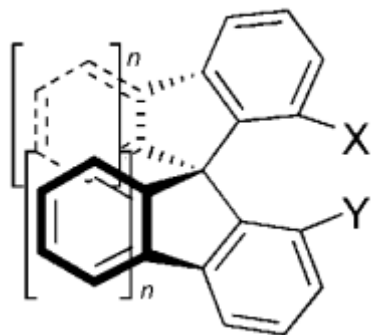


Chiral Spiro Ligands Developed by Zhou Qilin



Professor Zhou Qilin



1978-1982: B.Sc. degree, Lanzhou University

1982-1987: Ph.D. degree, SIOC, advisor: Yao-Zeng Huang

1987-1996: Postdoctoral, East China University of Science and Technology; Max-Planck Institute of Polymer Science; Basel University; Trinity University

1996-1999: East China University of Science and Technology, Associate professor; Professor

1999-present: Nankai University, Professor

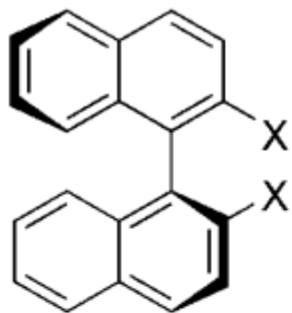
2009: Member of Chinese Academy of Sciences

2018: Future Science Prize---The Physical Science Prize

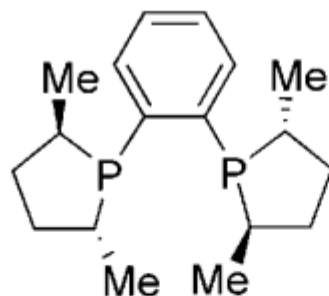
Research interests:

Synthetic methodology, organometallics, asymmetric catalysis, and synthesis of biologically active compounds and chiral drugs.

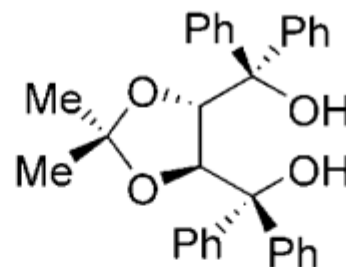
Examples of Privileged Chiral Ligands and Catalysts



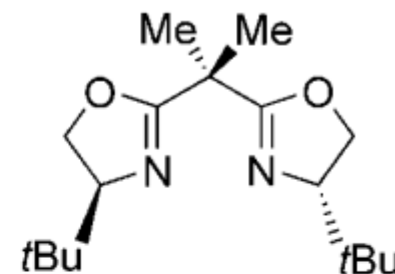
X = OH binol
X = PPh₂ binap



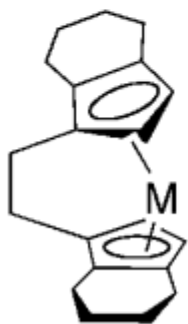
MeDuphos



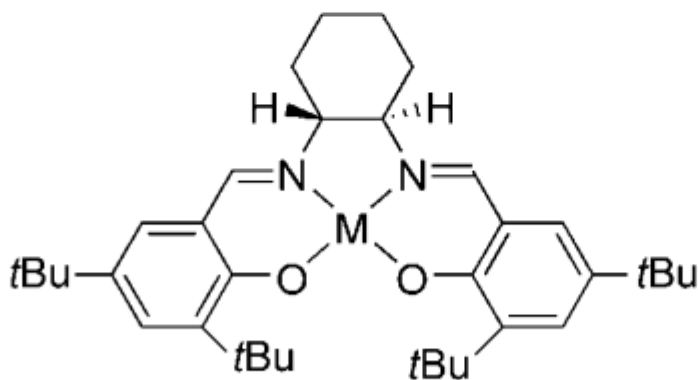
taddol



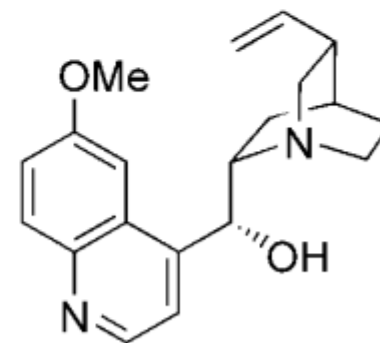
bis(oxazoline)



