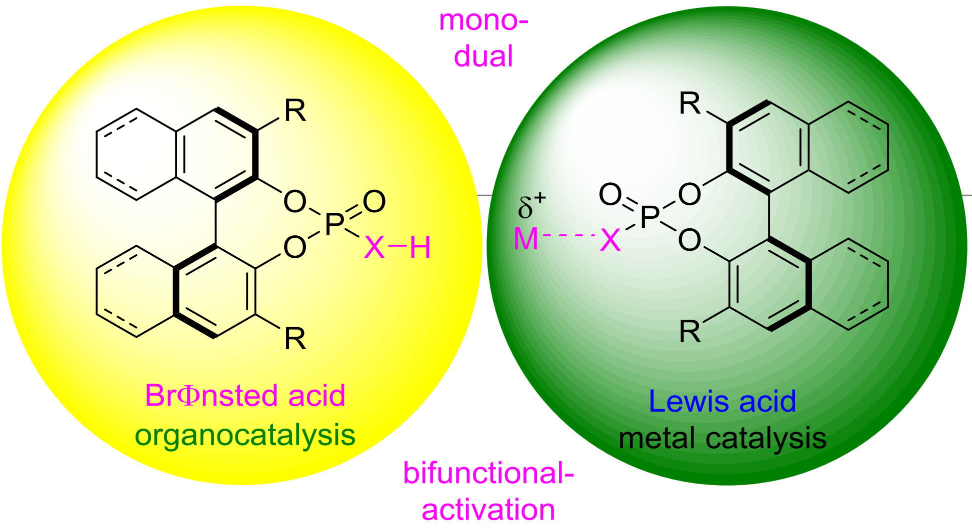
Complete Field Guide to Asymmetric BINOL-Phosphate Derived Brønsted Acid and Metal Catalysis



Reporter: Fangfang Guo
Supervisor : Prof.Huang
Date: 9/18/2017

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2.Modes of Activation

2.1 Mono Activation

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1. Introduction

pKa = (MeCN)

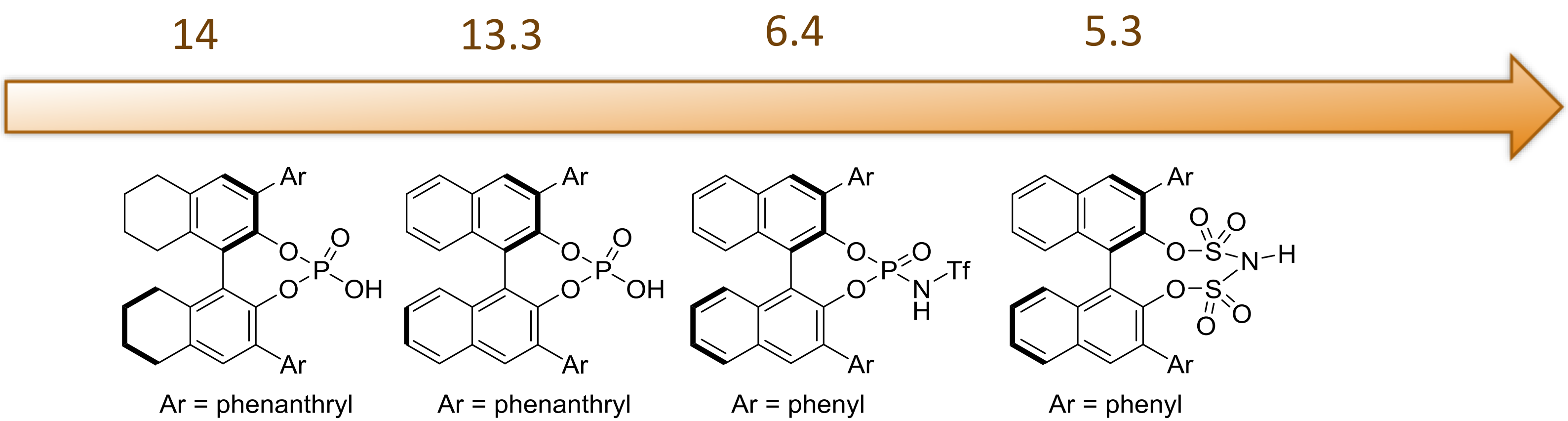


Figure 1. Acidity scale for selected BINOL-derived Brønsted acids.

Table 1. pKa's of Common Acids in MeCN

acid	pKa in MeCN
sacharin	14.6
picric acid	11
HCl	10.3
TsOH	8.5
4-$NO_2C_6H_4$-SO_3H	6.7
HBr	5.5

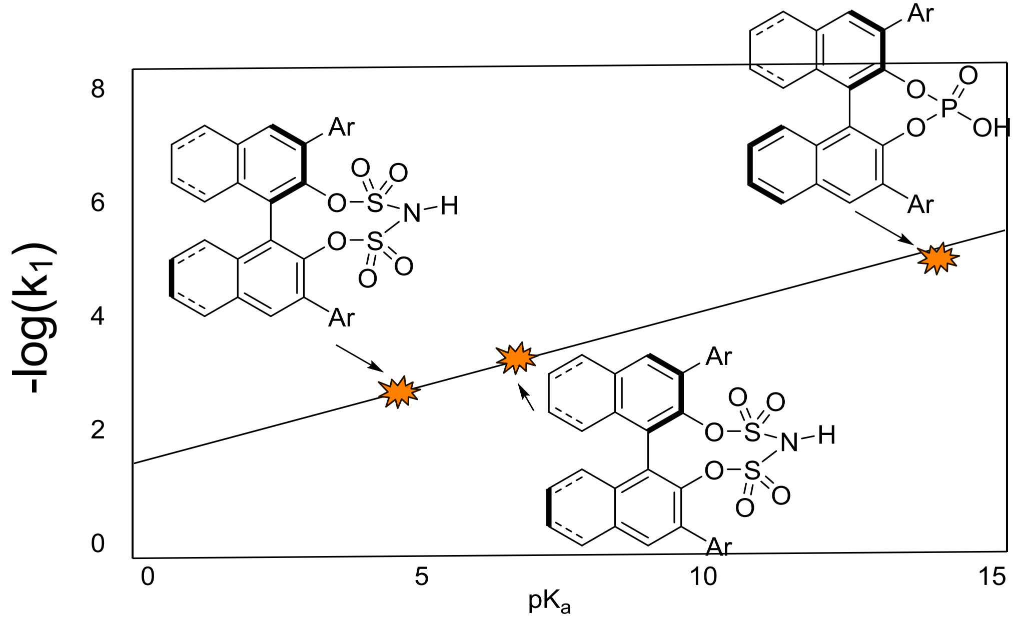
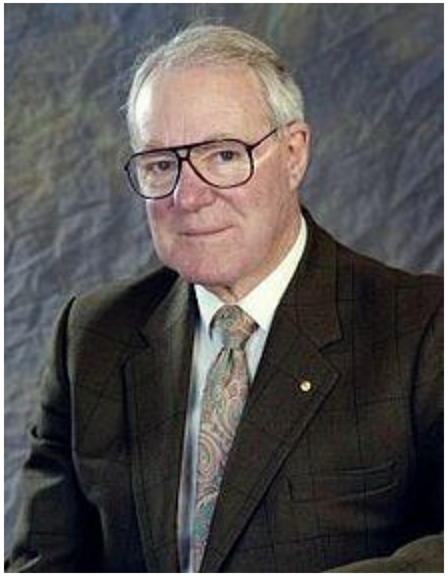


Figure 2. A plot of the rate of a reaction versus acidity of catalyst



John Cornforth, Jr., (7 September 1917 – 8 December 2013) was an Australian–British chemist who won the Nobel Prize in Chemistry in 1975 for his work on the stereochemistry of enzyme-catalysed reactions.

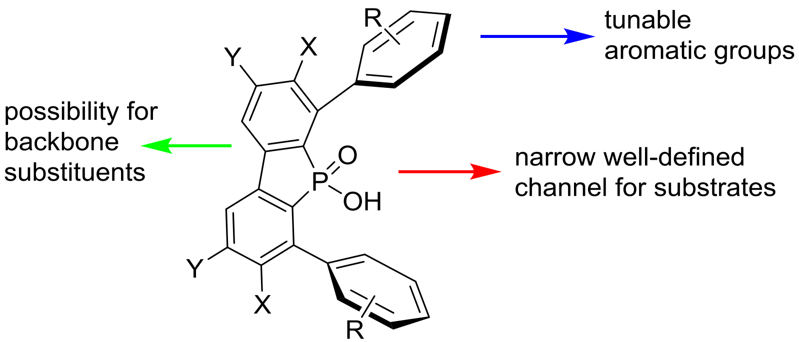


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Figure 3. Phosphoric acid catalysts developed by Cornforth (1978)

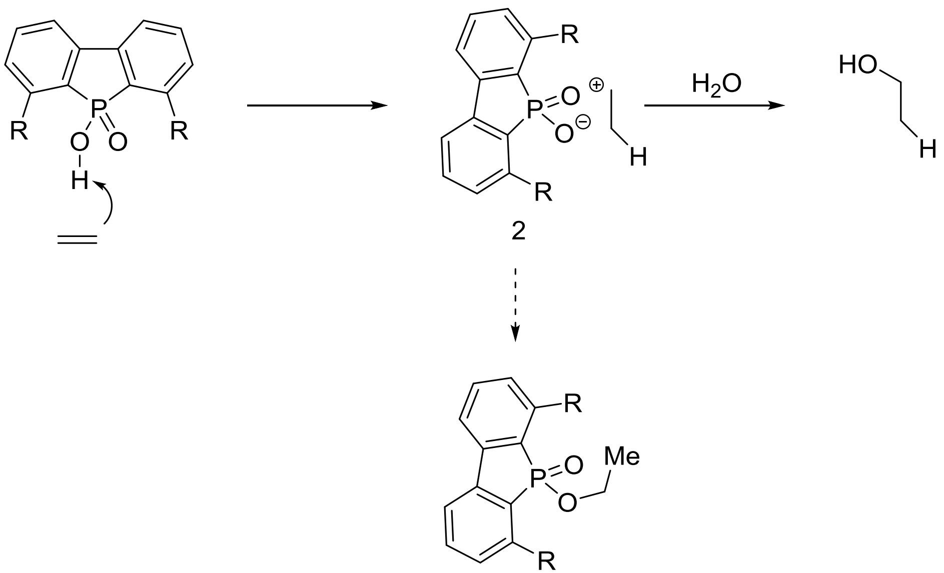
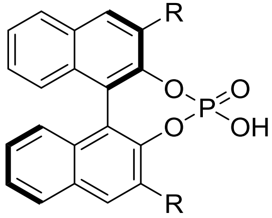
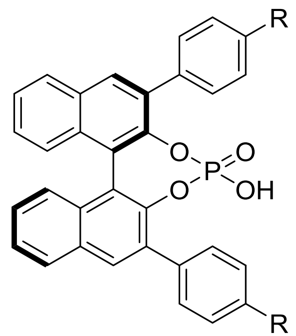


Figure 4. Potential reactivity of phosphoric acids with olefins.

