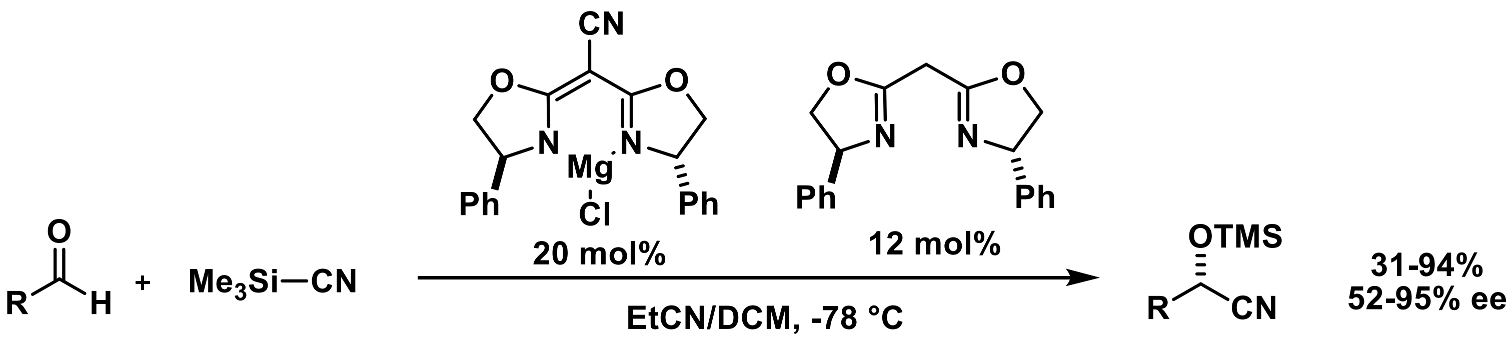
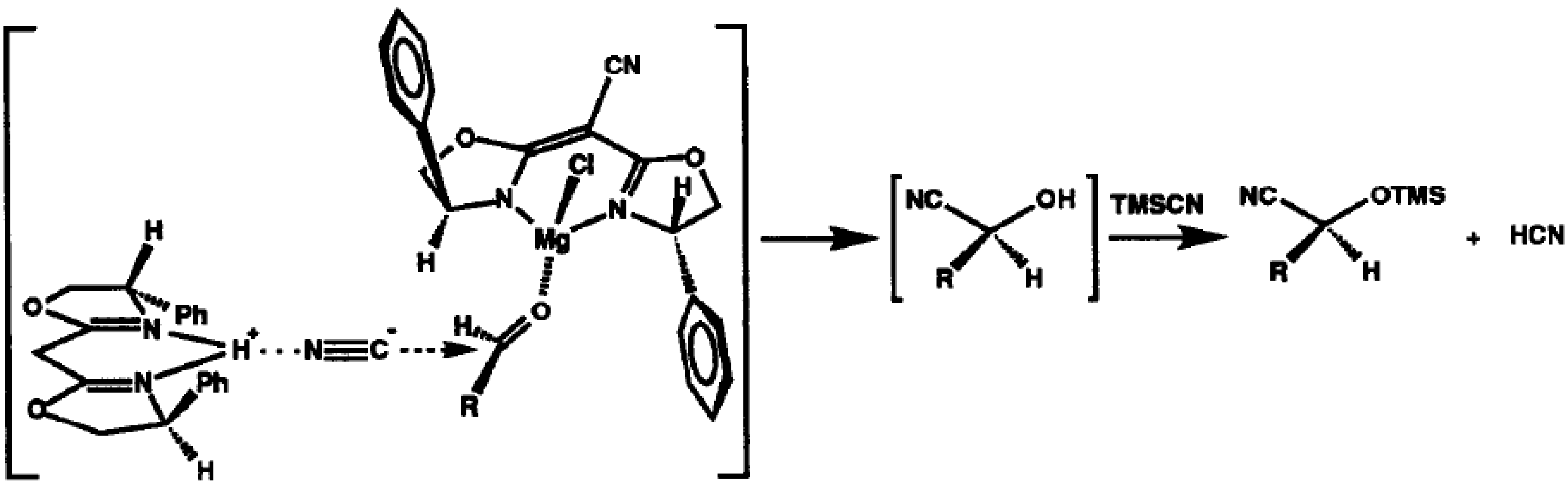
4.3 Metal-Ligand Dual Activation

4.3. Metal-Ligand Dual Activation: Cyanide Addition

Corey: Asymmetric Cyanhydrin Synthesis: Dual Activation with Lewis Acid and Basic Ligand



