

From Directing Group to Bifunctional Catalyst / Ligand: Achieving Selectivity in Organic Reactions

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Dr. Prof. Dong's Group
University of Texas at Austin
April, 11, 2012



Outline

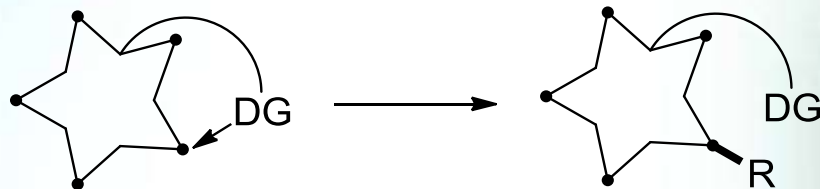
A bamboo pipe is shown pouring water into a glass. The pipe is green and has a hole cut into it. Water is flowing out of the hole. The glass is clear and has a wooden handle. The background is a soft, out-of-focus green and blue.

1. Introduction
2. Directing group
 - Substrate readily with directing group
 - Removable directing group
3. Bifunctional catalyst / ligand
 - Covalent bonding
 - Hydrogen bonding
4. Conclusion
5. Acknowledgement

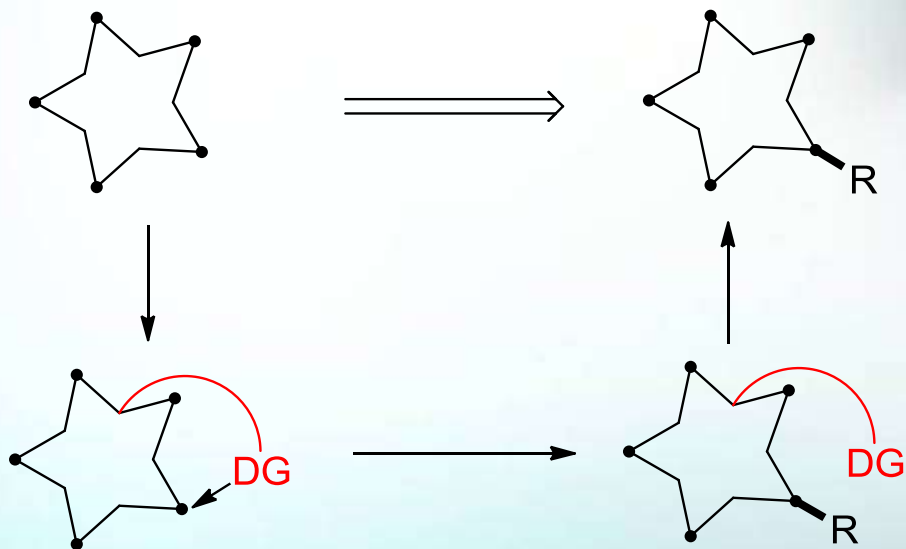
1. Introduction

❖ Directing group

Directing group readily on substrate

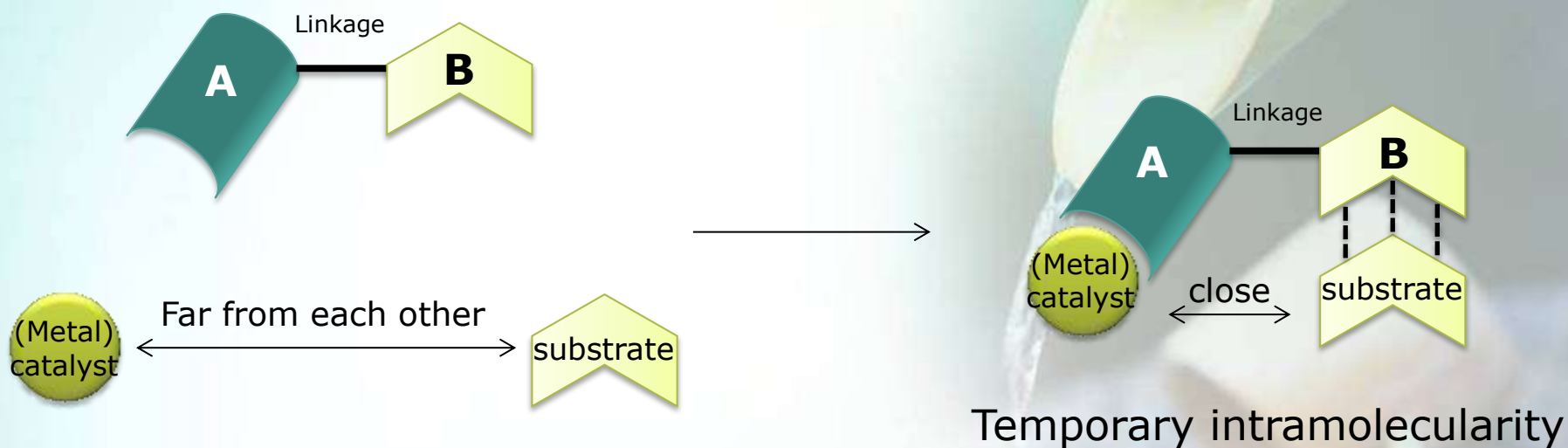


Removable directing group



1. Introduction

❖ Bifunctional catalyst / ligand

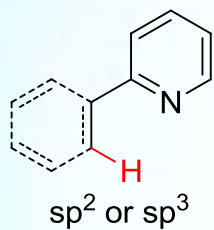


Make active species closer to substrate or one site of substrate.

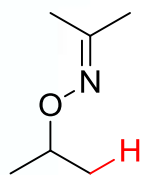
2. Directing group

- Hetero atoms: N, O, S, Si.....

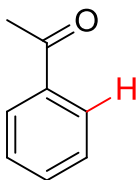
Representativity:



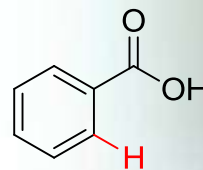
Sanford, "Pd"



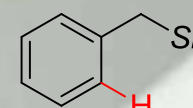
Dong, "Pd"



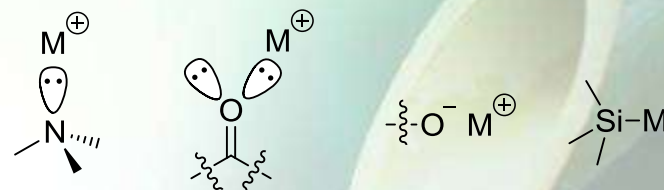
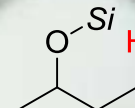
Murai, "Ru"



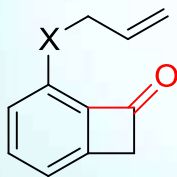
Yu, "Pd"



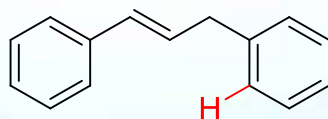
Hartwig, "Ir"



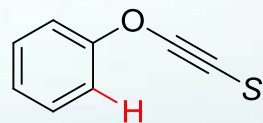
- Carbon: alkene, alkyne.....



Dong, "Rh"



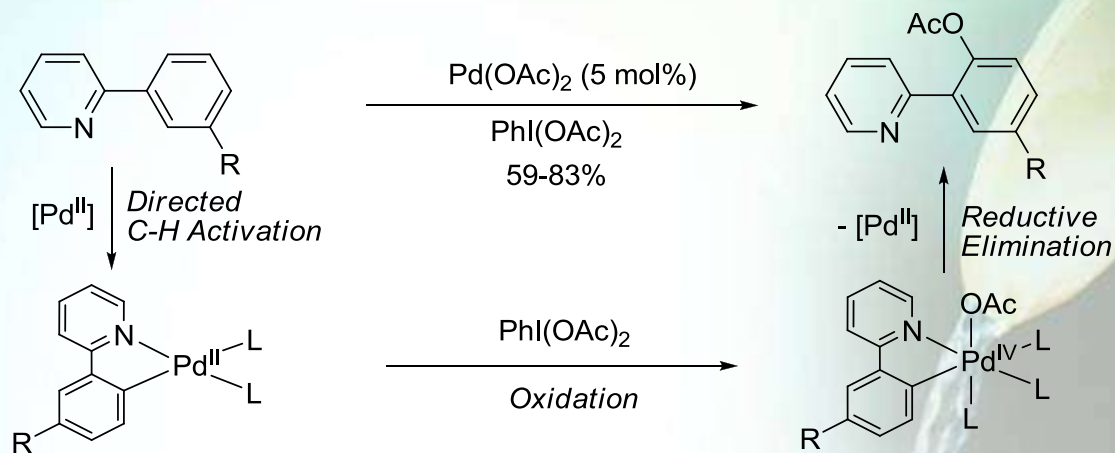
Cheng, "Pd"