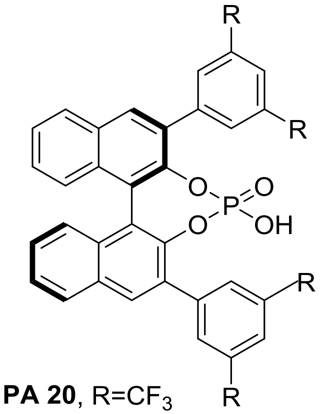
Cornforth, J.; Cornforth, R. H.; Gray, R. T. *J. Chem. Soc.,Perkin Trans*. 1982, 2289.



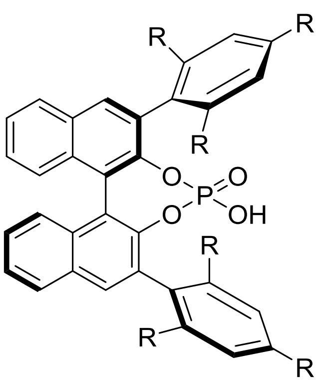
PA 1, R=H
PA 2, R=$SiPh_3$
PA 3, R=Si(4-*t*$BuC_6H_4)_3$
PA 4, R=adamanthyl
PA 5, R=1-naphthyl
PA 6, R=2-naphthyl
PA 7, R=9-anthracenyl
PA 8, R=9-phenanthryl
PA 9, R=1-pyrenyl



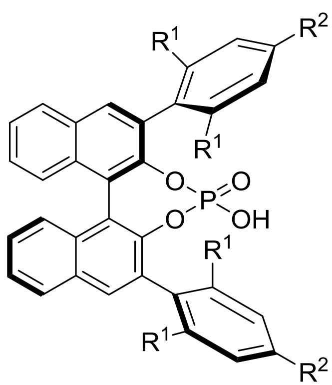
PA 10, R=H
PA 11, R=*t*Bu
PA 12, R=F
PA 13, R=Cl
PA 14, R=OMe
PA 15, R=NO_2
PA 16, R=Ph
PA 17, R=3,5-$(CF_3)_2C_6H_3$
PA 18, R=2,3,4,5-F_5C_6
PA 19, R=2-naphthyl



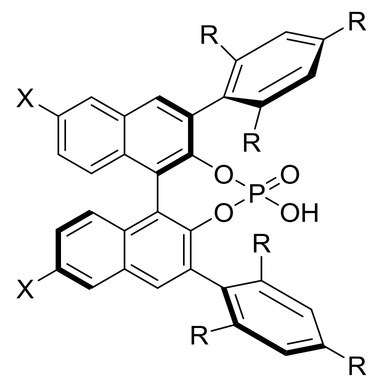
PA 20, R=CF_3
PA 21, R=SF_5
PA 22, R=Ph
PA 23, R=2,4,6-$(Me)_3C_6H_2$



PA 24, R=Me
PA 25, R=*i*Pr

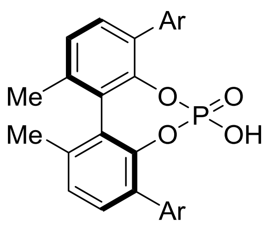


PA 26, R^1=Me, R^2=OMe
PA 27, R^1=*i*Pr, R^2=*t*Bu
PA 28, R^1=*i*Pr, R^2=4-*t*BuC_6H_4
PA 29, R^1=*i*Pr, R^2=9-anthracenyl

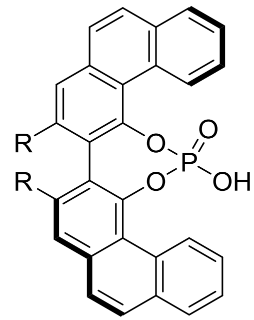


PA 30, R=*i*Pr, X=I
PA 31, R=*i*Pr, X=NO_2
PA 32, R=*i*Pr, X=Si(iPr)$_3$
PA 33, R=*i*Pr, X=C_8H_{17}

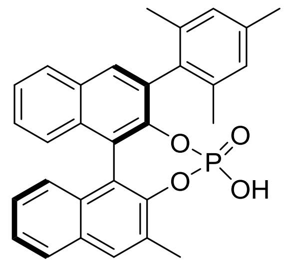
Figure 5. BINOL-phosphoric acid (PA) catalysts used in the majority of reactions



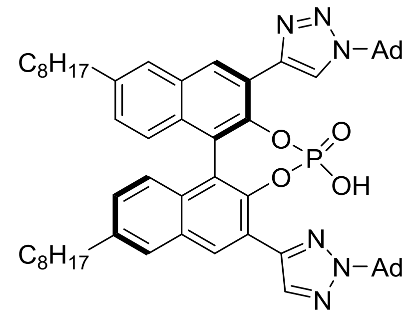
PA 34, Ar=2,4-$(CF_3)_2C_6H_3$
PA 35, Ar=9-anthracenyl



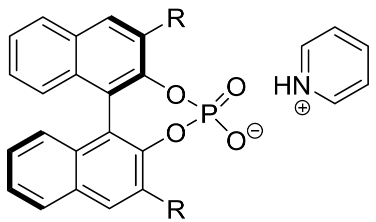
PA 36, R=H
PA 37, R=Ph



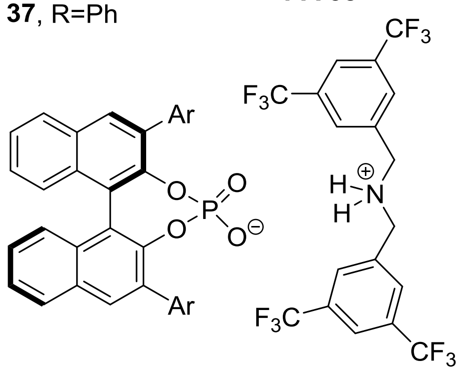
PA 38



PA 39

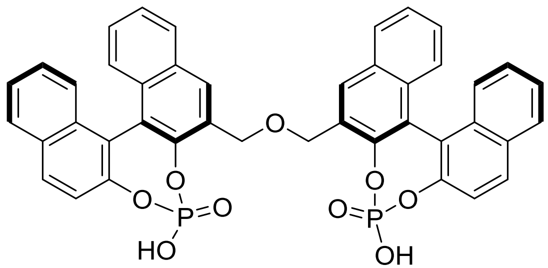


PA 40, R=9-anthracenyl

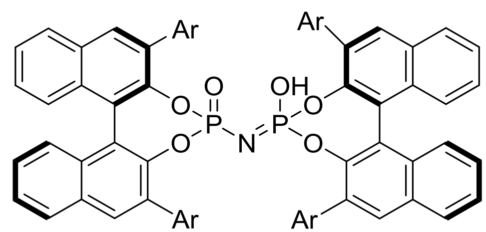


PA 41, Ar=2,4,6-$C_6H_2(i\text{Pr})_3$

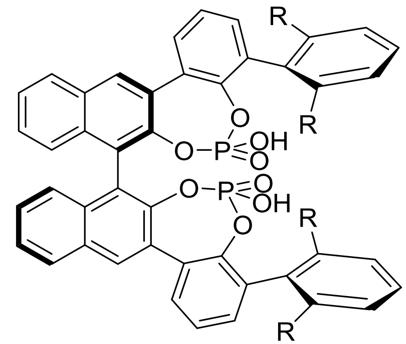
Figure 6. Miscellaneous chiral phosphoric acid catalysts.



PA 42



PA 43, Ar=2,4,6-$Et_3C_6H_2$



PA 44, R=*i*Pr

Figure 7. Multiple chiral axis containing phosphoric acid catalysts.

