Unit 3
Stereocontrolled Conjugate Addition

★ Catalytic Asymmetric Conjugate Addition I: Unstabilized Nucleophiles
  Hayashi-Miyaura Rh-Catalyzed Conjugate Addition Reactions
  Cu-Catalyzed Conjugate Addition of Organozinc Compounds
  Organocatalytic Conjugate Addition of Activated Aromatic Compounds
★ Catalytic Asymmetric Conjugate Addition II: Conjugate Reduction
★ Catalytic Asymmetric Conjugate Addition III: Stabilized Nucleophiles
  Michael Reactions Using Heterobimetallic Catalysts (Shibasaki)
  Organocatalytic Michael Reactions (Jorgensen)

Organocatalytic Conjugate Addition of Activated Aromatic Compounds

Reviews: See Berkessel and Gröger
Catalytic Asymmetric Conjugate Reduction

**Buchwald Cu-Catalyzed Conjugate Reduction:** *J. Am. Chem. Soc.* 2003, 125, 11,253 and refs cited

![Chemical reaction](image)

- PMHS (4 equiv)
- $t$-AmOH (4 equiv)
- CuCl$_2$ (0.1 mol%)
- $t$-BuONa (0.2 mol%)
- (S)-$p$-tolBINAP (0.1 mol%)
- c-hexane, 23°C.
- 95%, 86% ee

**MacMillan Organocatalytic Conjugate Reduction:** *J. Am. Chem. Soc.* 2005, 127, 32

![Chemical structures](image)

Enantioselective Organocatalytic Hydride Reduction (EOHR)

- Imidazolidinone
- Iminium Catalyst
- Hantzsch Ester
- Hydride Source
- Figures by MIT OCW.
Catalyst 2

EOHR
Origins of Enantiocontrol with Catalyst 2

Enal Hantzsch Ester
Catalyst 2

\[ + H^- \]

\[ + H^+ \]

Figures by MIT OCW.
Catalytic Asymmetric Conjugate Addition of Stabilized Nucleophiles

I. Shibasaki: "Heterobimetallic Catalysts"

II. Jorgensen: Organocatalytic Conjugate Addition  
*Angew. Chem. Int. Ed.* 2003, 42, 661 and 4955

![Reaction Scheme]

III. Jacobsen: Enantioselective Conjugate Additions Catalyzed by (Salen)Al Complexes  

IV. Corey: Organocatalytic Conjugate Addition of Imino Esters  

![Reaction Scheme]

Figure by OCW