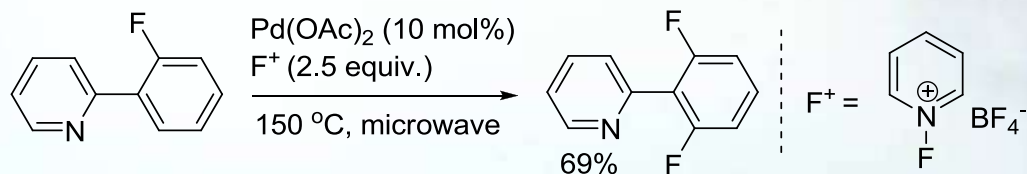
Hiyama, "Pd"

2. Directing group

2.1 Substrate readily with directing group



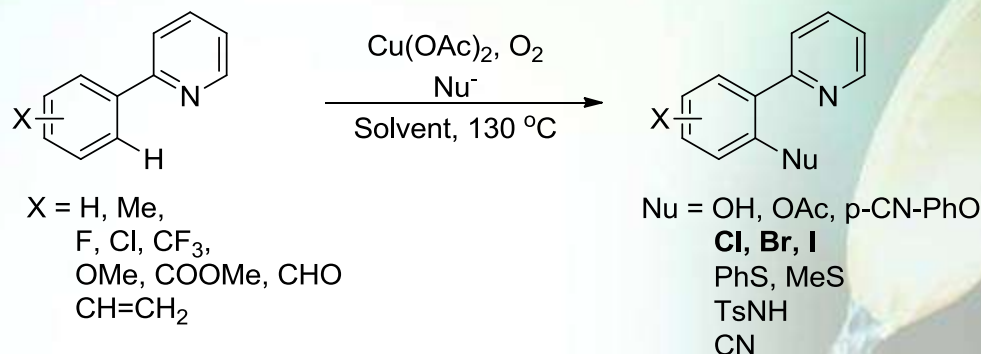
Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *126*, 2300.



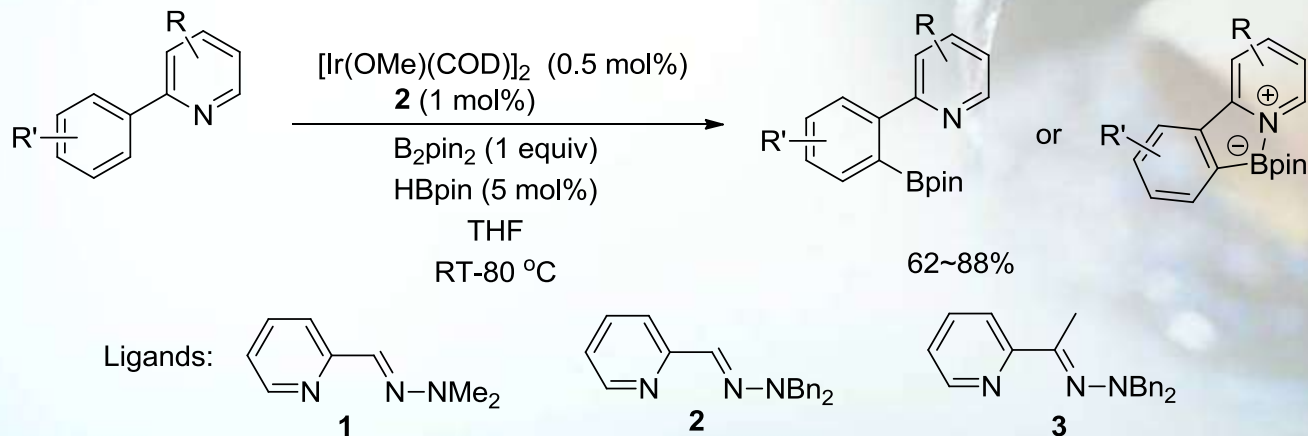
Hull, K. L.; Anani, W. Q.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 7134.

2. Directing group

2.1 Substrate readily with directing group



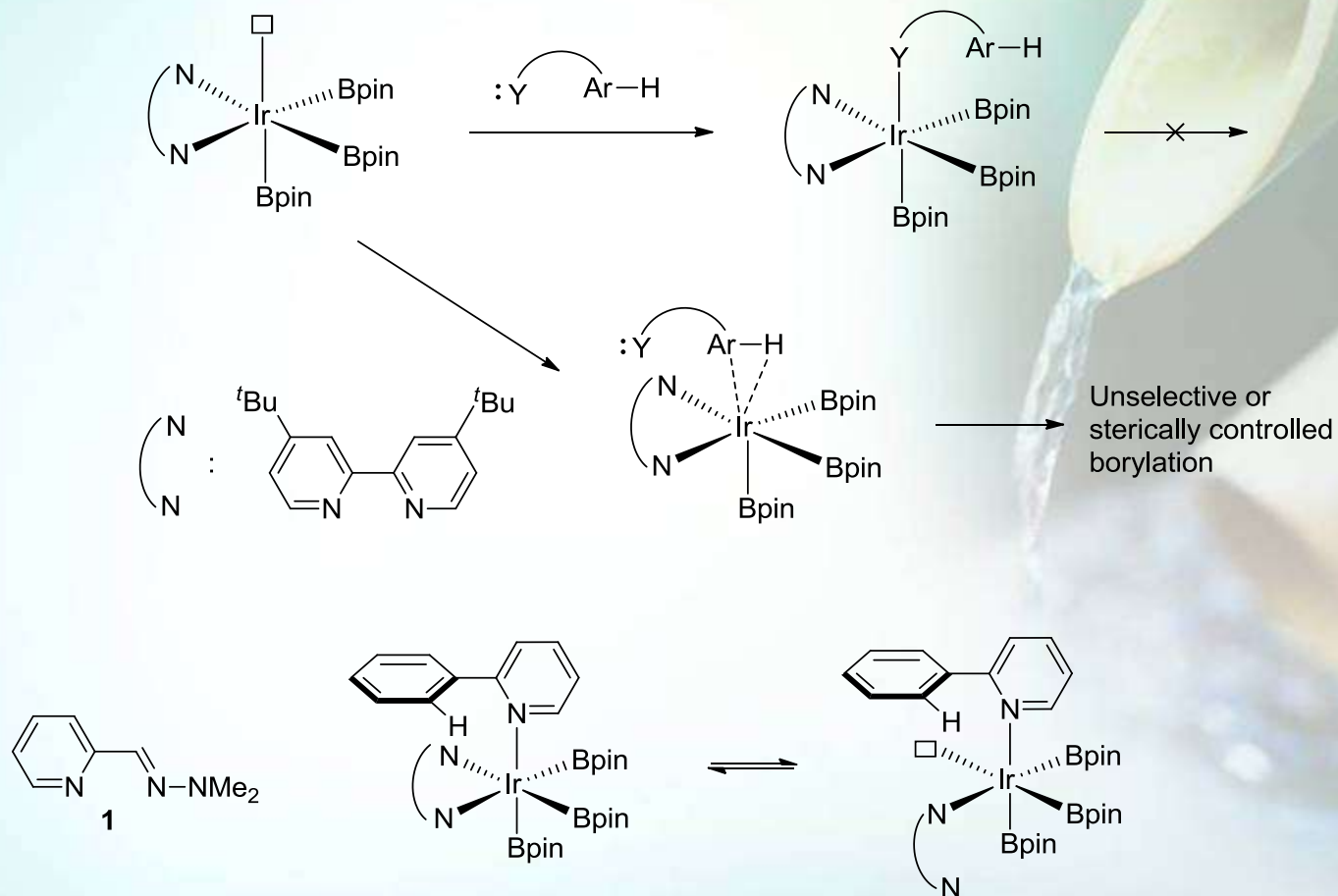
Chen, X.; Hao, X. S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *126*, 6790.



Ros, A.; Estepa, B.; López-Rodríguez, R.; Álvarez, E.; Fernández, R.; Lassaletta, J. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11724.