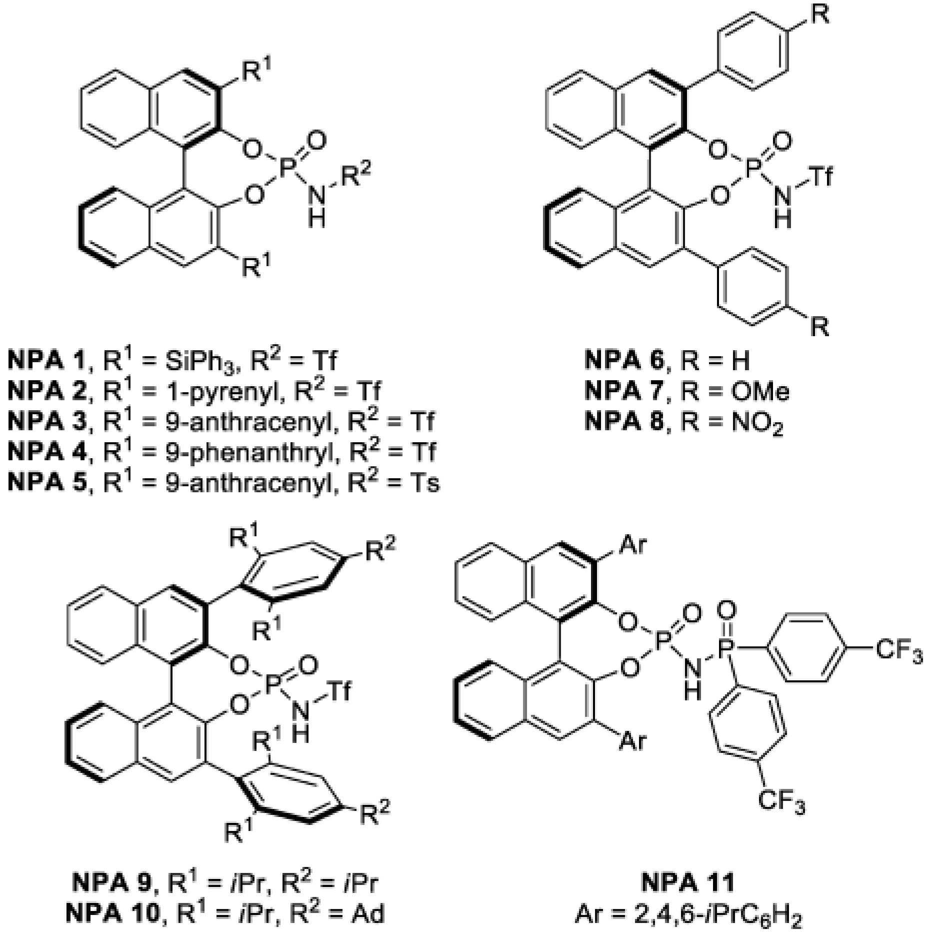
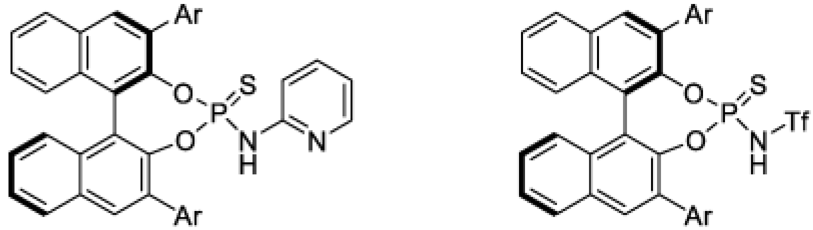


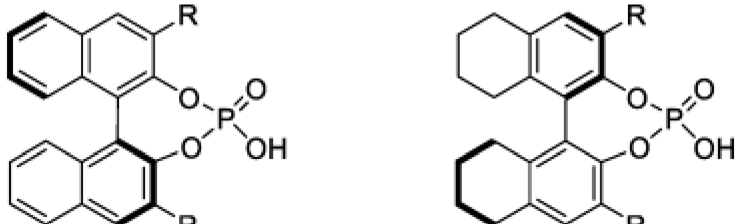
Figure 8. N-Phosphoramide catalysts



NTA 1
Ar = 3,5-$CF_3C_6H_3$

NTA 2
Ar = 2,4,6-(iPr)$_3C_6H_2$
NTA 3
Ar = 4-tBu-2,6-(iPr)$_2C_6H_2$

Figure 9. N-Thiophosphoramide catalysts



(*S*)-PA **[H_8]-PA**

Figure 10. Alternative variants of catalysts

2.1 Mono Activation

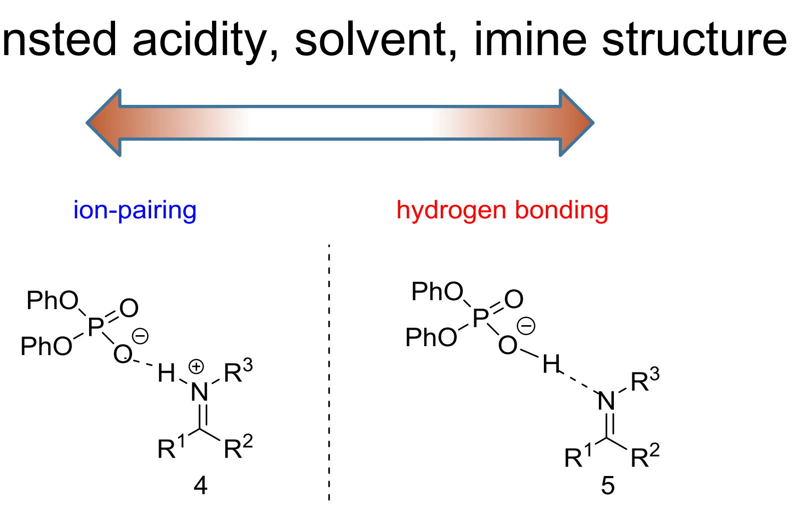


Figure11. Different modes of monoactivation.

Appel, R.; Chelli, S.; Tokuyasu, T.; Troshin, K.; Mayr, H. *J. Am.Chem. Soc.* **2013**, *135,* 6579

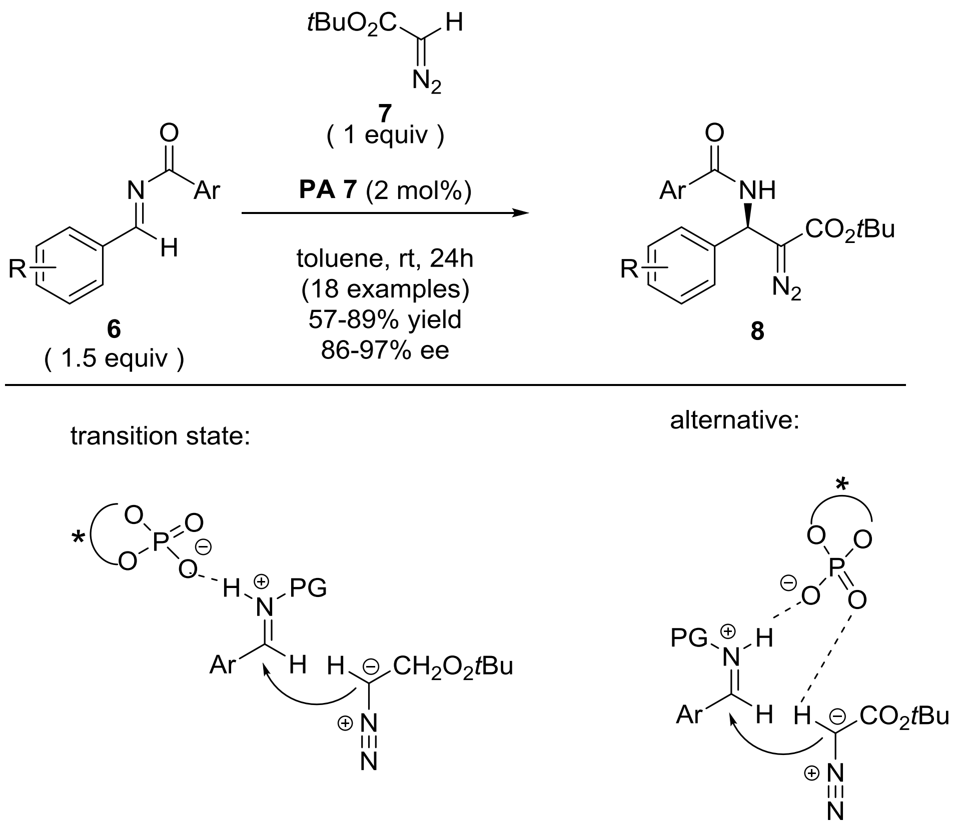


Figure 12. Alkylation of diazoesters with imines by Terada (2005)

(a) Uraguchi, D.; Sorimachi, K.; Terada, M. *J. Am. Chem. Soc.*.**2005**, *127*, 9360.
(b) (b) So, S. S.; Mattson, A. E. *Chem. -Asian. J.* **2014**, *3*,425.

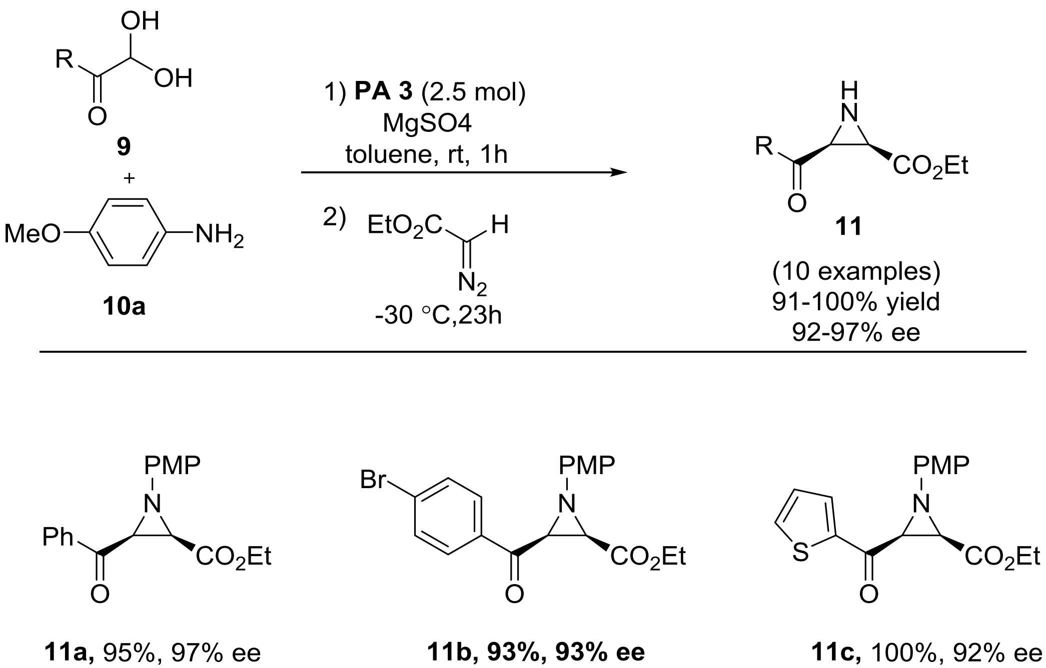
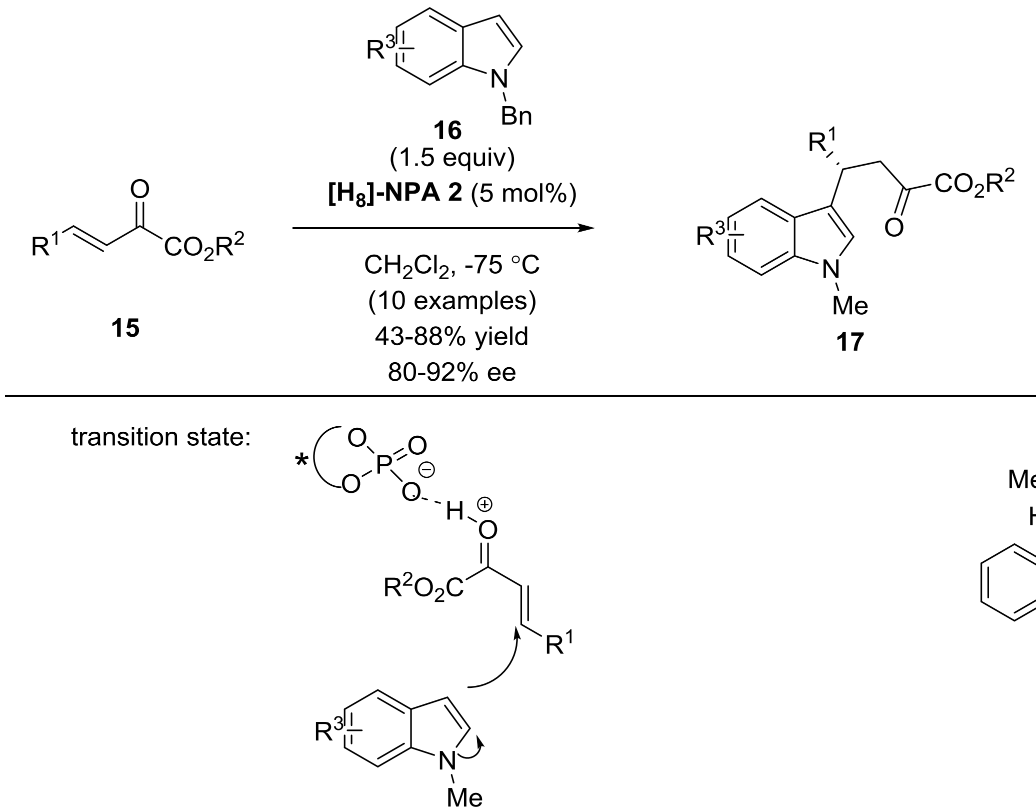


