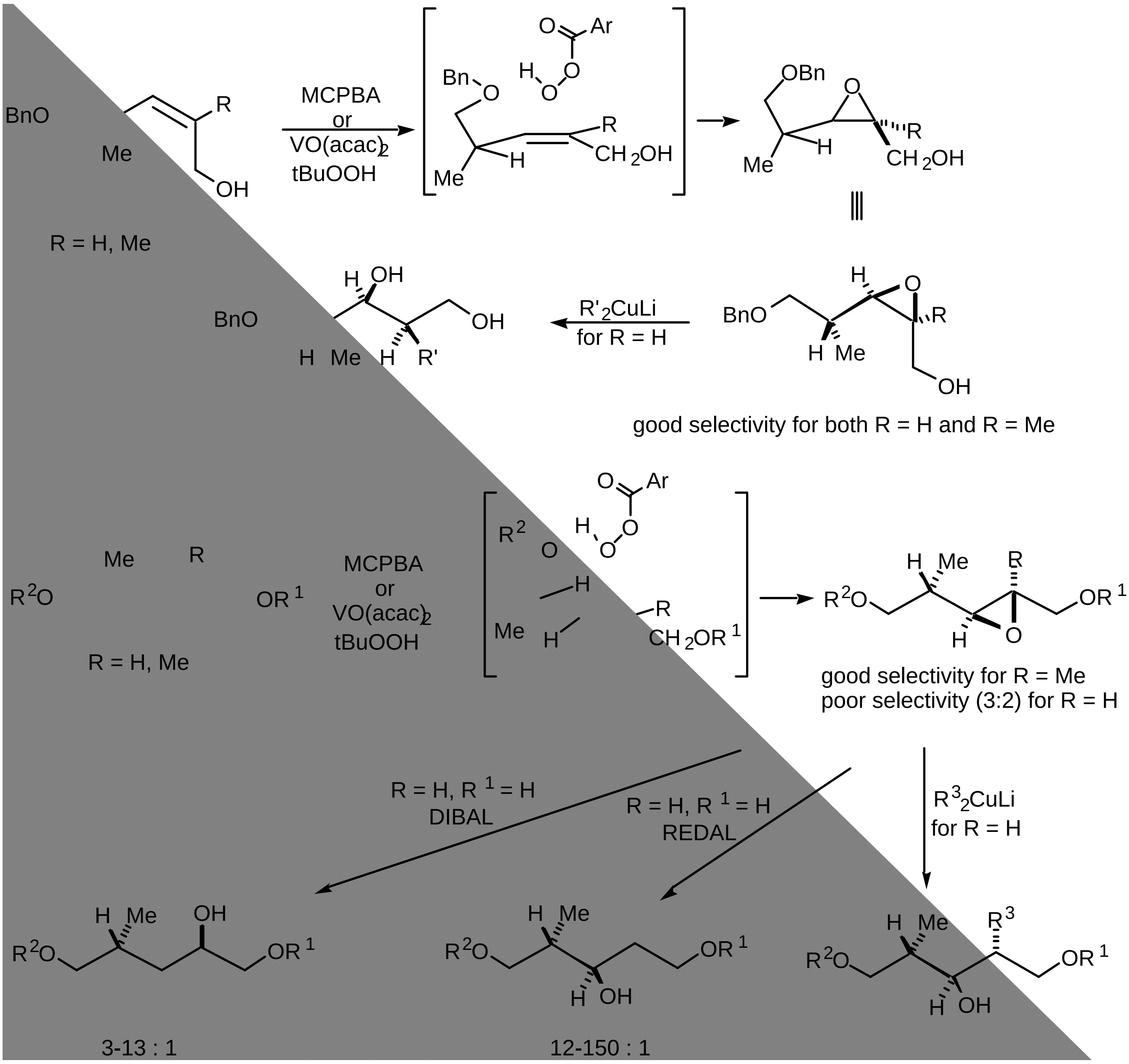
Chemistry 144

M. E. Jung
Organic Synthesis

Acyclic Stereocontrol

Kishi Epoxidation (*Tetrahedron Lett.* **1979**, 4343, 4347; **1982**, *23*, 2719)