Brintzinger's
complexes

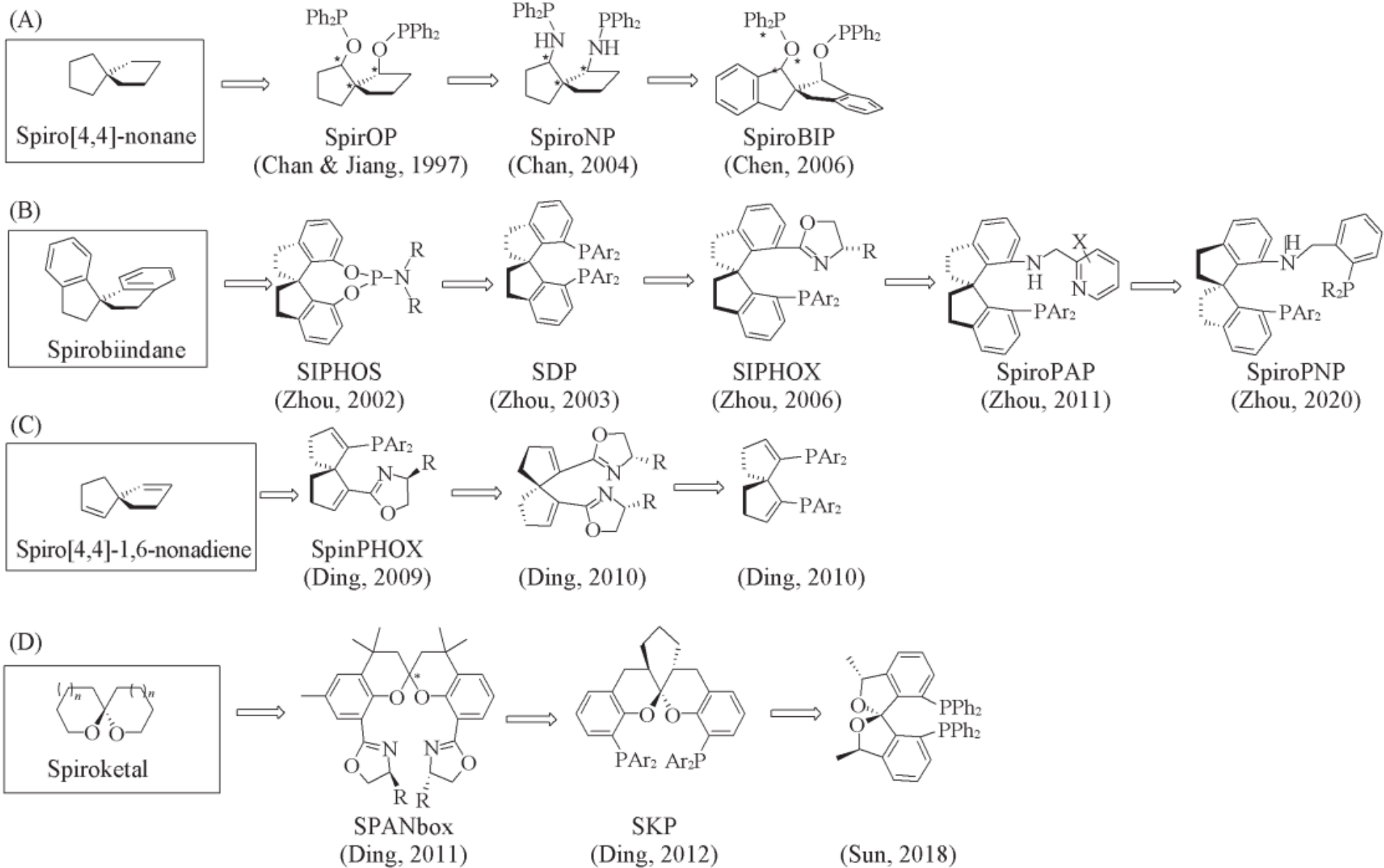


salen complexes



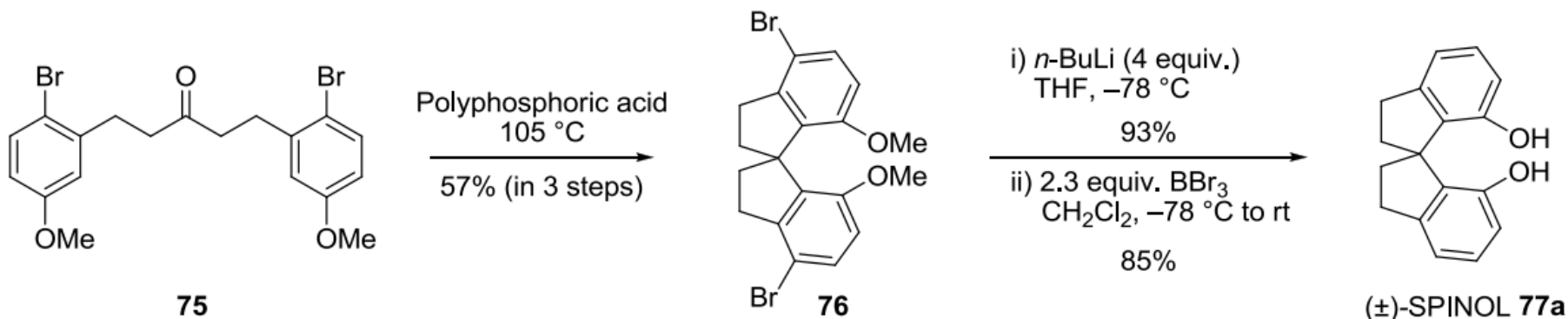
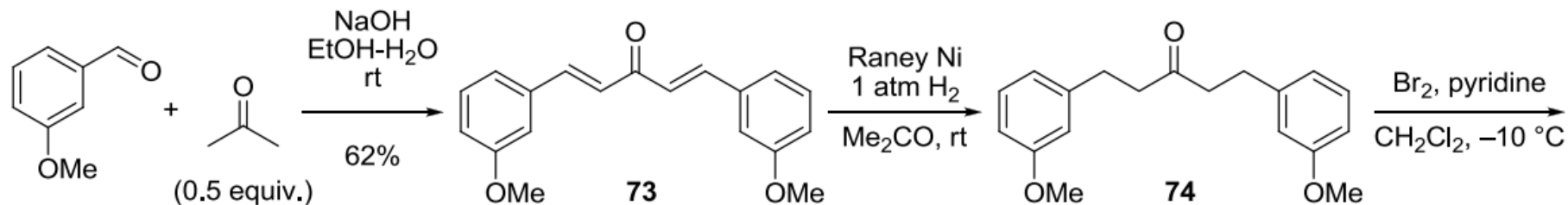
Cinchona alkaloids