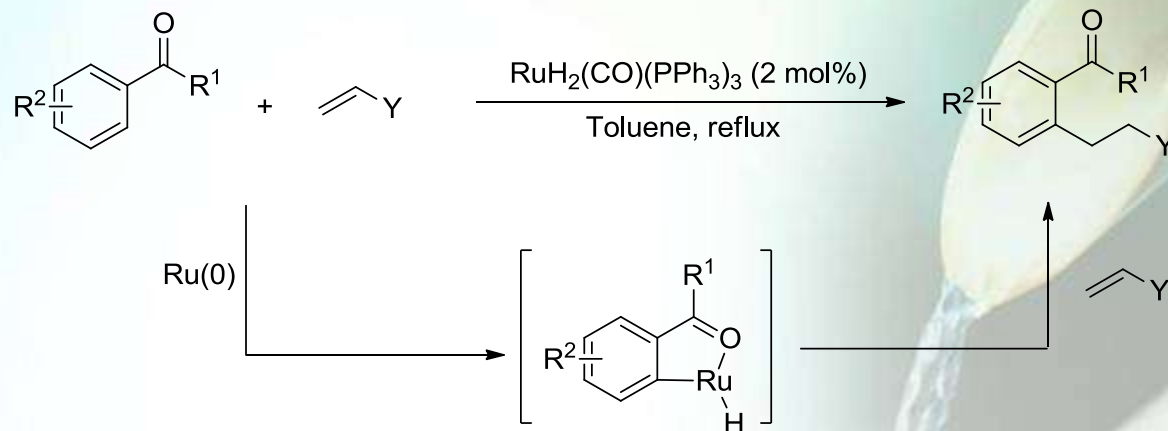
2. Directing group

2.1 Substrate readily with directing group



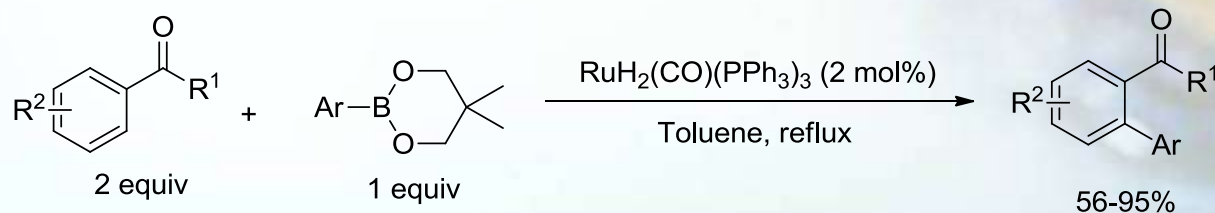
2. Directing group

2.1 Substrate readily with directing group



Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, 366, 529.

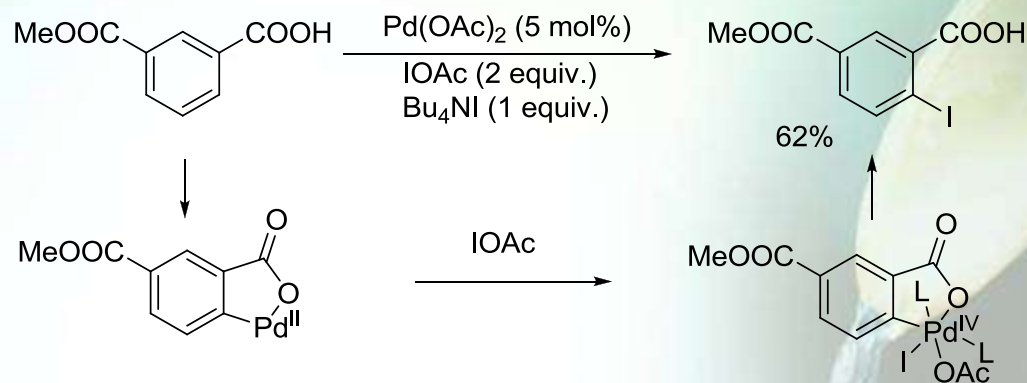
Citation 443 references



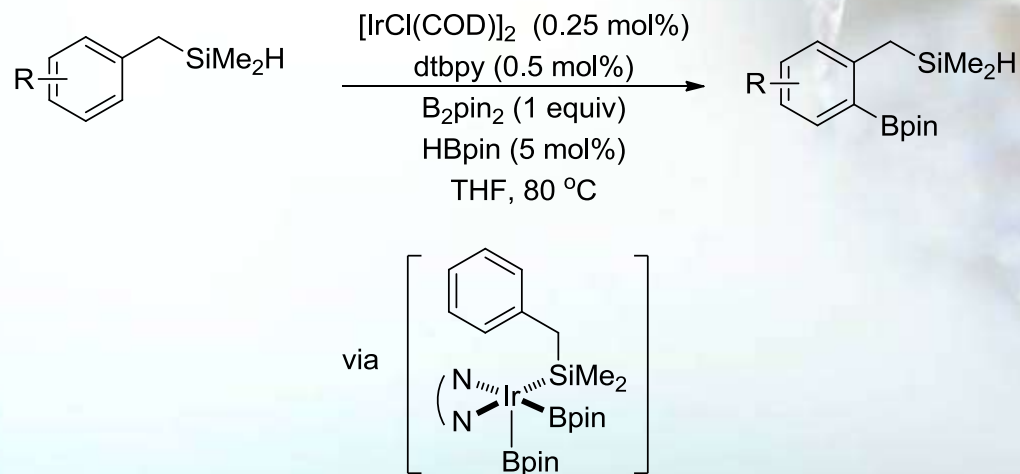
Kakiuchi, F.; Kan, S.; Igi, K.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **2003**, 125, 1698.

2. Directing group

2.1 Substrate readily with directing group



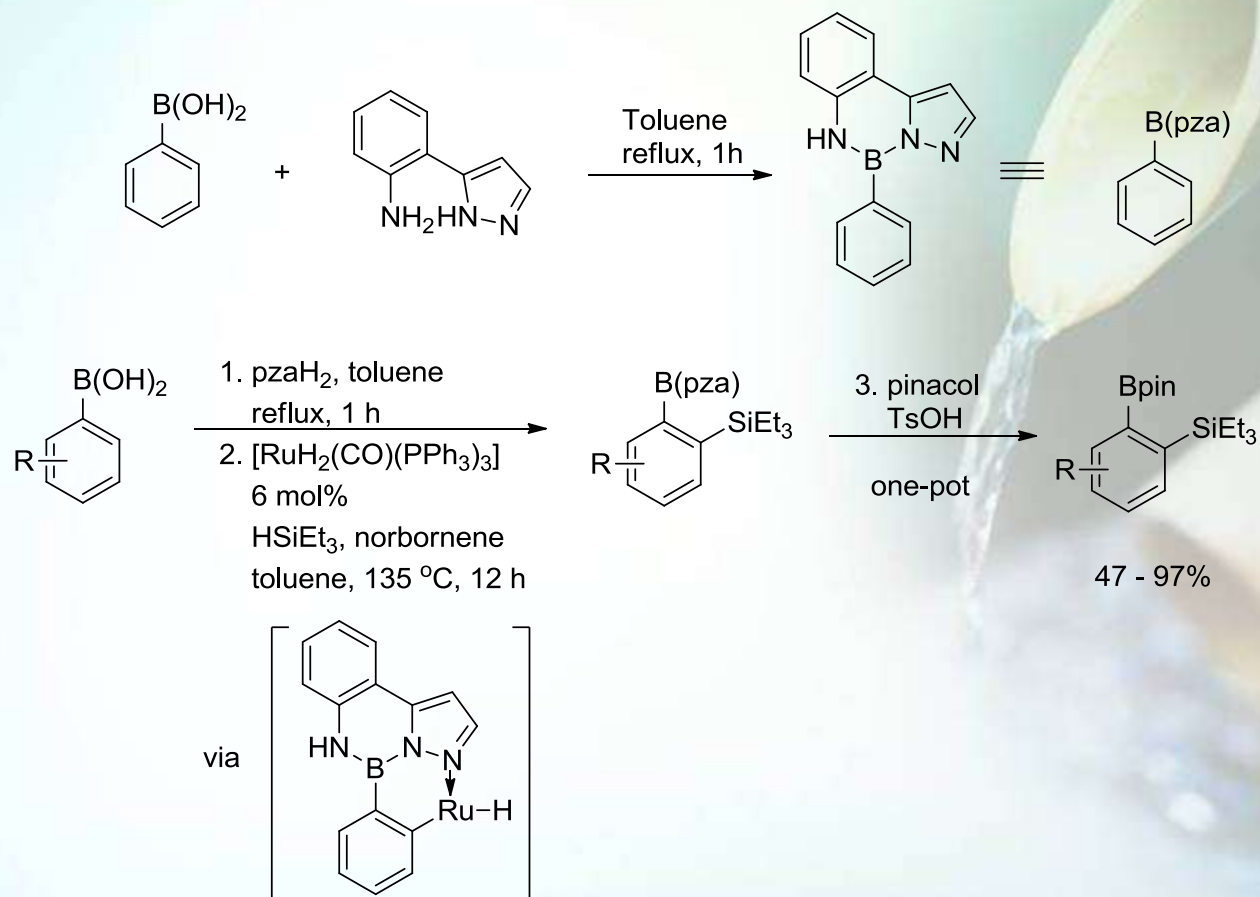
Mei, T. -S.; Giri, R.; Maugel, N.; Yu, J. -Q. *Angew. Chem. Int. Ed.* **2008**, *47*, 5215.



Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534.

2. Directing group

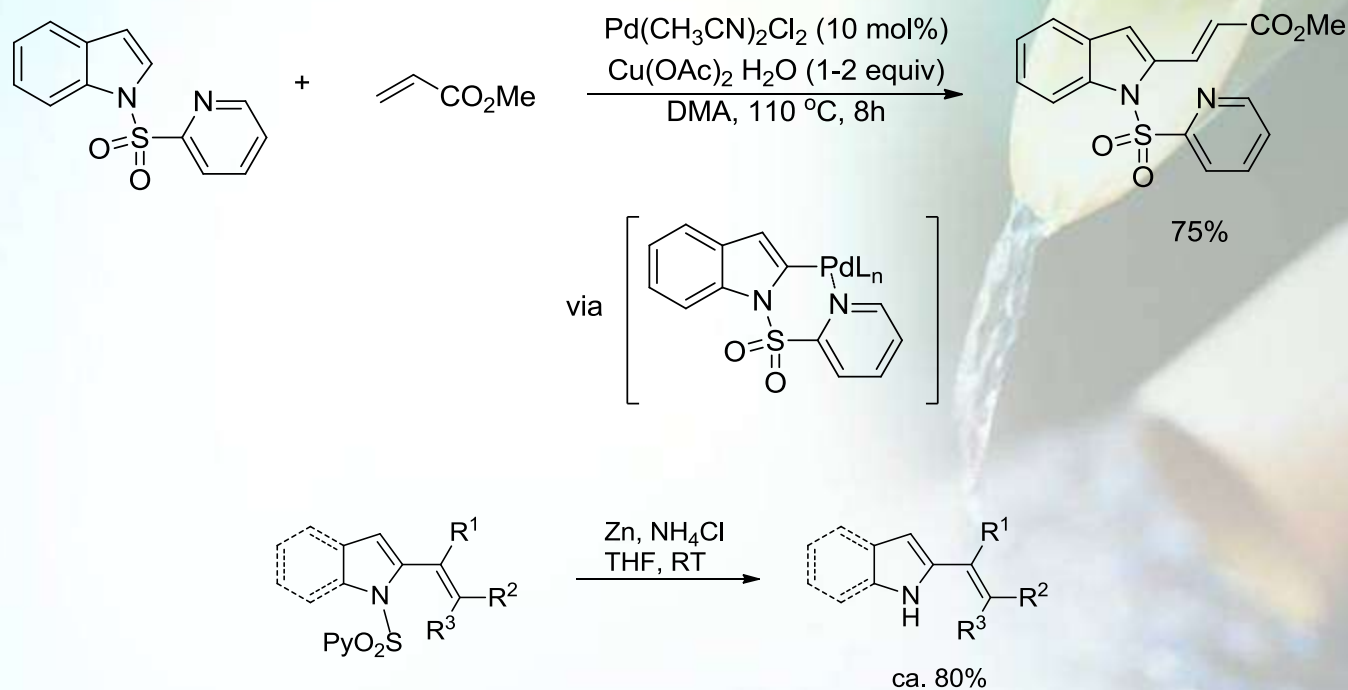
2.2 Removable directing group



Ihara, H.; Suginome, M. *J. Am. Chem. Soc.* **2009**, *131*, 7502.

2. Directing group

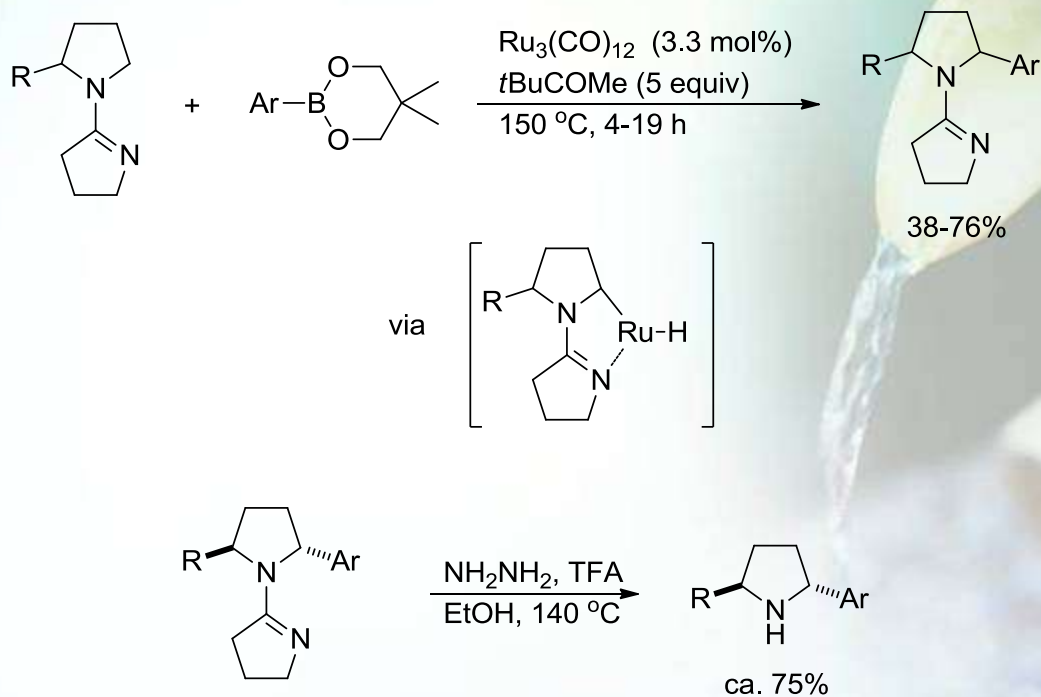
2.2 Removable directing group



García-Rubia, A.; Gómez Arrayás, R.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 6511.

2. Directing group

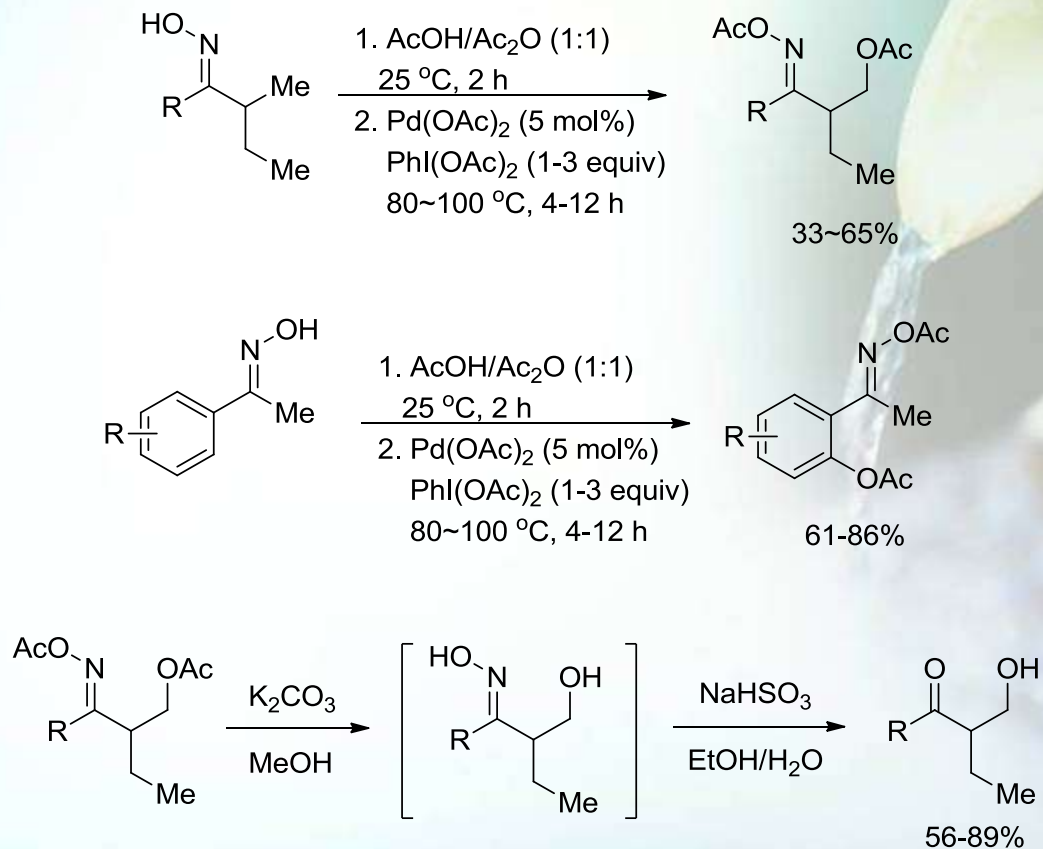
2.2 Removable directing group



Pastine, S. J.; Gribkov, D. V.; Sames, D. *J. Am. Chem. Soc.* **2006**, *128*, 14220.