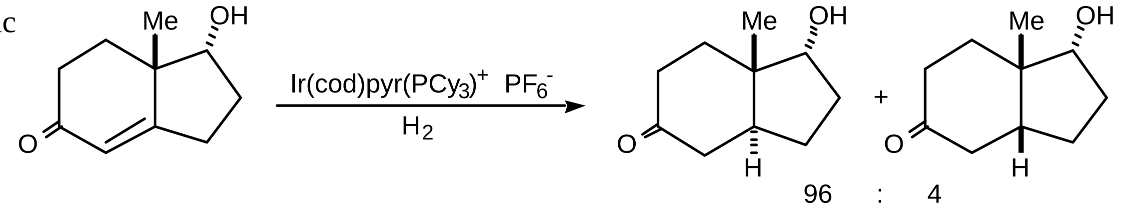
Chemistry 144

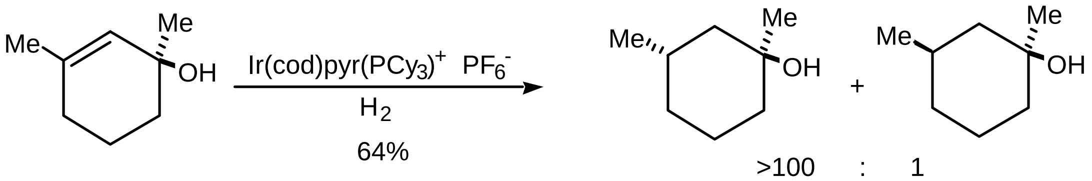
M. E. Jung
Organic Synthesis

Cyclic and Acyclic Stereocontrol

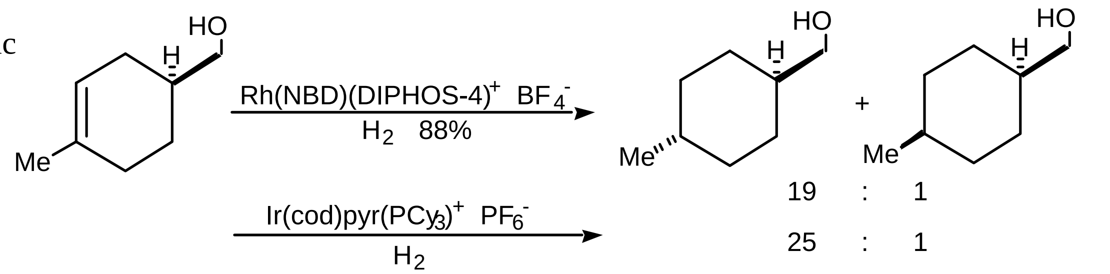
Hydroxyl-Directed Hydrogenation
Stork, G.; *et al. J. Am. Chem. Soc.* **1983**, *105*, 1072.
Evans, D. A.; *et al. J. Am. Chem. Soc.* **1984**, *106*, 3866; *Tetrahedron Lett.* **1985**, *26*, 6005;
Tetrahedron Lett. **1984**, *25*, 4637.
Crabtree, R.; *et al. J. Organomet. Chem.* **1979**, *168*, 183; *Organometallics* **1983**, *2*, 681.
Schultz, A. G.; *et al.*, *J. Org. Chem.* **1985**, *50*, 5905.
Review: Brown, J. M. *Angew. Chem. Int. Ed. Eng.* **1987**, *26*, 190.