Development of Chiral Spiro Ligands

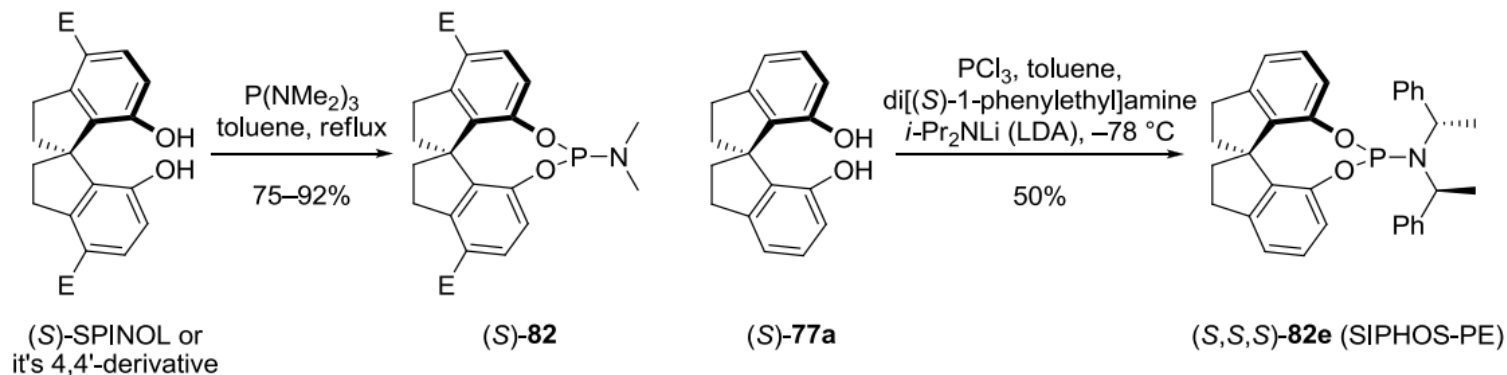


Development of Chiral Ligands with Spirobiindane Skeletons

Birman, 1999

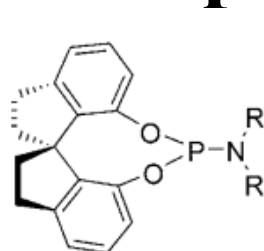


Zhou, 2002



(S)-82a (SIPHOS-Me) (E = H)
 (S)-82b (DiBr-SIPHOS) (E = Br)
 (S)-82c (DiPh-SIPHOS) (E = Ph)
 (S)-82d (DiMeO-SIPHOS) (E = MeO)

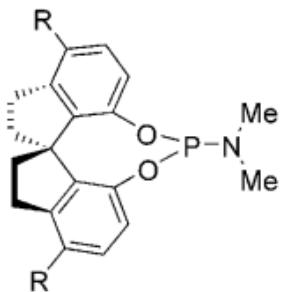
Development of Chiral Ligands with Spirobiindane Skeletons



4a R = Me ((S)-siphos)

4b R = (S)-1-phenylethyl

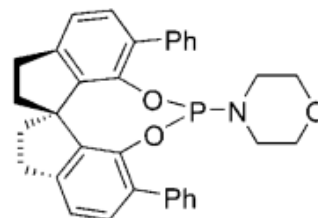
4c R = (R)-1-phenylethyl



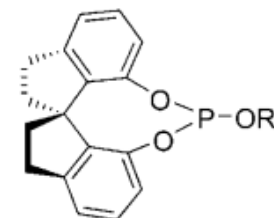
5a R = Br

5b R = Ph

5c R = MeO



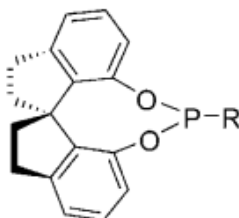
(R)-6



7a R = C₆H₅ ((S)-ShiP)