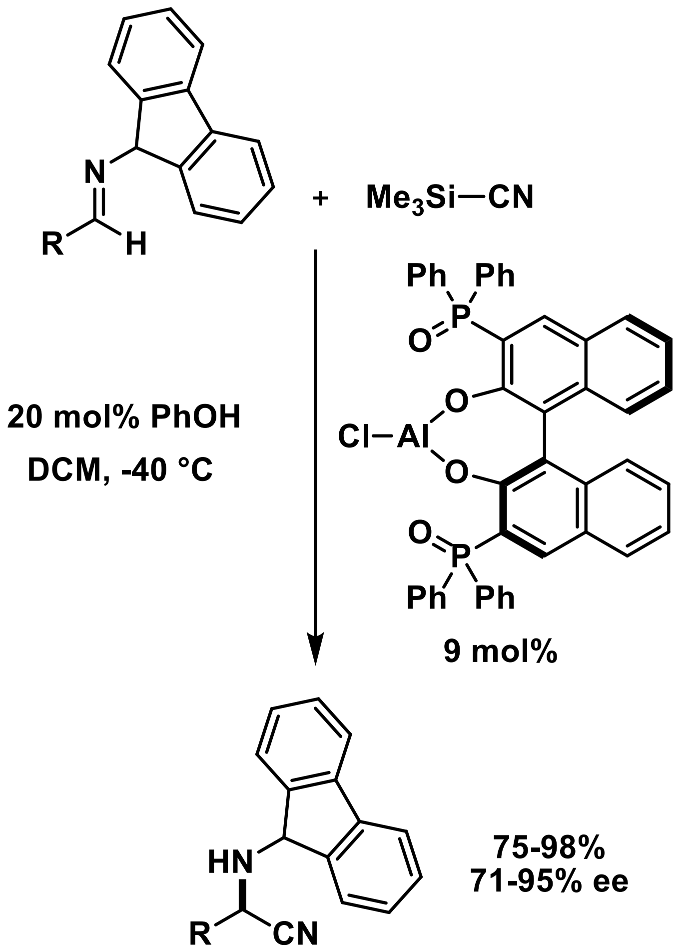
Model for Dual Activation



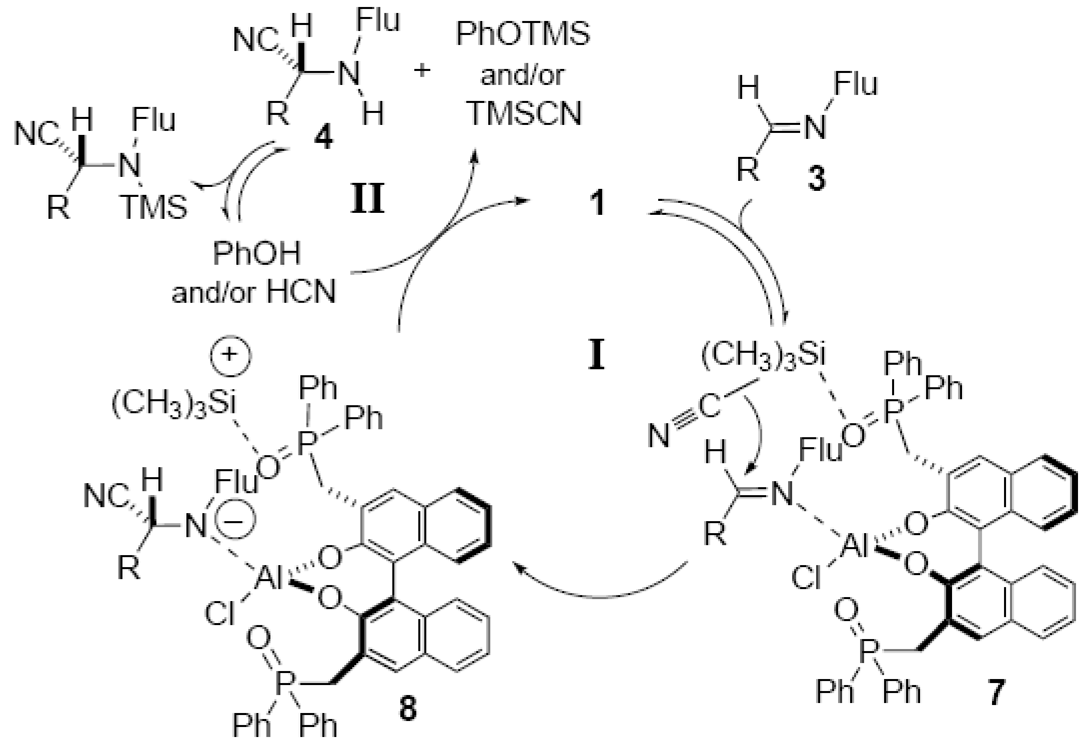
(1) Corey, E. J.; Wang, Z. *Tetrahedron Lett.* **1993,** *34,* 4001-4004.