Stork - cyclic

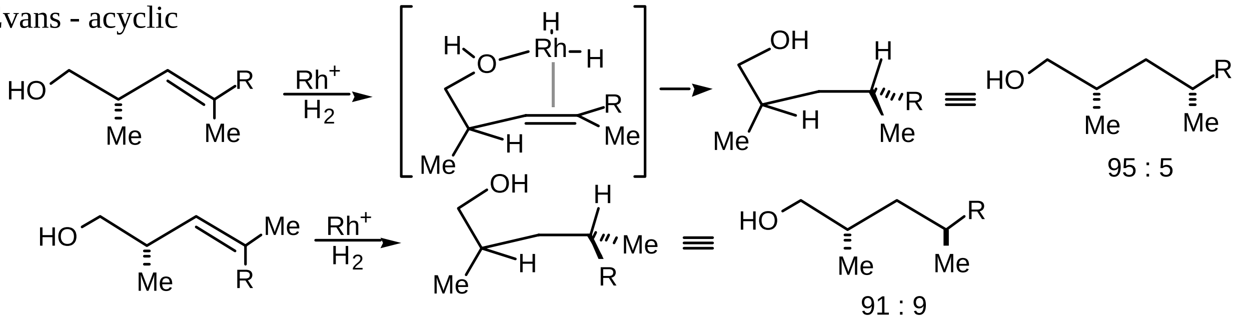




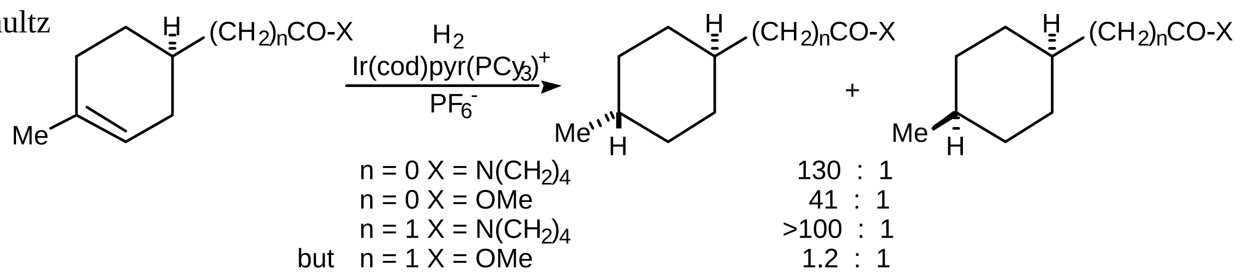
Evans - cyclic



Evans - acyclic



Schultz

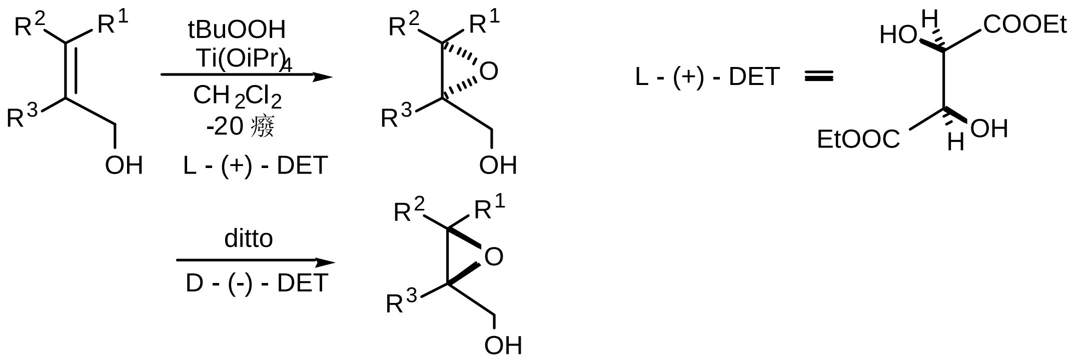


Chemistry 144
M. E. Jung
Organic Synthesis

Acyclic Enantiocontrol

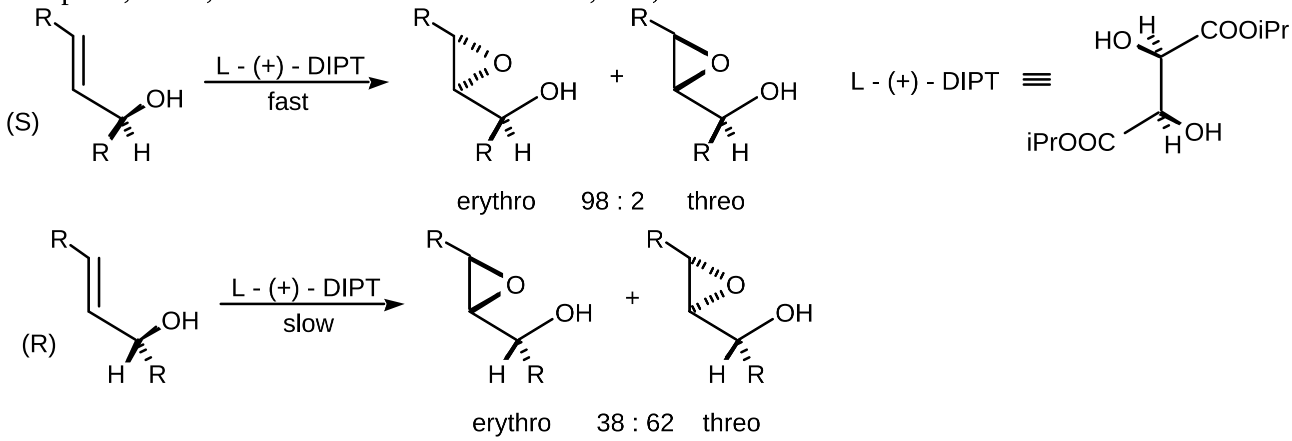
Sharpless Asymmetric Epoxidation and Kinetic Resolution