2. Directing group

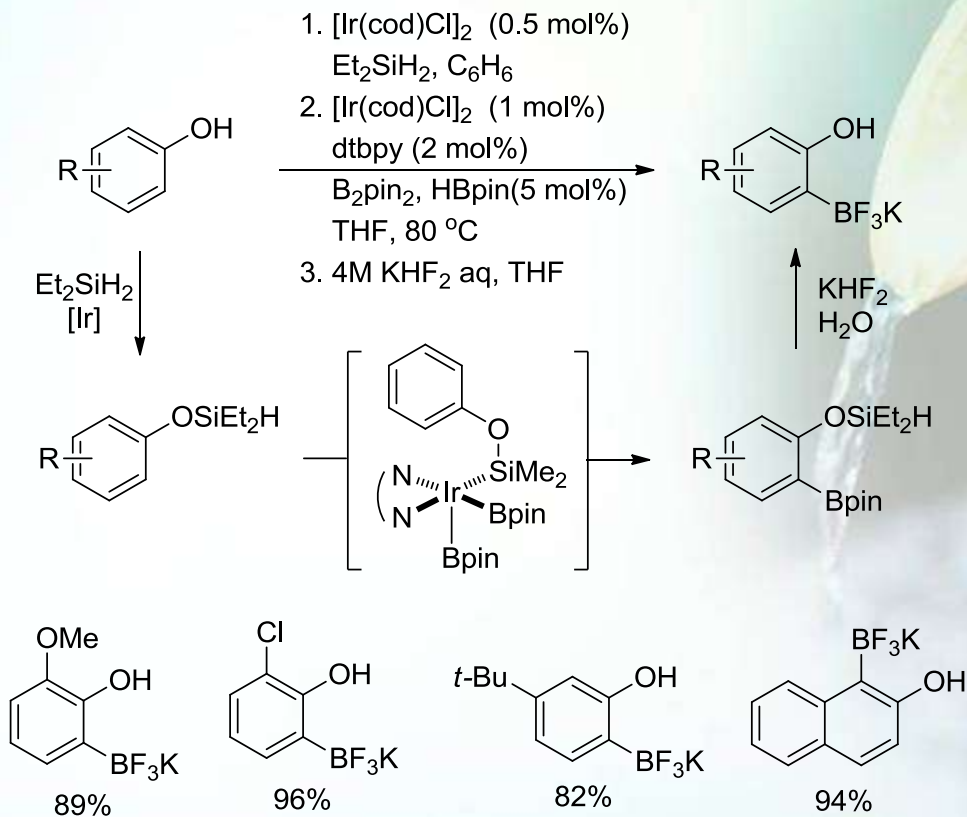
2.2 Removable directing group



Neufeldt, S. R.; Sanford, M. S. *Org. Lett.* **2010**, *12*, 532.

2. Directing group

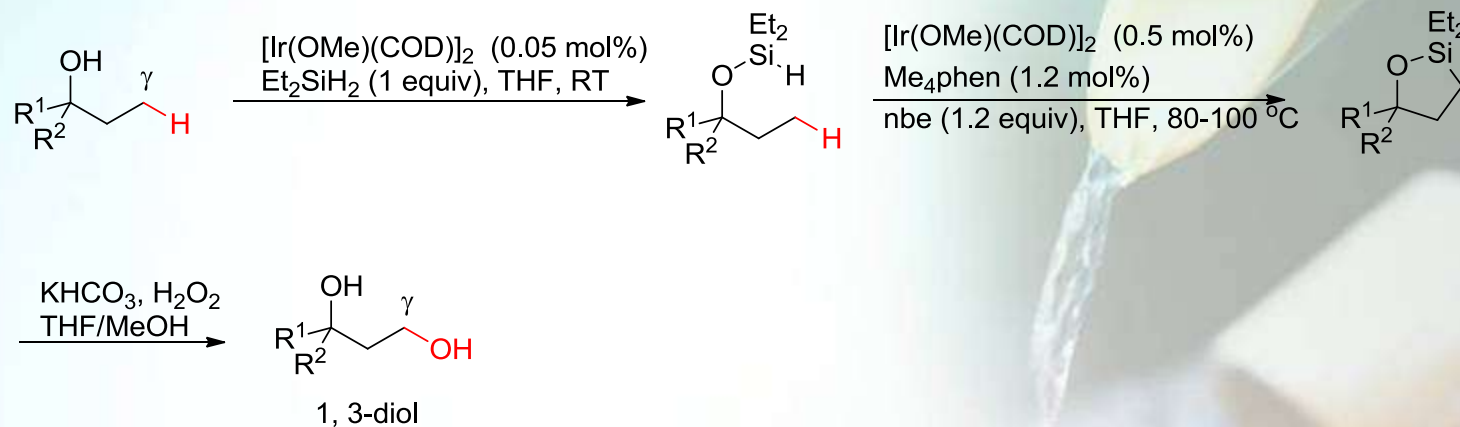
2.2 Removable directing group



Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534.

2. Directing group

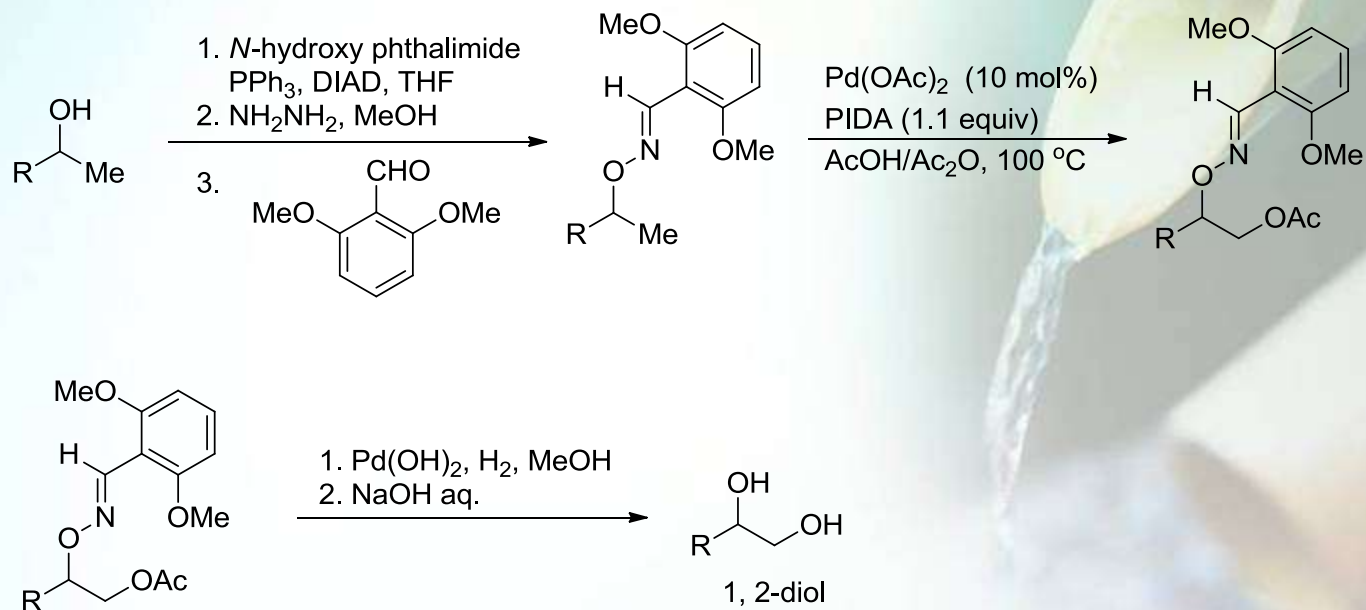
2.2 Removable directing group



Simmons, E.M.; Hartwig, J.F. *Nature* **2012**,483, 70.