7b R = 2-naphthyl

7c R = 4-MeOC₆H₄



8a R = C₆H₅ ((S)-FuP)

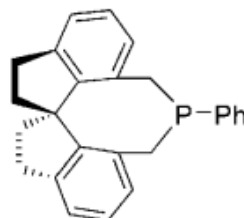
8b R = 4-MeC₆H₄

8c R = 4-MeOC₆H₄

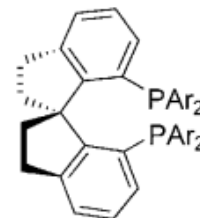
8d R = 4-ClC₆H₄

8e R = 4-CF₃C₆H₄

8f R = *t*Bu



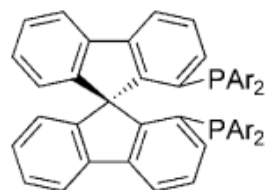
(R)-sitcp 9



10a Ar = C₆H₅ ((S)-sdp)

10b Ar = 3,5-(Me)₂C₆H₃ (Xyl-sdp)

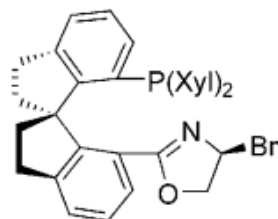
10c Ar = 3,5-(Me)₂-4-MeOC₆H₂



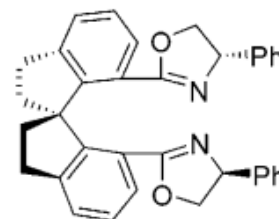
11a Ar = 4-MeC₆H₄ (Tol-sfdp)

11b Ar = 3,5-(Me)₂C₆H₃ (Xyl-sfdp)

11c Ar = 3,4,5-(Me)₃C₆H₂ (tm-sfdp)



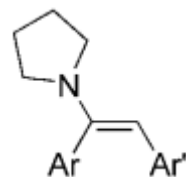
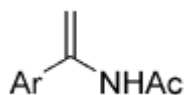
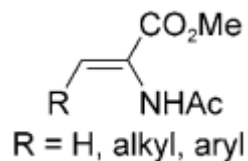
(S_a,S)-siphox 12



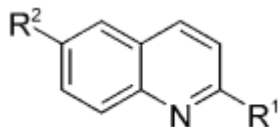
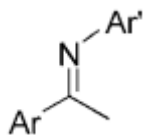
(S_a,S,S)-SpiroBOX 13

Applications

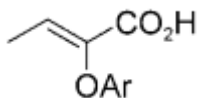
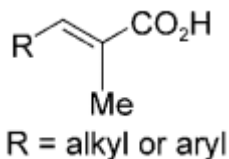
Enantioselective Hydrogenations



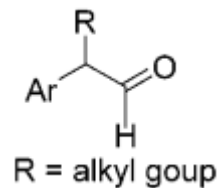
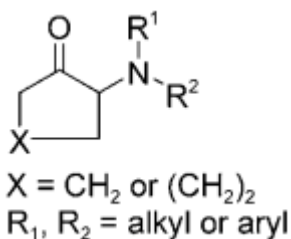
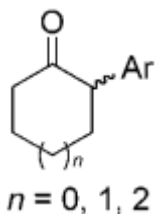
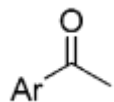
enamides and enamines