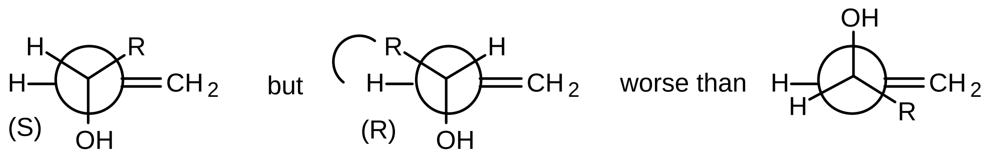
Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974; Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 464.



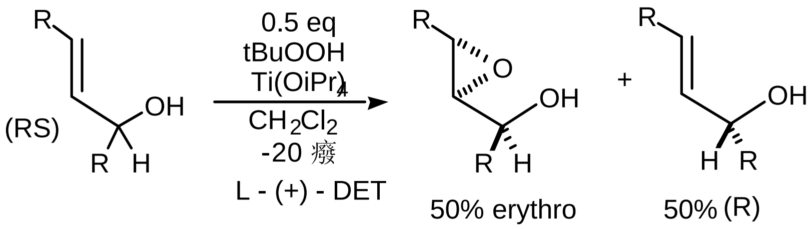
Sharpless Kinetic Resolution

Sharpless, K. B.; *et al. J. Am. Chem. Soc.* **1981**, *103*, 6237.

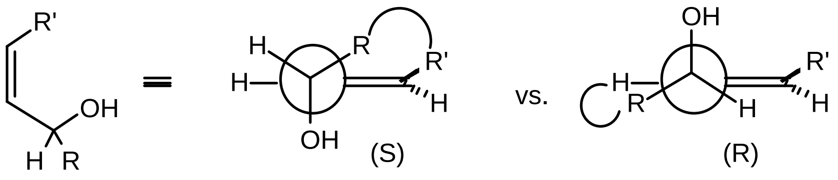




Therefore, when you epoxidize a racemic mixture of the secondary allylic alcohol at -20 °C using
only 0.5 equivalent of tBuOOH, all of the (S) enantiomer is epoxidized to give the erythro epoxy alcohol while the (R) enantiomer remains unreacted. These two compounds can be easily separated by simple chromatography. Therefore in this process you have <u>kinetically resolved</u> the racemic allylic alcohol (resolved by a difference in the rates of reaction of the enantiomers)!