2. Directing group

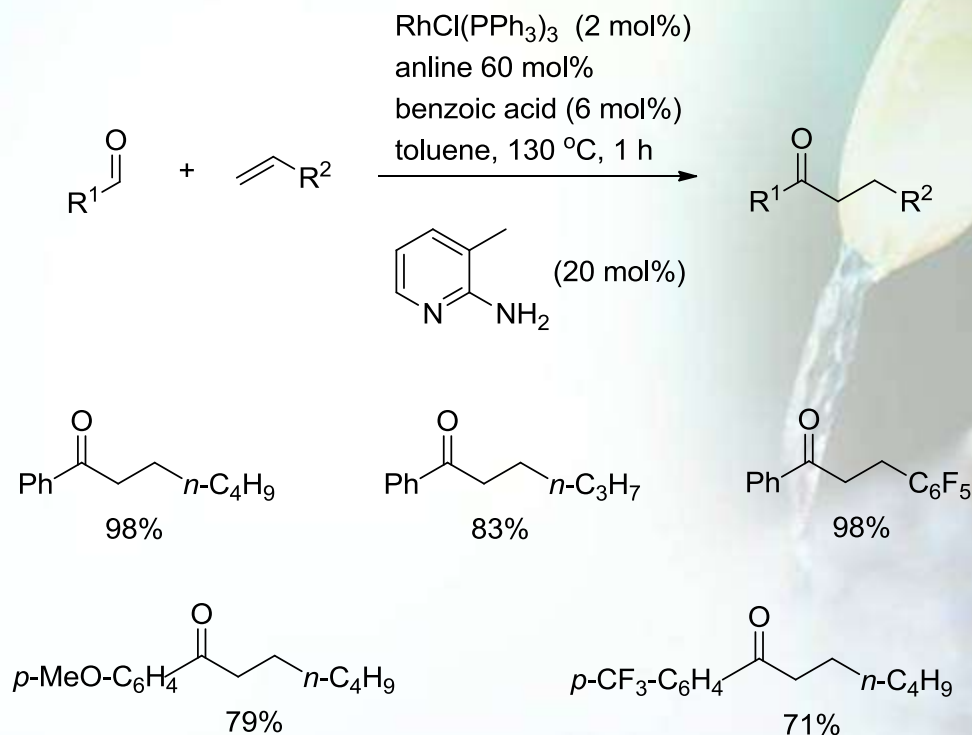
2.2 Removable directing group



Zack's work, Dong's group, unpublished result.

3. Bifunctional catalyst / ligand

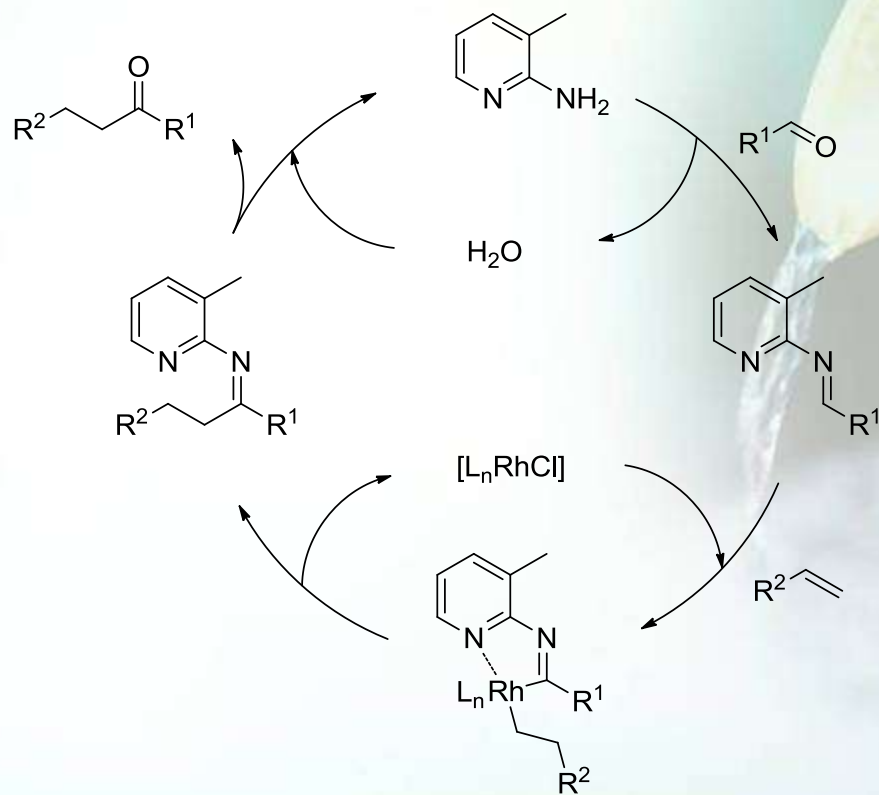
3.1 Covalent bonding



Jun, C. -H.; Lee, D. -Y.; Lee, H.; Hong, J. -B. *Angew. Chem. Int. Ed.* **2000**, *39*, 3070.

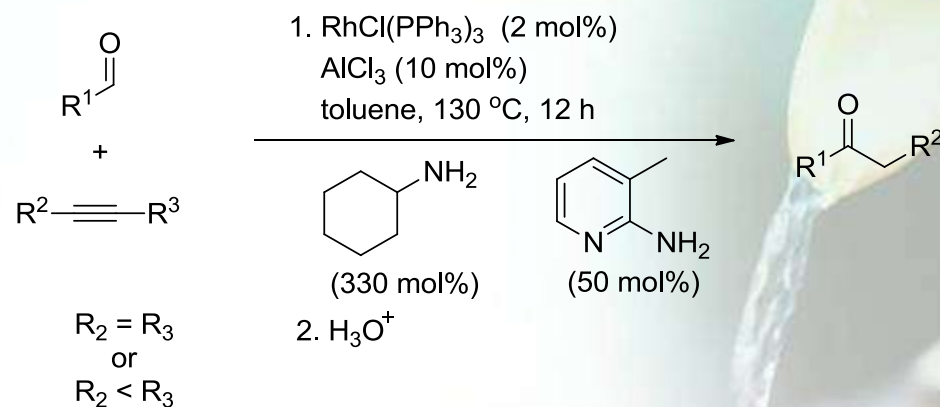
3. Bifunctional catalyst / ligand

3.1 Covalent bonding



3. Bifunctional catalyst / ligand

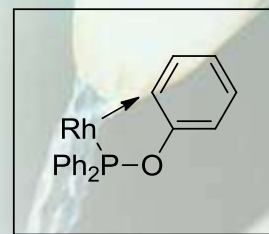
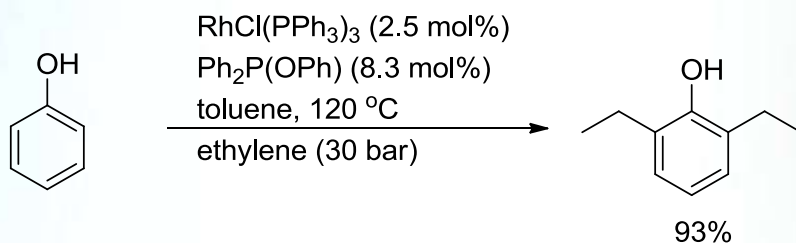
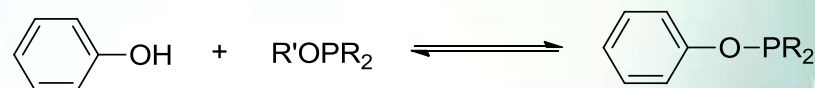
3.1 Covalent bonding



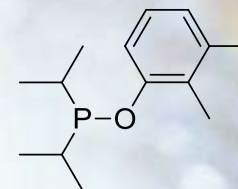
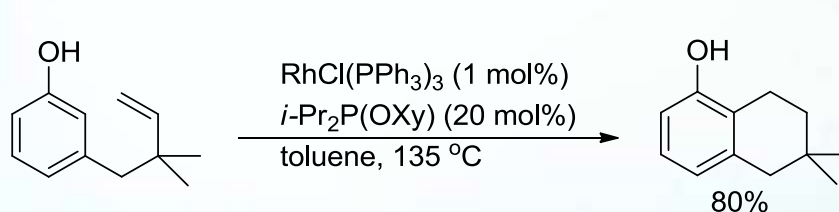
Lee, D. -Y.; Hong, B. -S.; Cho, E. -G.; Lee, H.; Jun, C. -H.; *J. Am. Chem. Soc.* **2003**, *125*, 6372.