imines and quinolines



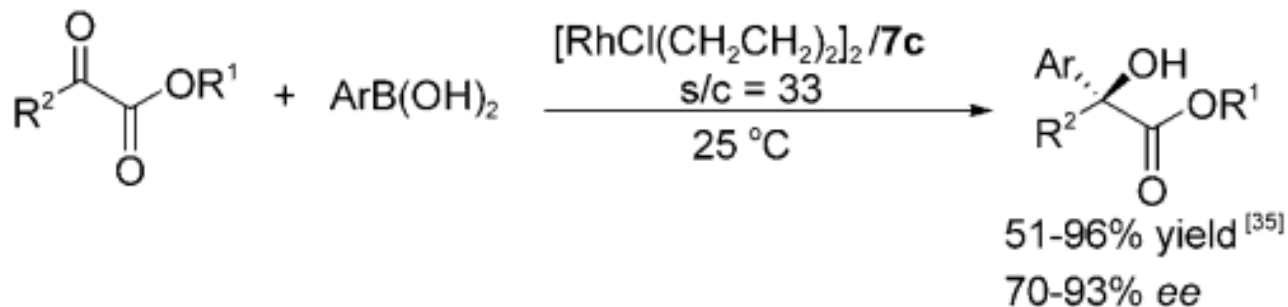
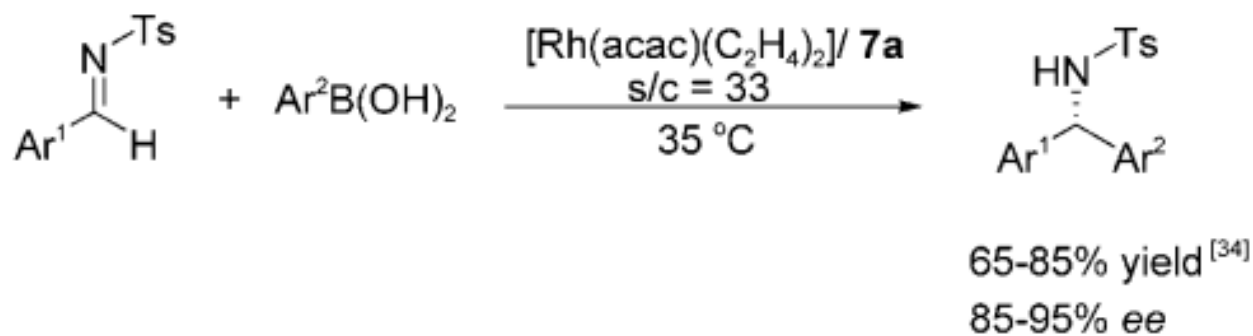
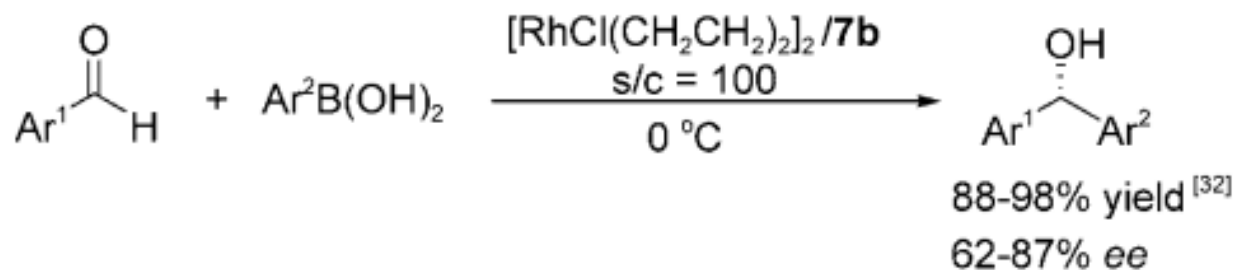
α, β -unsaturated carboxylic acids