but cis-substituted
has steric problems
and gives low ee's
in kinetic resolution



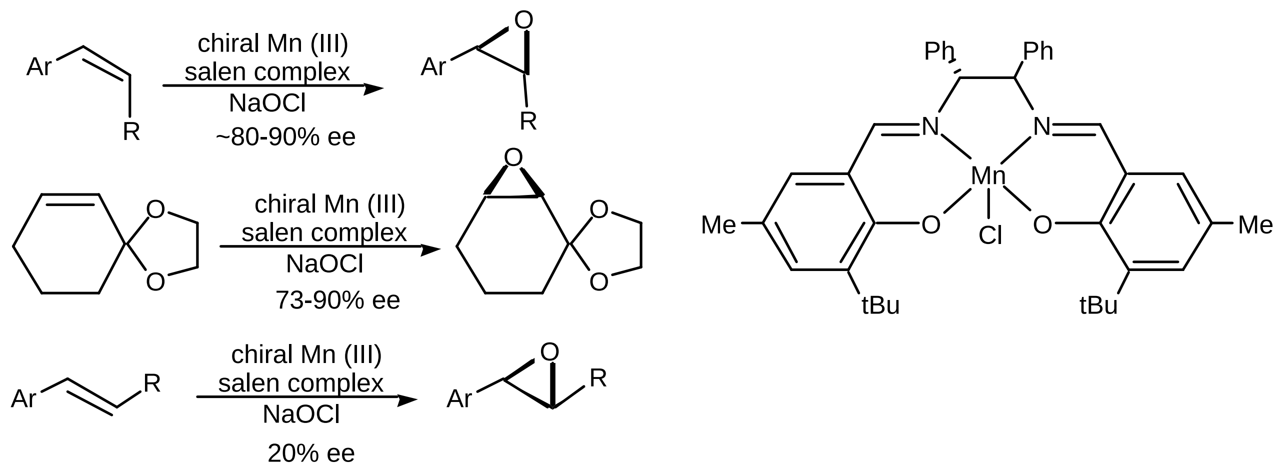
Chemistry 144

M. E. Jung
Organic Synthesis

Acyclic Enantiocontrol

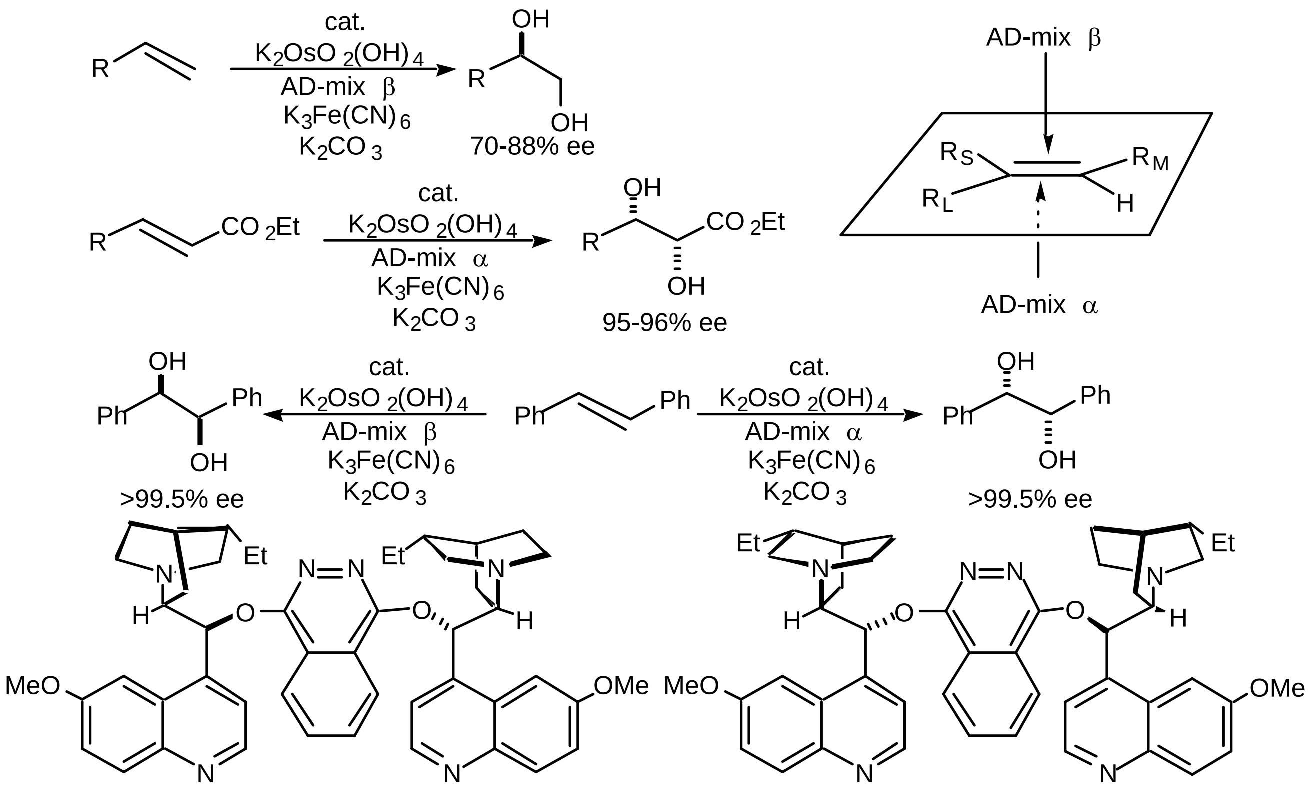
<u>Jacobsen Asymmetric Epoxidation</u>

Jacobsen, E. N.; *et al. J. Am. Chem. Soc.* **1990**, *112*, 2801; **1991**, *113*, 7063; *J. Org. Chem.* **1991**, *56*, 2296.



<u>Sharpless Asymmetric Dihydroxylation</u>

Sharpless, K. B.; *et al. J. Org. Chem.* **1992**, *57*, 2768; **1993**, *58*, 844. Corey, E. J. *et al. J. Am. Chem. Soc.* **1993**, *115*, 3828.



$(DHQD)_2$-PHAL (AD-mix β) $(DHQ)_2$-PHAL (AD-mix α)