3. Bifunctional catalyst / ligand

3.1 Covalent bonding



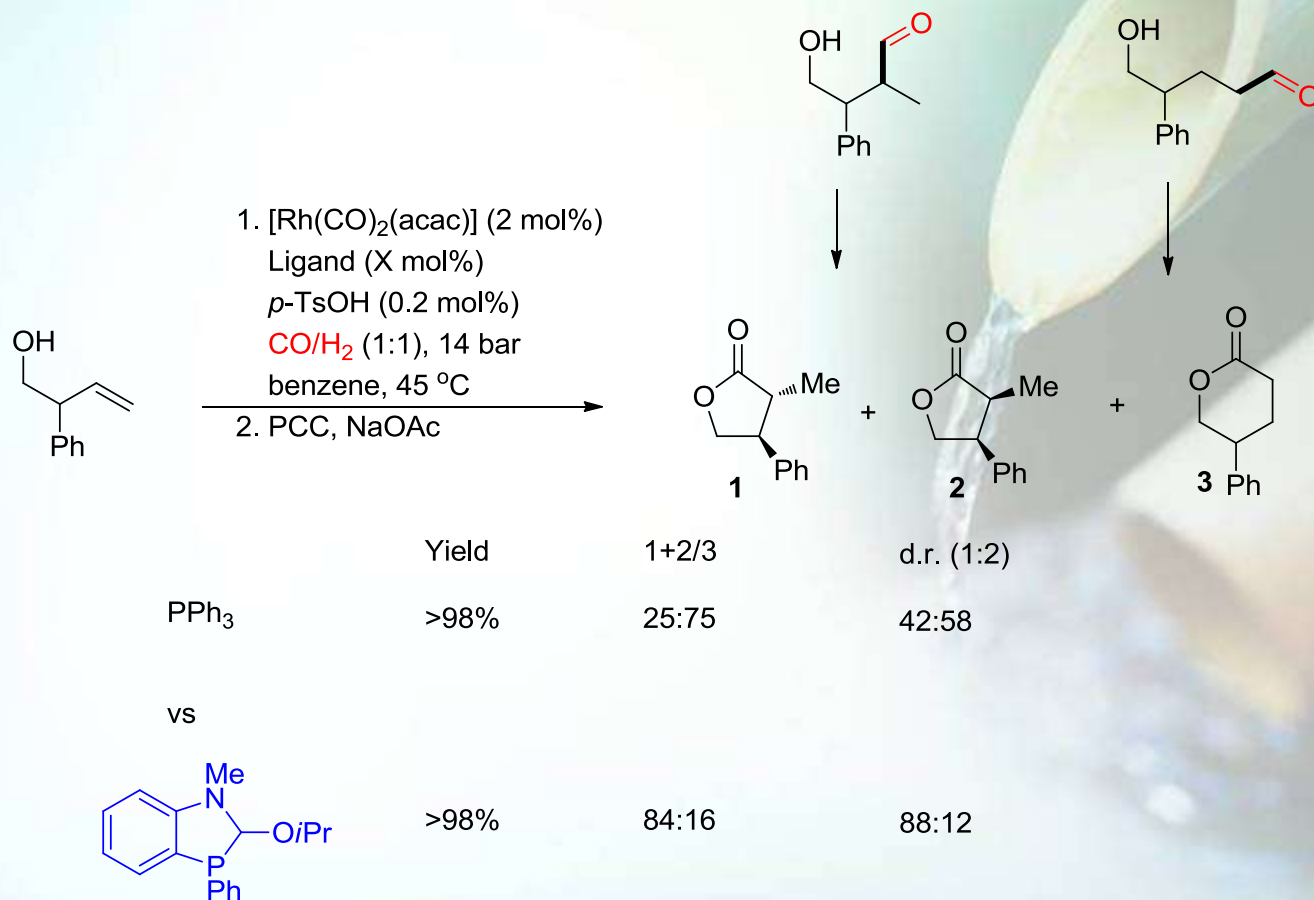
Carrion, M. C.; Cole-Hamilton, D. J. *Chem. Commun.* **2006**, 43, 4527.



Lewis, J. C; Wu, J.; Bergman, R. G.; Ellman, J. A. *Organometallics* **2005**, 24, 5737.

3. Bifunctional catalyst / ligand

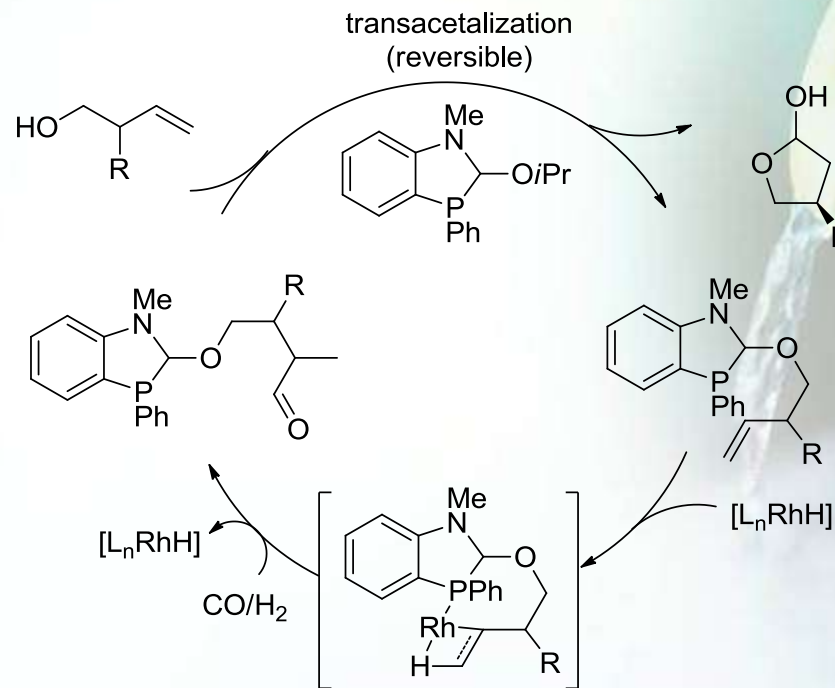
3.1 Covalent bonding



Lightburn, T. E.; Dombrowski, M. T.; Tan, K. L. *J. Am. Chem. Soc.* **2008**, *130*, 9210.

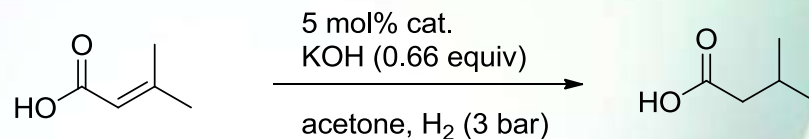
3. Bifunctional catalyst / ligand

3.1 Covalent bonding

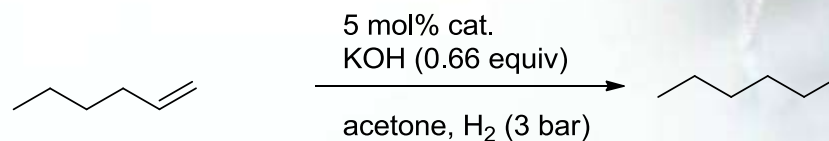
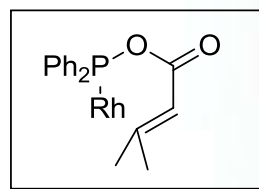


3. Bifunctional catalyst / ligand

3.1 Covalent bonding



RhCl(PPh₃)₃ = 27% conversion
RhCl(PPh₃)₂(Ph₂PO₂CH=CMe₂) = 80% conversion



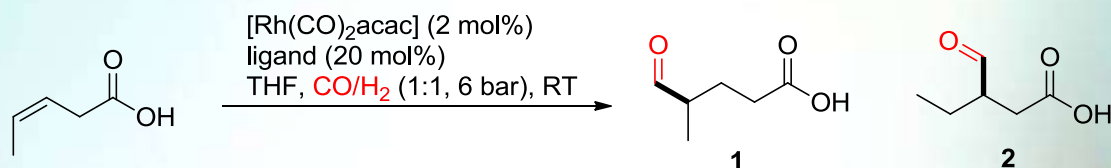
RhCl(PPh₃)₃ = 22% conversion
RhCl(PPh₃)₂(Ph₂PO₂CH=CMe₂) = 10% conversion

Preston, S. A.; Cupertino, D. C.; Palma-Ramirez, P.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1986**, 12, 977.