ketones and aldehydes

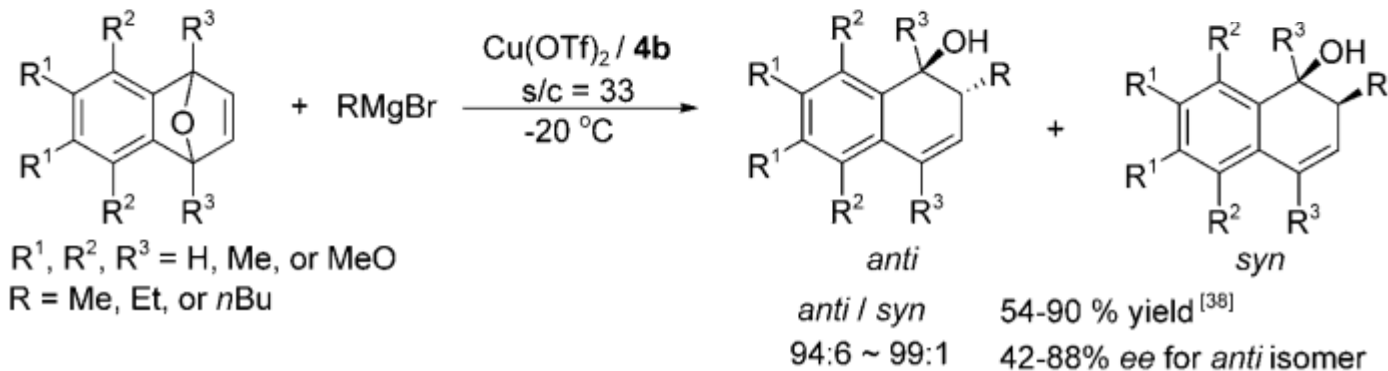
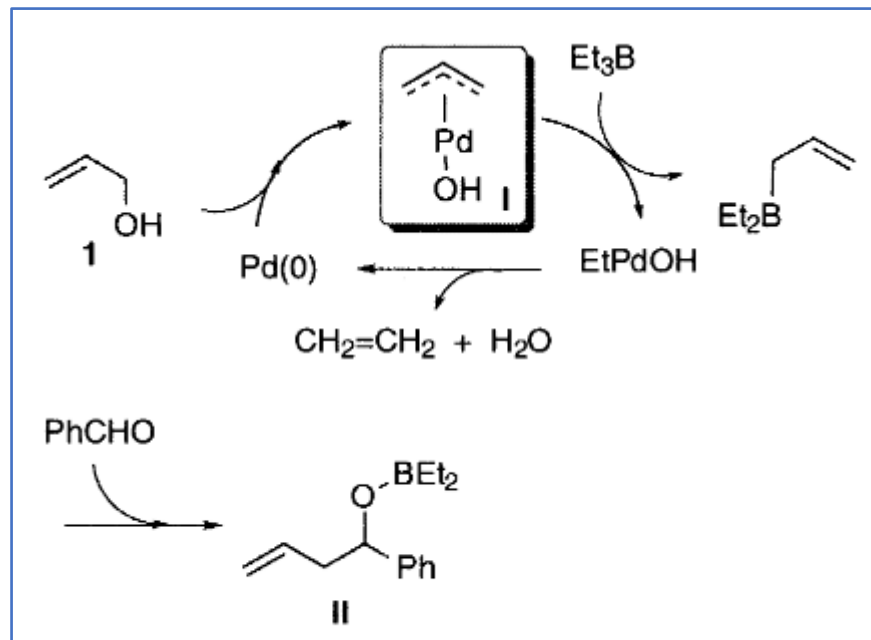
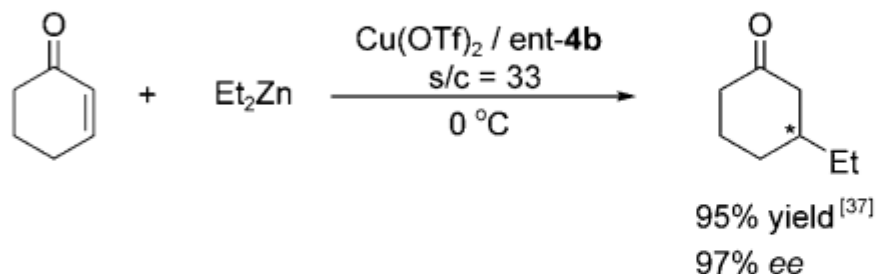
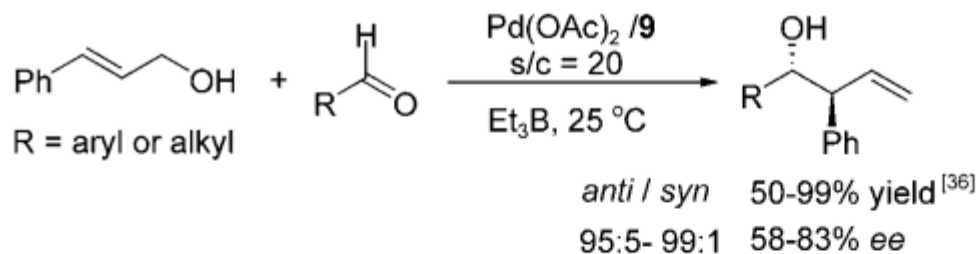
Applications

Asymmetric addition of arylboronic acids to aldehydes, imines, and α -ketoesters.