Figure 13. Aziridination of diazoesters using imines by Akiyama(2009).

Akiyama, T.; Suzuki, T.; Mori, K. *Org. Lett.* **2009**, *11,* 2445.



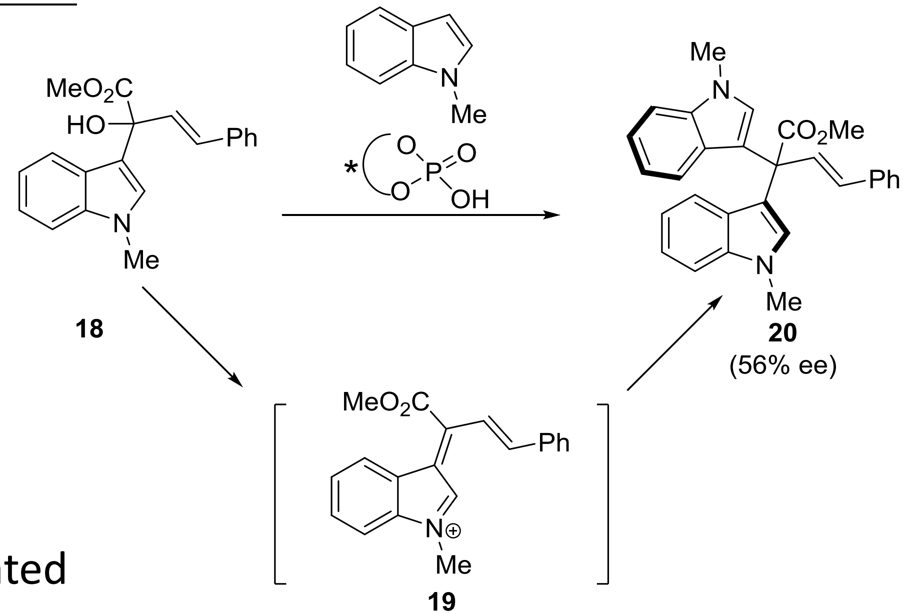


Figure 15. Friedel-Crafts reaction with α,β-unsaturated ketones by Rueping (2008)

Rueping, M.; Nachtsheim, B. J.; Moreth, S. A.; Bolte, M. *Angew. Chem., Int. Ed*. **2008**, *47*, 593

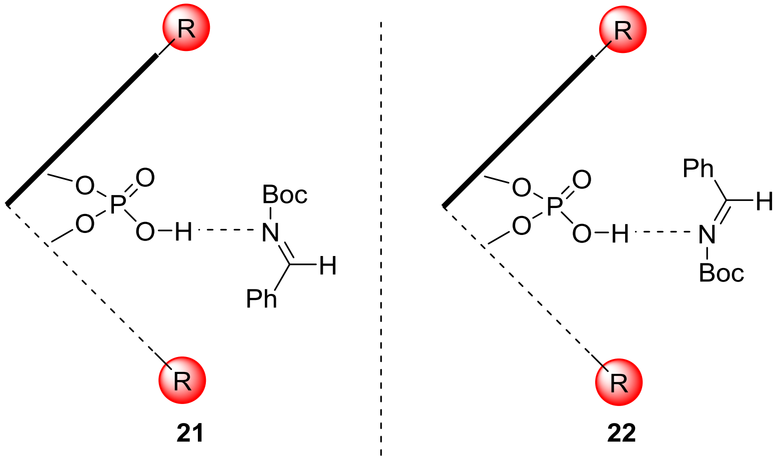


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Figure 16. Possible imine orientations for hydrogen-bonding activation (Terada).

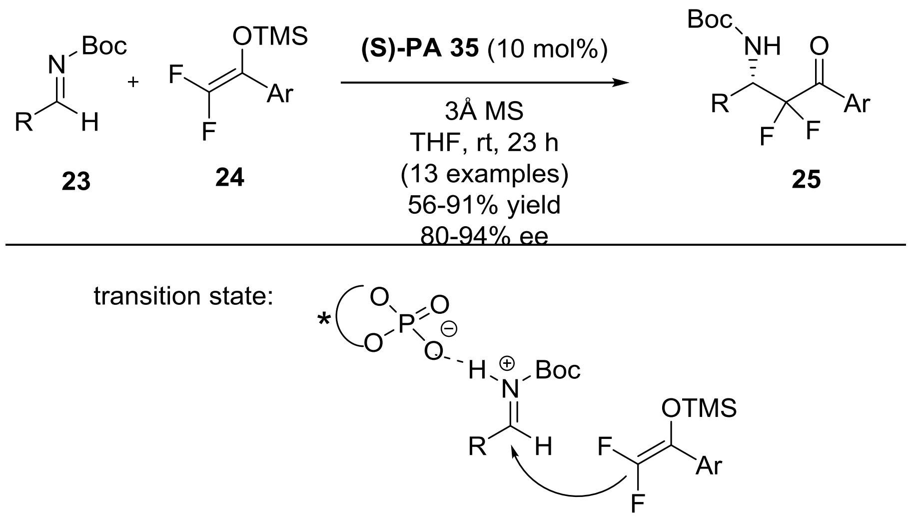


Figure 17. Synthesis of β-amino-α,α-difluoro carbonyl compounds by Akiyama (2011).

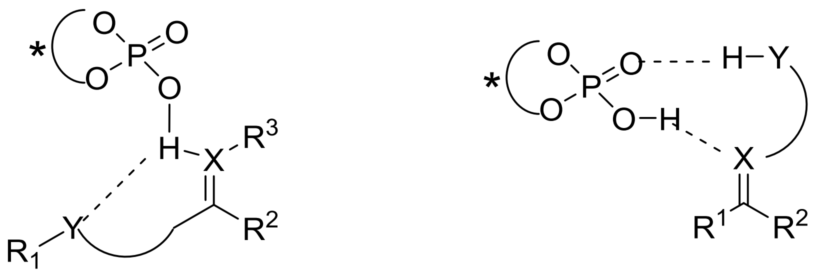
Kashikura, W.; Mori, K.; Akiyama, T. *Org. Lett*. **2011**, *13*, 1860

2.2 Dual Activation

Main activations modes featured under dual-activation

-two contacts to the acidic proton

-two contacts to the catalyst



26 **27**

Figure 18. Examples of different modes covered by dual activation.

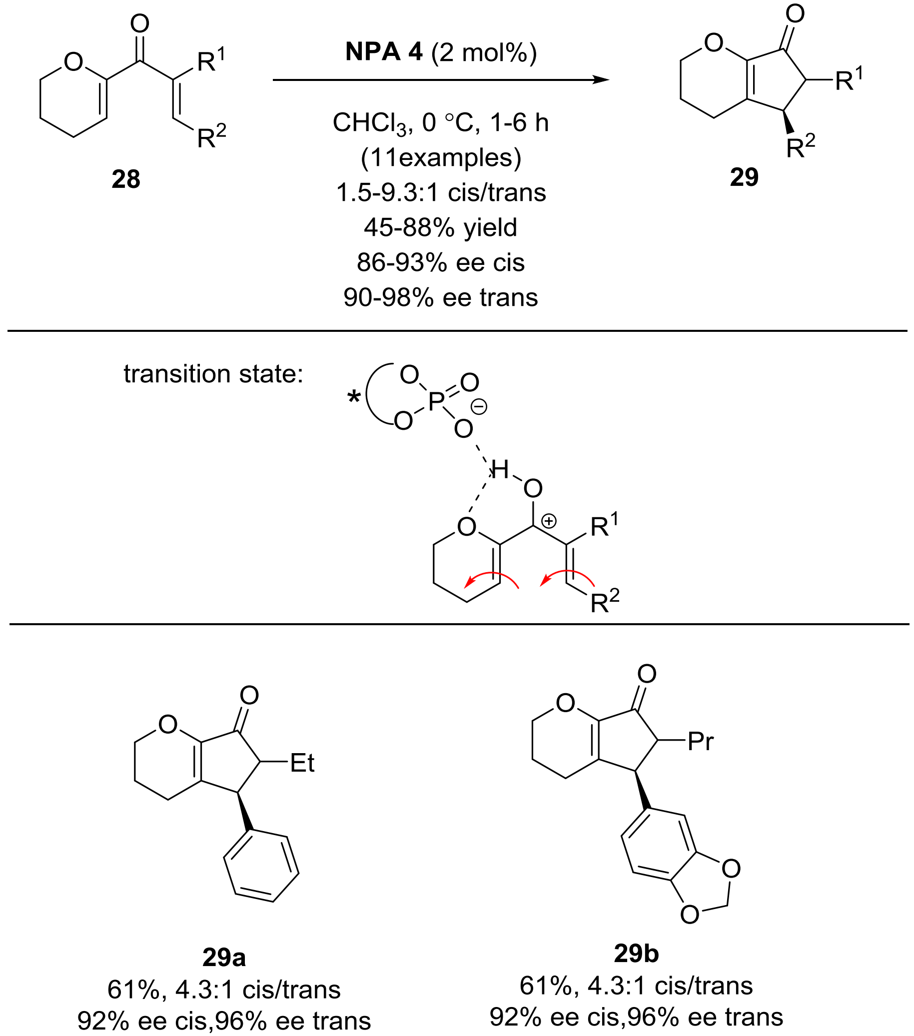


Figure 19. Nazarov cyclization by Rueping (2007).