Iraqi, A.; Fairfax, N. R.; Preston, S. A.; Cupertino, D. C.; Irvine, D. J.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1991**, 8, 1929.

3. Bifunctional catalyst / ligand

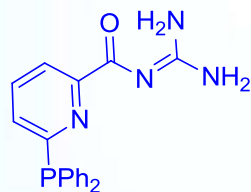
3.2 Hydrogen bonding



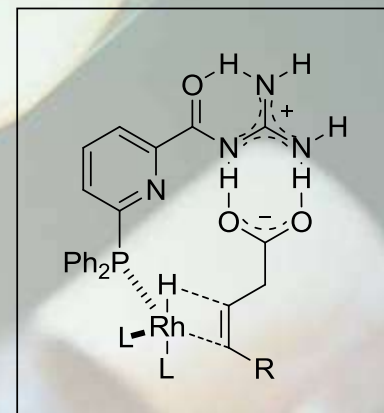
Conversion **1:2**

PPh₃ 20% 1:1.7

vs



80.5 11:1



Šmejkal, T.; Breit, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 311.

3. Bifunctional catalyst / ligand

3.2 Hydrogen bonding

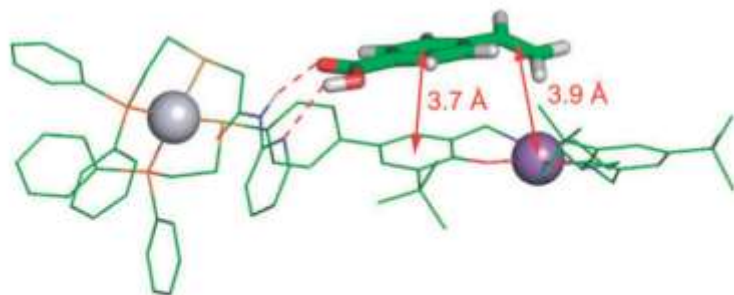
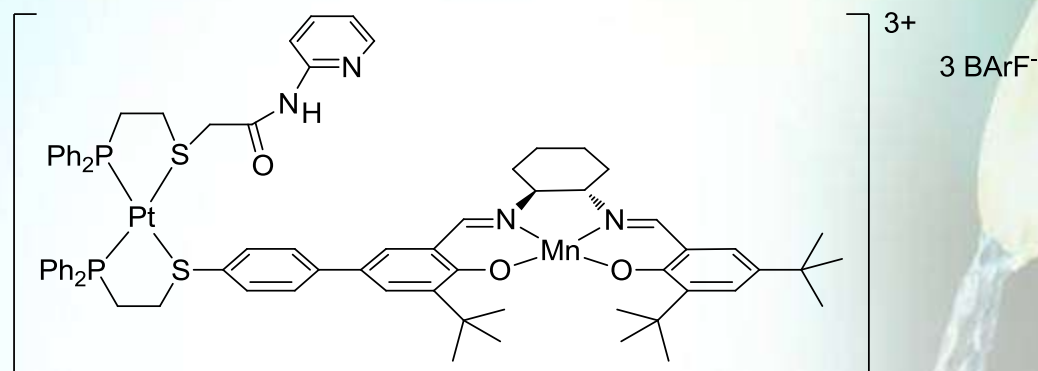
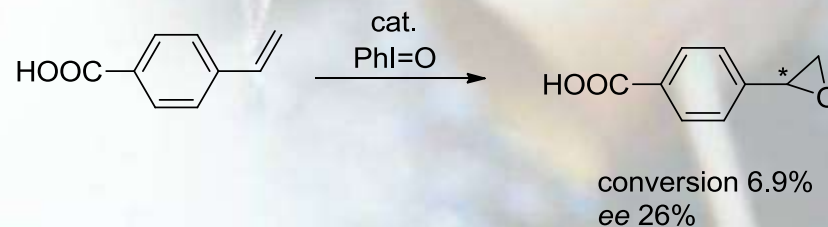
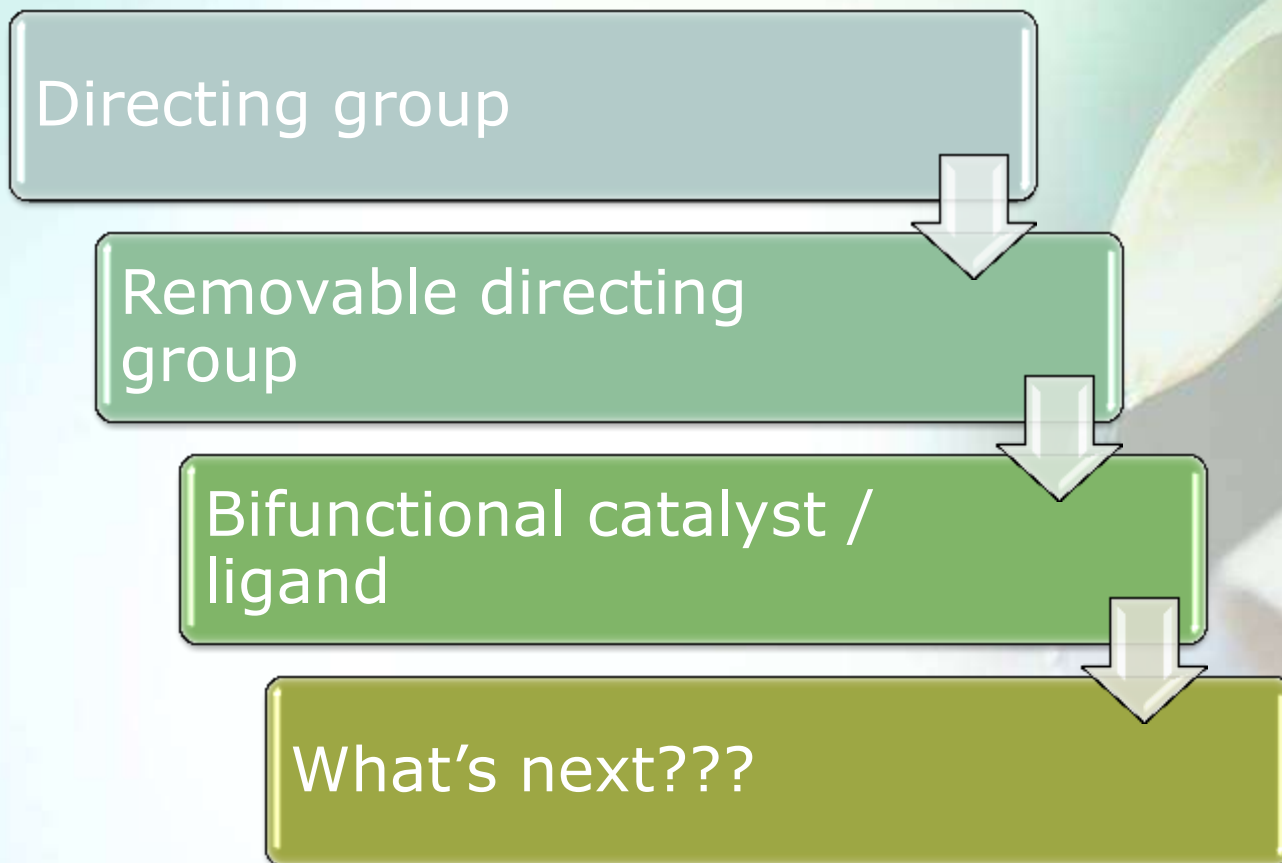


Fig. 1 Global minimum structure obtained from conformation search simulations of a hydrogen bonded supramolecular complex between catalyst **4** and 4-vinylbenzoic acid **7**.



Ulmann, P. A.; Braunschweig, A. B.; Lee, O.-S.; Wiester, M. J.; Schatz, G. C.; Mirkin, C. A. *Chem. Commun.* **2009**, 5121.

4. Conclusion and Outlook



Please see Dong Group publications in the near future!!!

We are **Dong Group**
We do **Directing Group**

5. Acknowledgement

Thank the whole group family ~ ~ !