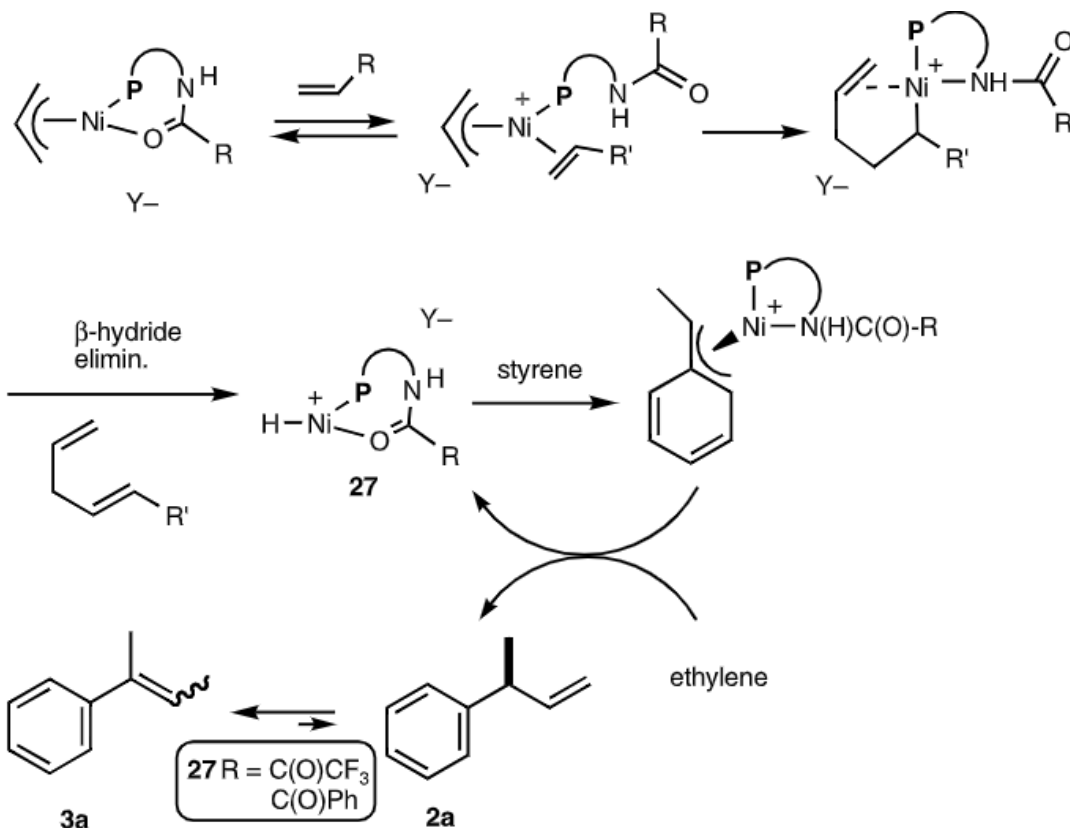
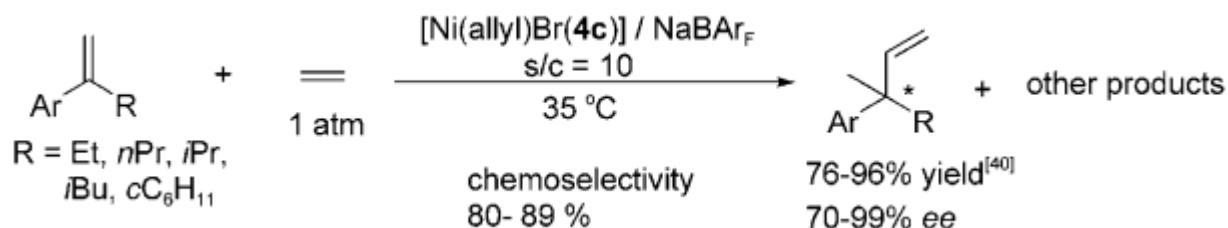
Applications

Asymmetric alkylation of aldehydes, α,β -unsaturated ketones or meso oxabicyclic alkenes.



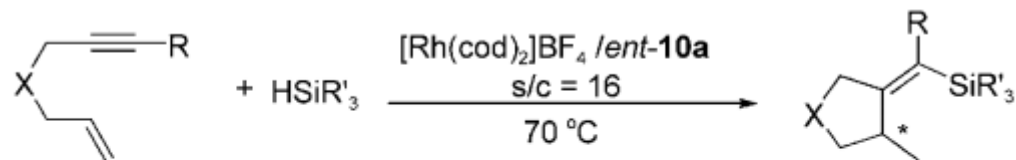
Applications

Asymmetric hydrovinylation and cyclization of olefin derivatives.



Applications

Asymmetric hydrovinylation and cyclization of olefin derivatives.