Rueping, M.; Ieawsuwan, W.; Antonchick, A. P.; Nachtsheim,B. J. *Angew. Chem*., Int. Ed. **2007**, *46,* 2097.

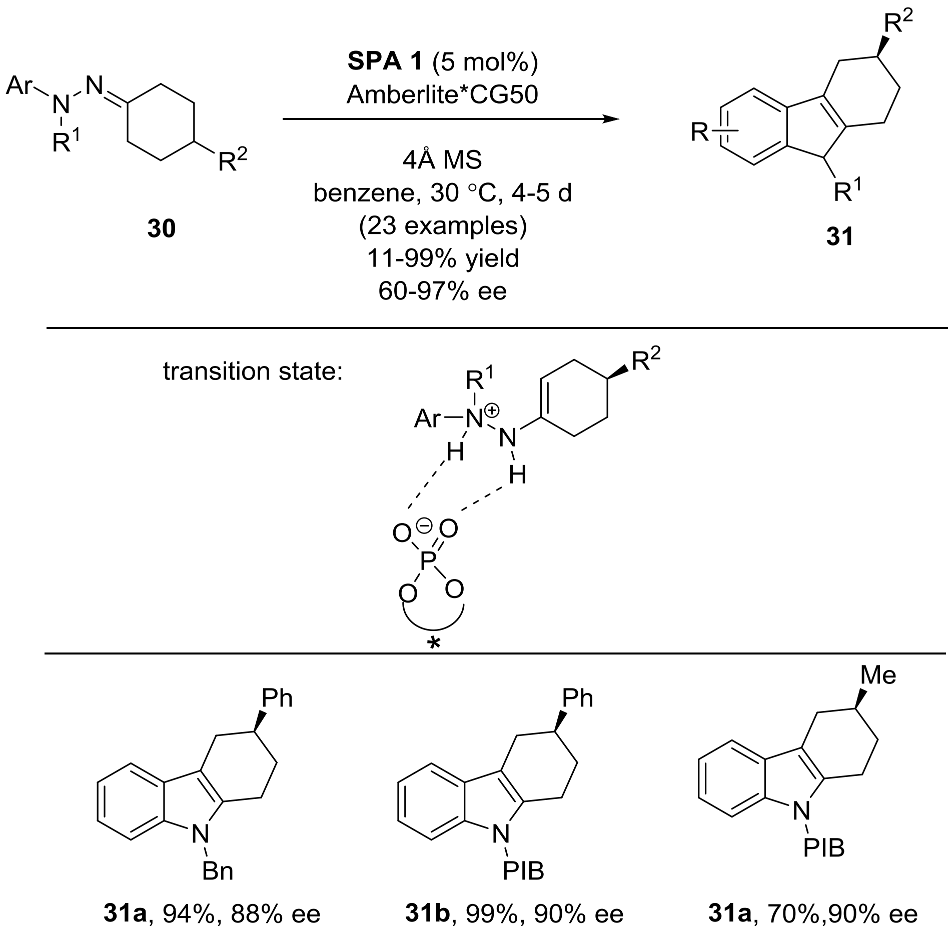


Figure 20. Fischer indole reaction by List (2011).

2.3 Bifunctional Activation

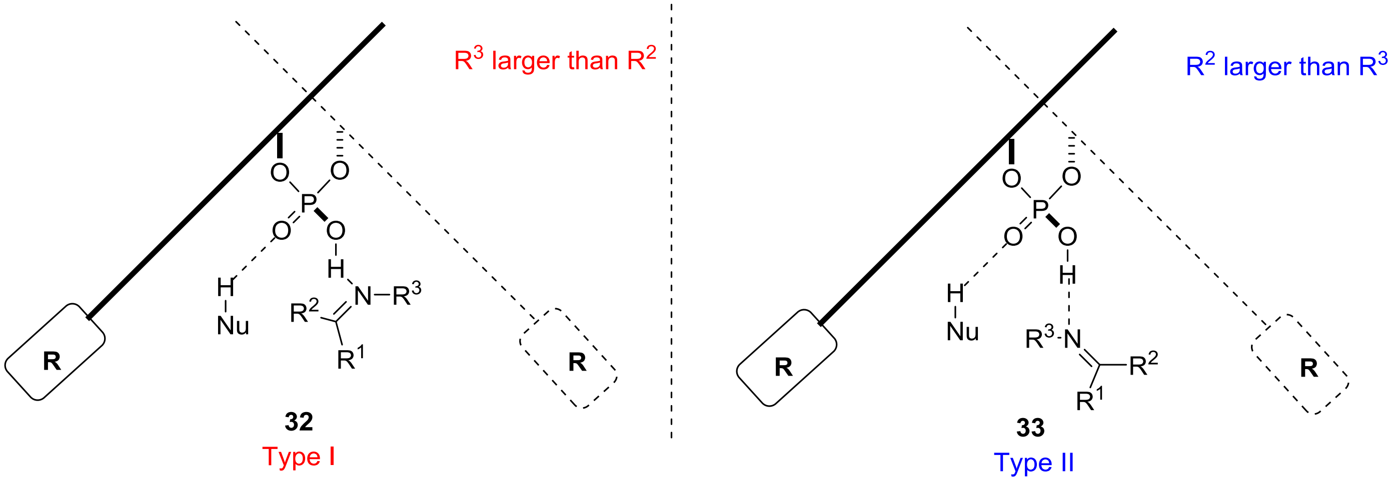


Figure 21. Models for bifunctional activation (Goodman).

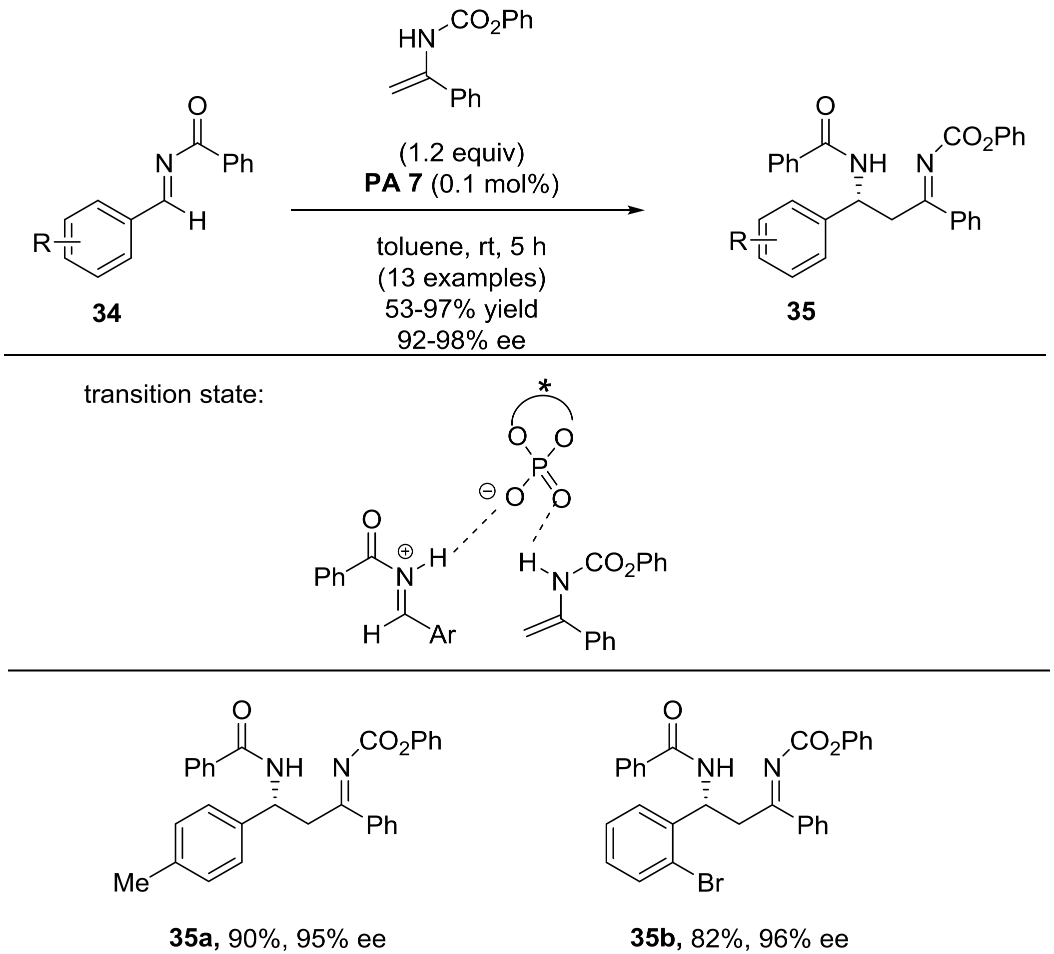


Figure 22. Aza-ene reaction by Terada (2006).