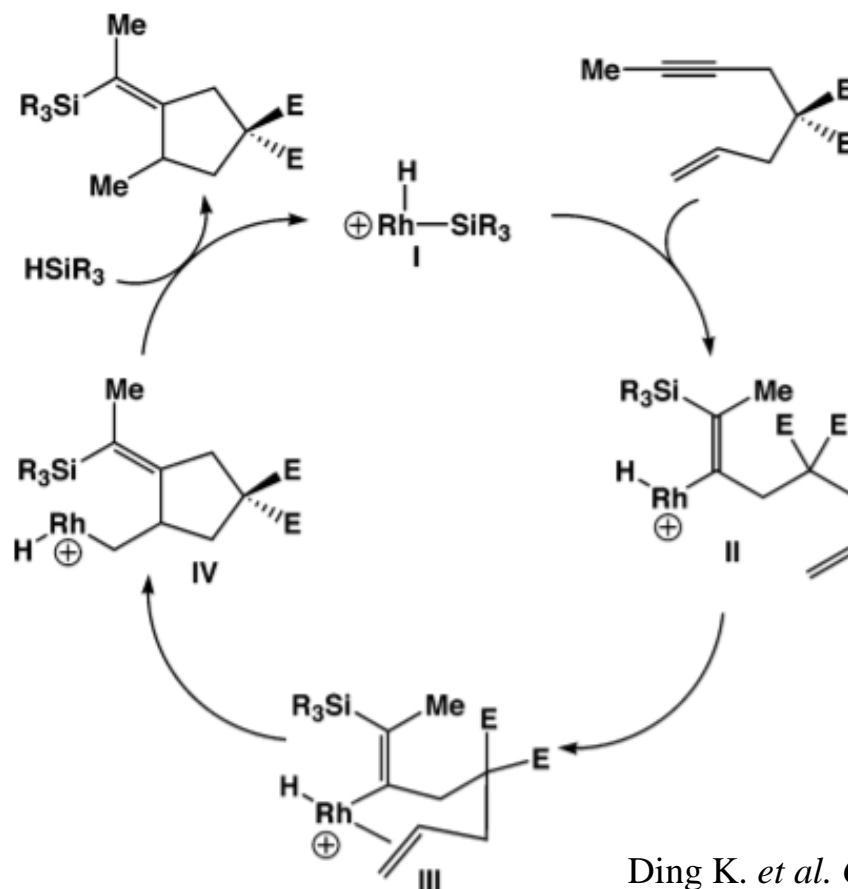
X = MsN, NsN, TsN, (EtO₂C)₂C, (NC)₂C

R = H or Me

R' = Et, *n*Pr, MeO or EtO, etc.

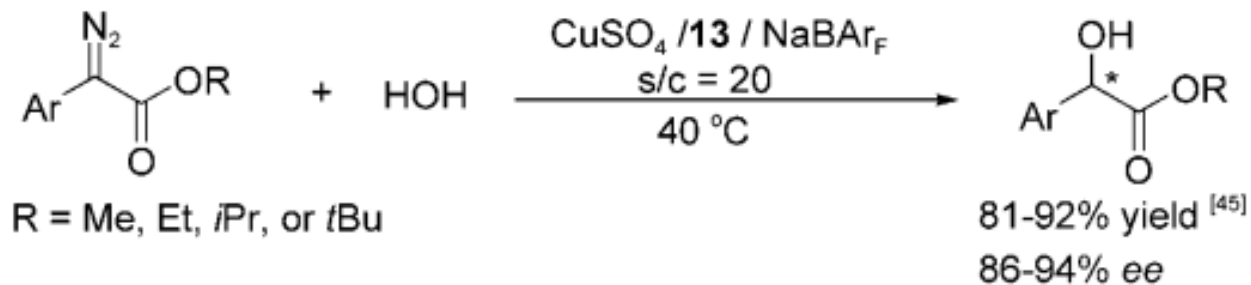
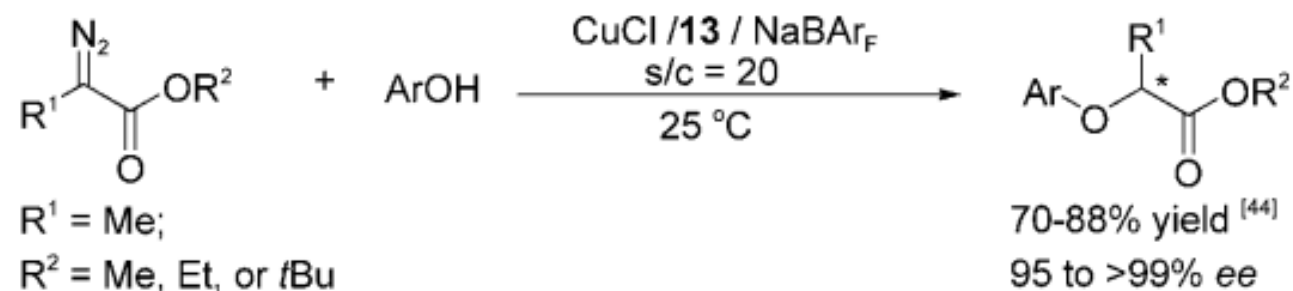
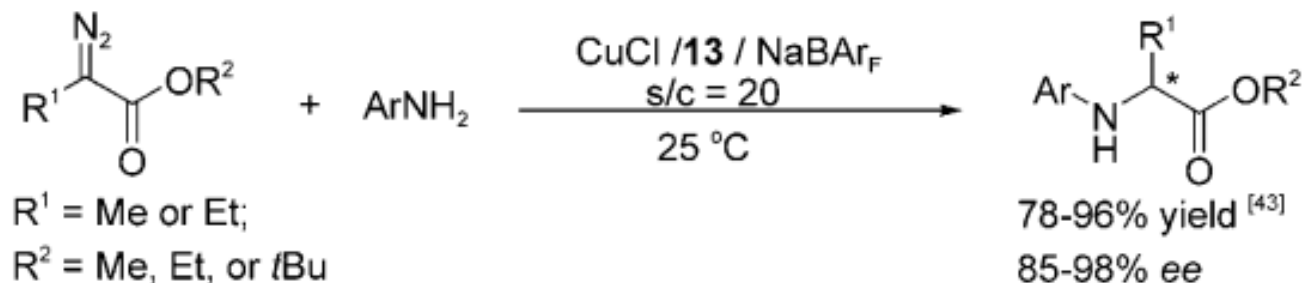
41-93% yield^[42]

89 to >99% ee



Applications

Asymmetric insertion of α -diazooesters into the NH or OH bonds of amines, phenols, or H₂O.



Applications

Application of chiral spiro ligands as organocatalyst.