Terada, M.; Machioka, K.; Sorimachi, K. *Angew. Chem., Int. Ed.* ***2006***, *45*, 2254

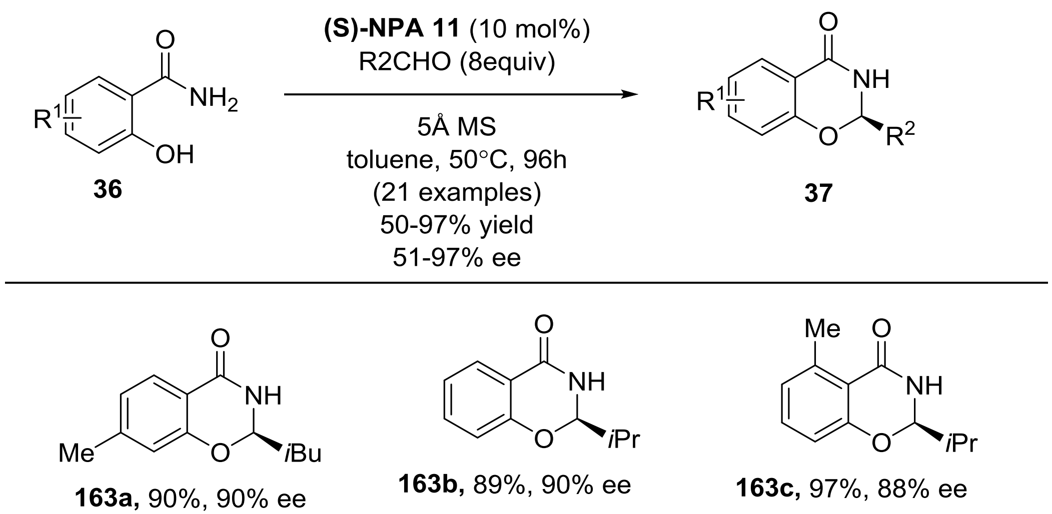


Figure 23. Addition of phenols to in situ formed imines by List (2010).

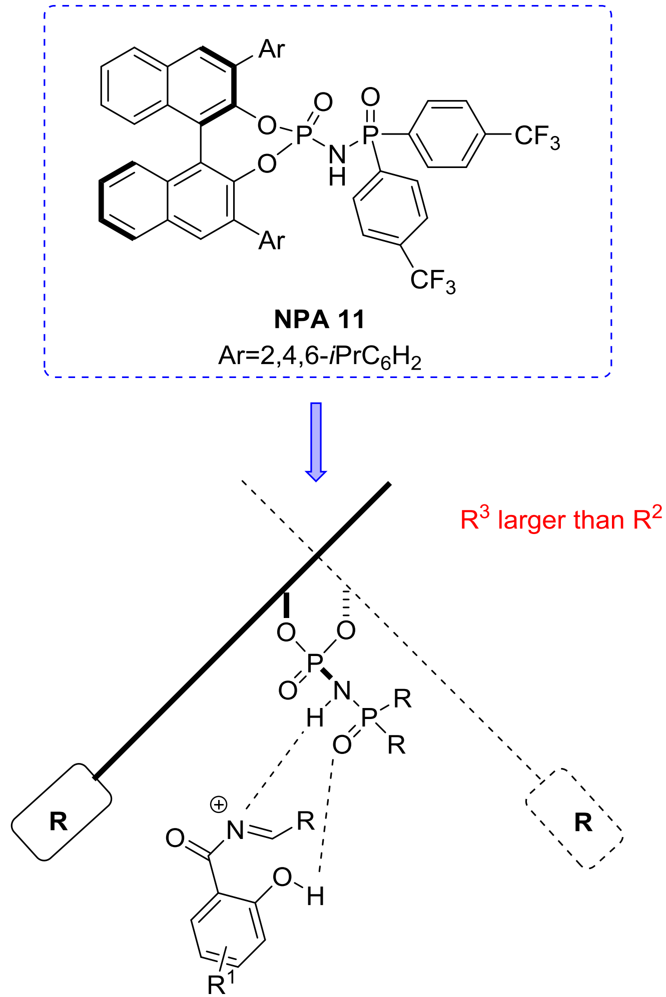


Figure 24. Proposed interaction of N-phosphinyl catalyst (List).

Vellalath, S.; Coric, I.; List, B. *Angew. Chem., Int. Ed*. **2010**, *49,*9749

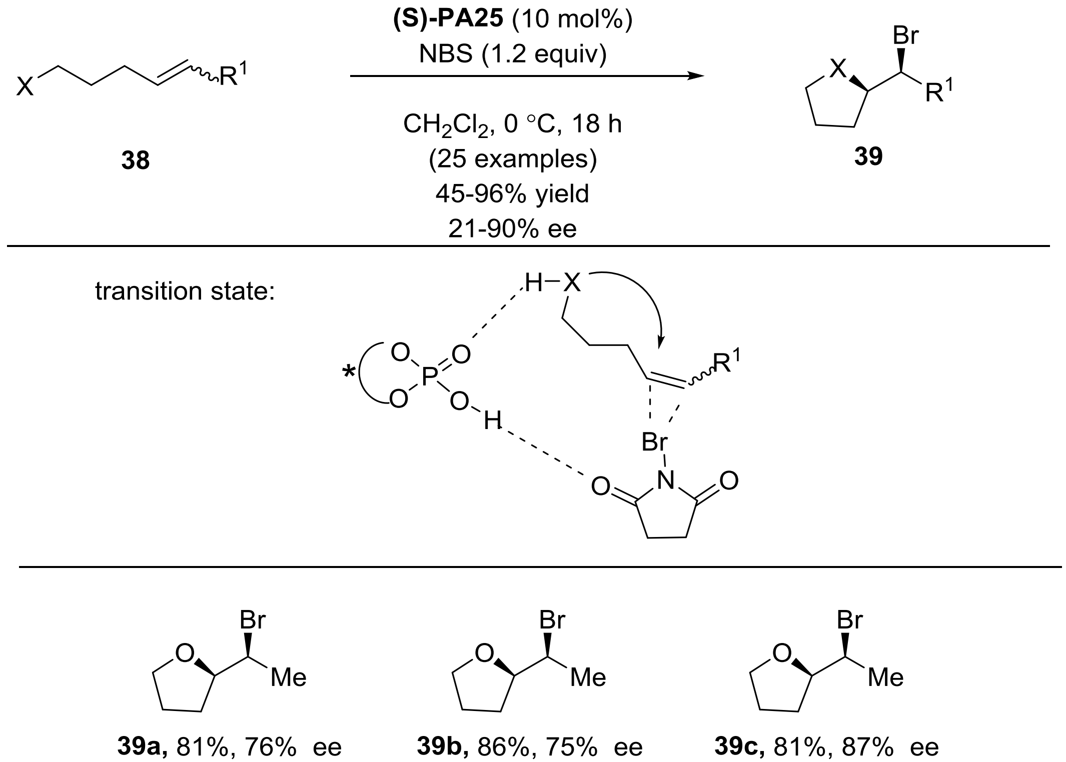


Figure 25. Bromocyclization using alkenes by Shi (2011).

Huang, D.; Wang, H.; Xue, F.; Guan, H.; Li, L.; Peng, X.; Shi,Y. *Org. Lett*. **2011**, *13*, 6350

2.4 Counterion Catalysis

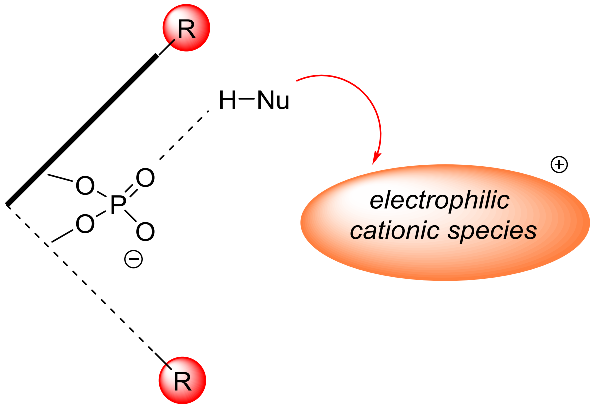
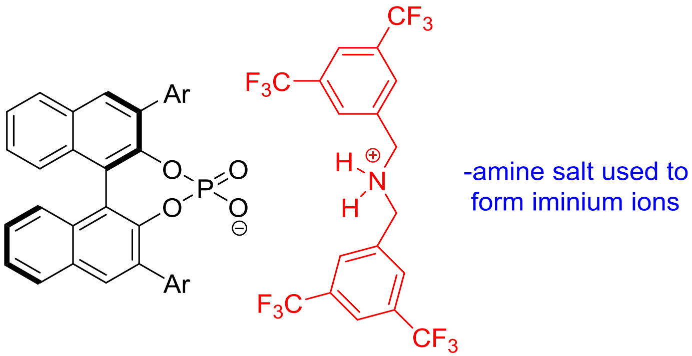


Figure 26. A generic schematic for chiral phosphate catalysis.



PA 41

Ar=2,4,6-C_6H_2(*i*Pr)$_3$

Figure 27. Phosphoric acid salt used by List.

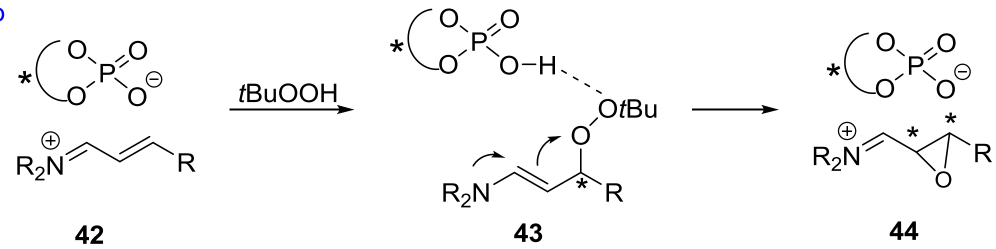


Figure29. Mechanism for epoxidation (List)

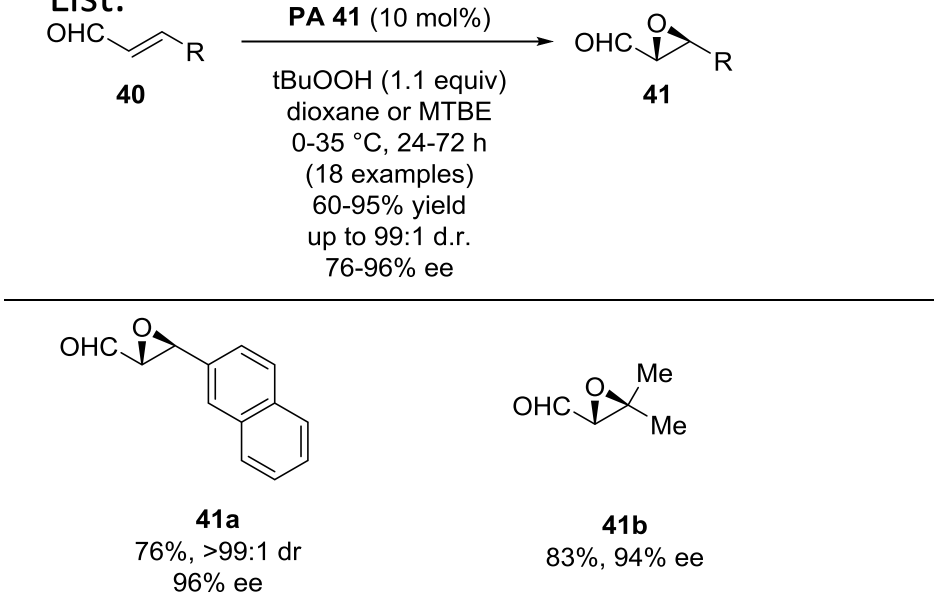


Figure 28. ACDC epoxidation by List (2008).

Wang, X.; Reisinger, C. M.; List, B. J. Am. Chem. Soc. **2008**, *130*

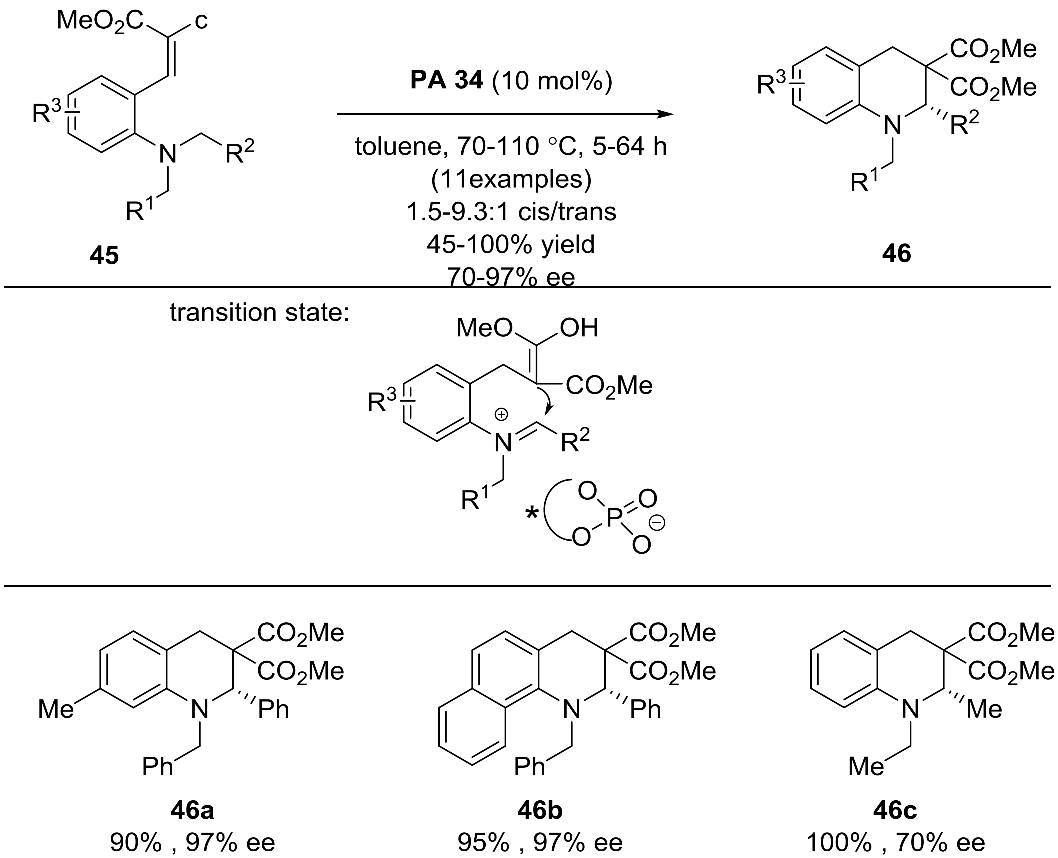


Figure 30. Activation of enantiotopic C(sp^3)-hydrogen atoms by Akiyama (2011).

Mori, K.; Ehara, K.; Kurihara, K.; Akiyama, T. *J. Am. Chem. Soc.* ***2011***, *133*, 6166.

3. Reaction in the Presence of Metals

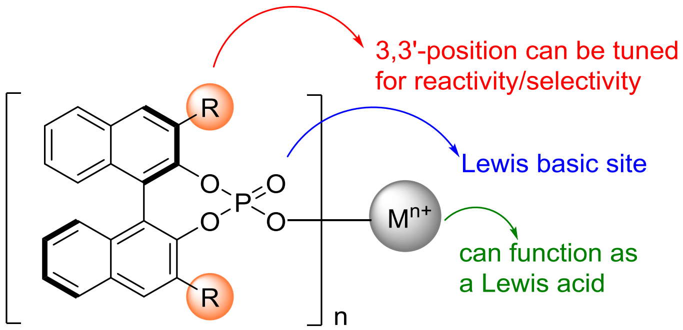


Figure 31. Potential of chiral phosphoric acid-metal complexes.

3.1 Lewis Acid Behavior

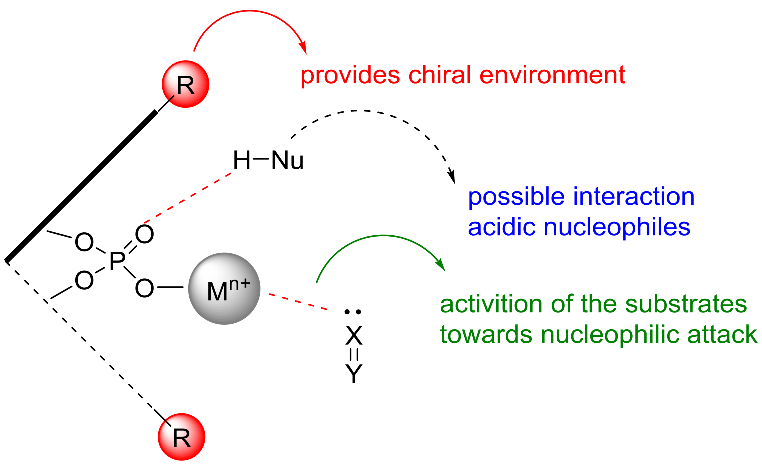


Figure 32. A generic model for Lewis acid activations using metal phosphates.

Yu, Z.; Jin, W.; Jiang, Q. *Angew. Chem., Int.Ed*. **2012**, *51*, 6060.

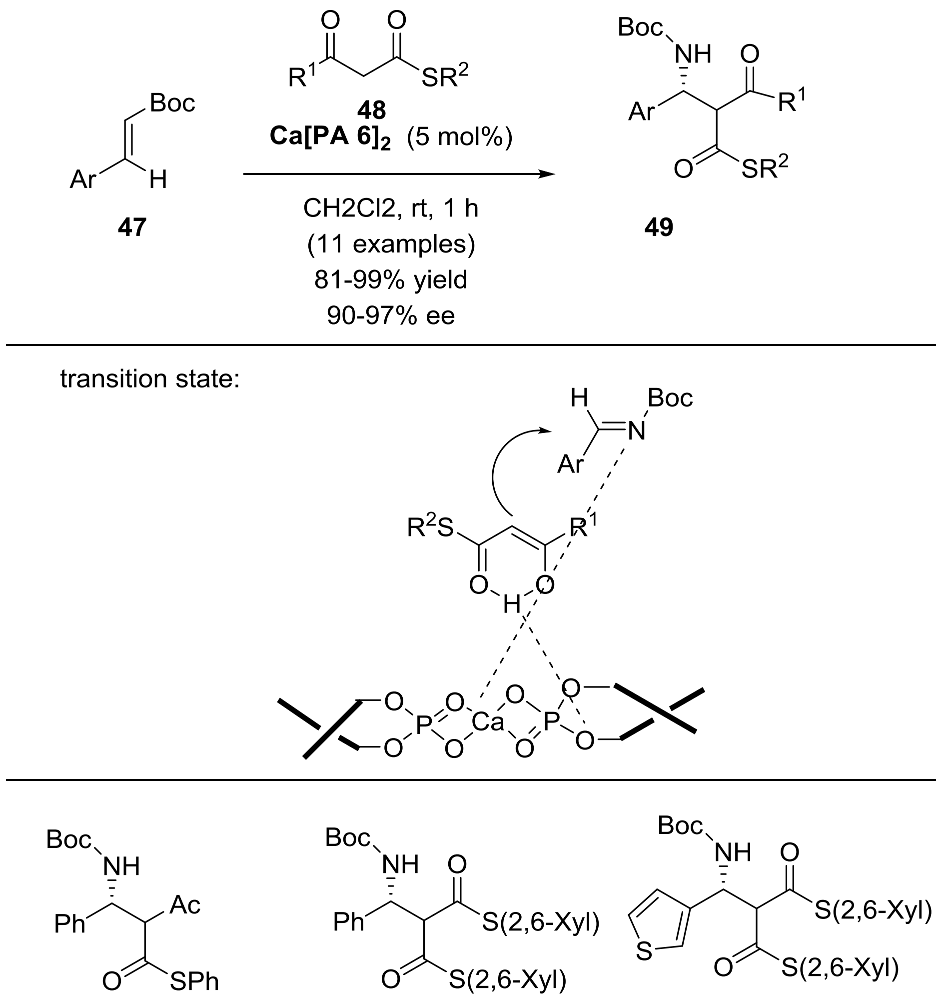
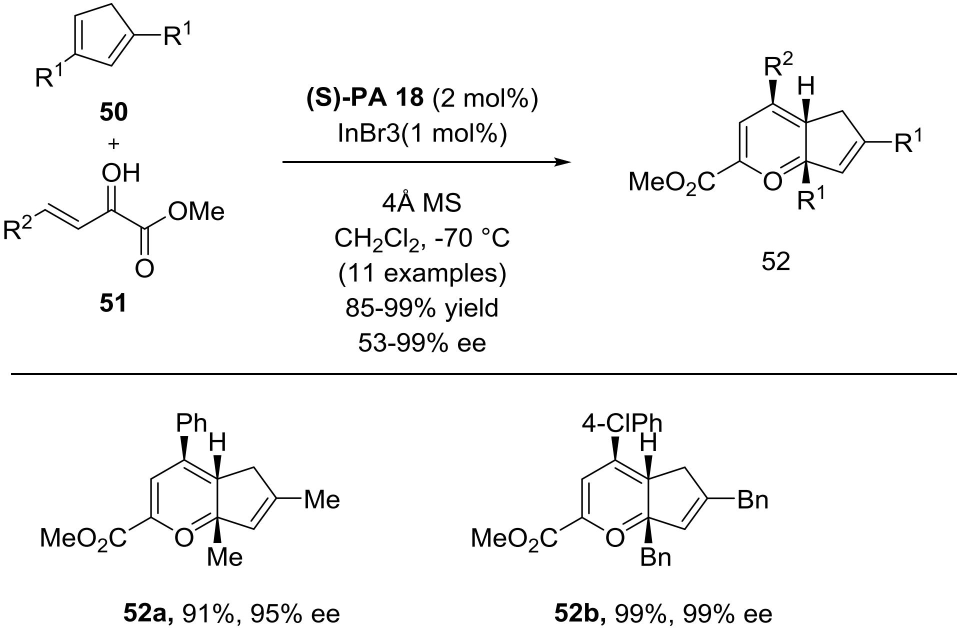


Figure 33. Mannich reaction using a calcium salt by Ishihara (2010).



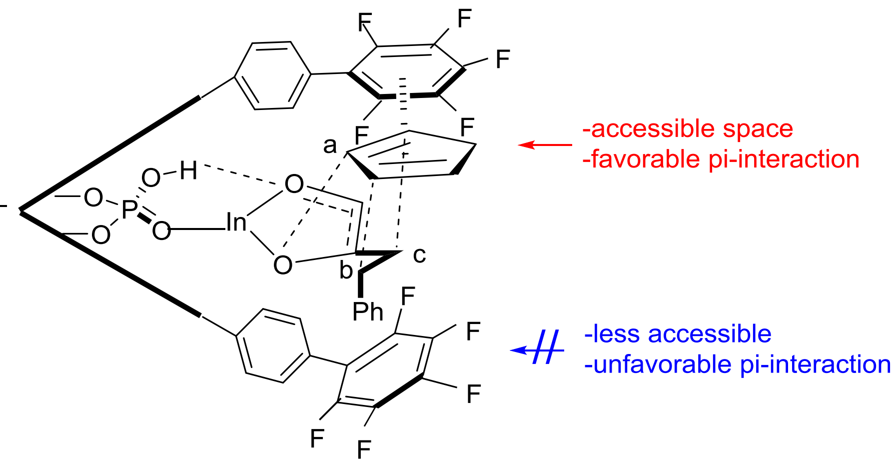


Figure34. Hetero-Diels-Alder reaction by indium salts by Luo(2012).

Figure 35. Proposed transition state.

Yu, Z.; Jin, W.; Jiang, Q. *Angew. Chem., Int.Ed*. **2012**, *51*, 6060.

3.2 Non-Lewis Acid Behavior

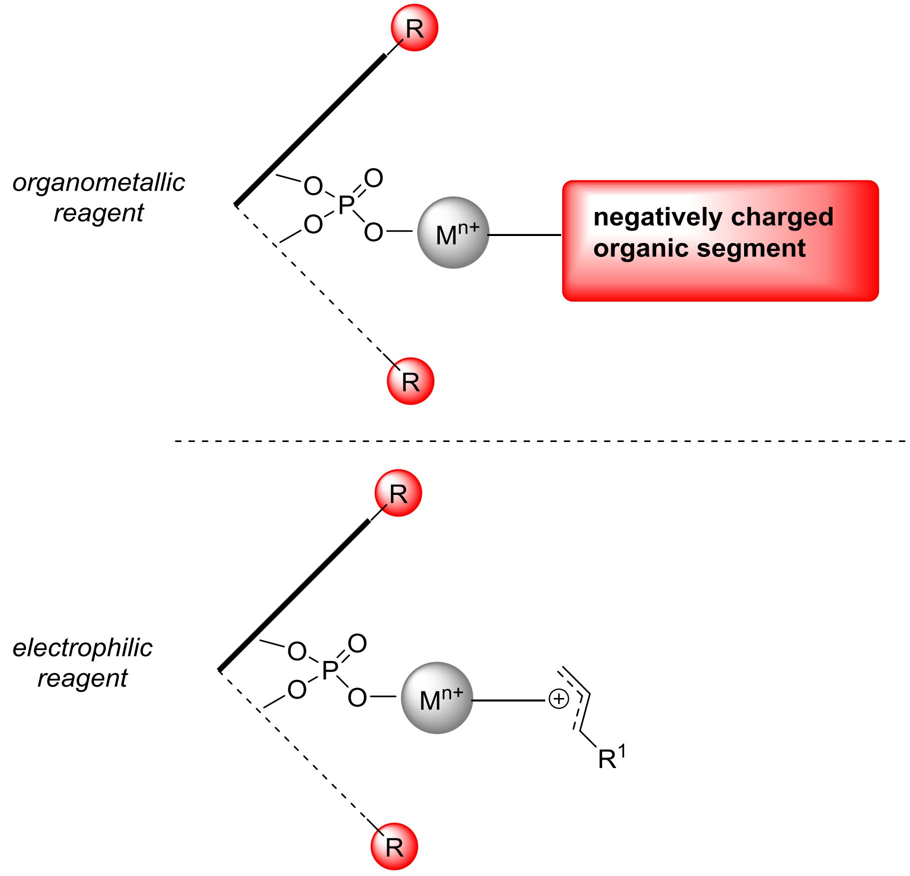
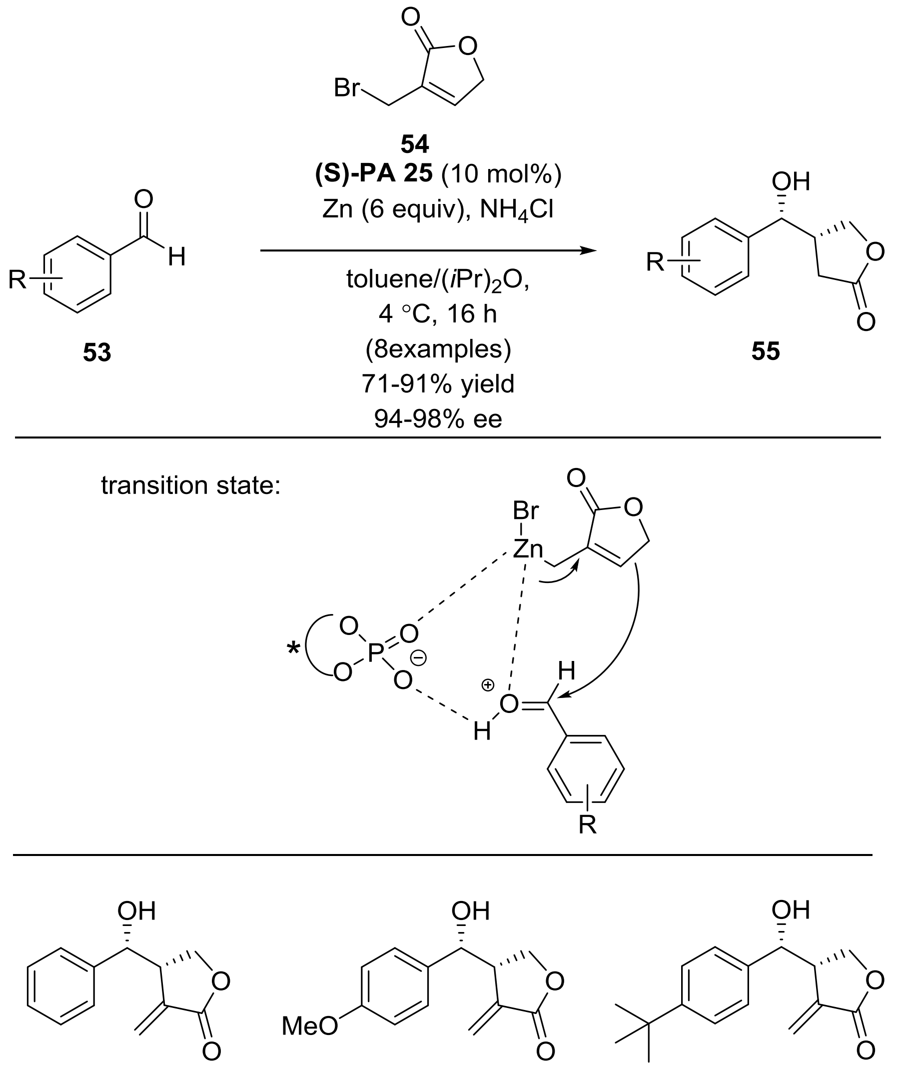


Figure 36. Examples of reactive non-Lewis acid intermediates



55a, 98%, 94% ee **55b,** 79%, 96% ee **55c,** 91%, >99% ee

Figure 37. Carbocyclization of 1,6-enynes using an iridium phosphate by Gandon (2011).

Fuchs, M.; Schober, M.; Orthaber, A.; Faber, K. Adv. Synth.Catal. **2013**, *355*, 2499.

4. Conclusion and Outlook

Conclusion:

Outlook:

1. Detailed experimental and computational studies are still required for further progress in the field.
2. Find way to lower catalyst loading.

5. Acknowledgement

- **Prof.Huang**
- **Dr. Chen**
- **All members in E201**

Thank you for your attention!