4.3. Metal-Ligand Dual Activation: Cyanide Addition

Shibasaki: Al-Phosphinoxide Bifunctional Catalysts



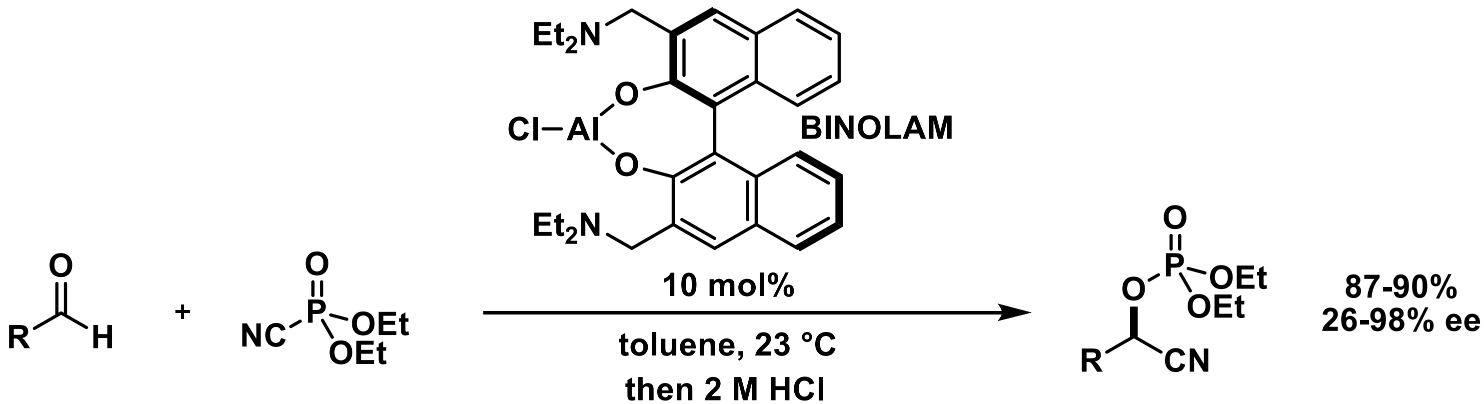
Mechanism



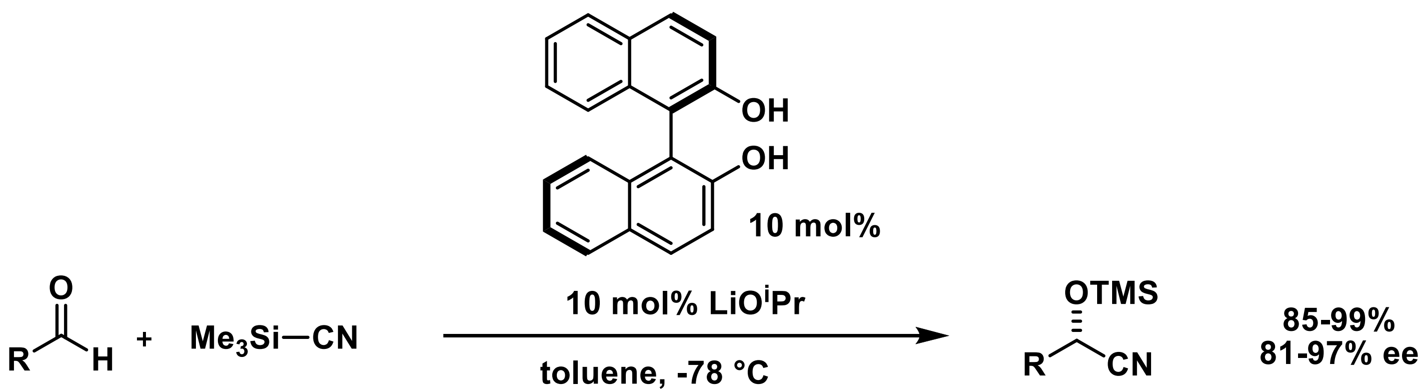
(1) Takamura, M.; Hamashima, Y.; Usuda, H.; Kanai, M.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2000,** *39,* 1650-1652.

4.3. Metal-Ligand Dual Activation: Cyanide Addition

Saa: Bifunctional Al-Amine Catalyst for Cyanophosphorylation of Aldehydes[1]



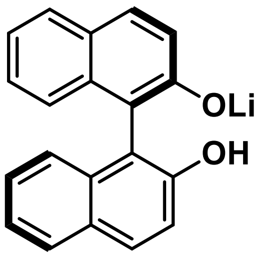
Shibasaki: Cyanohydrin Synthesis with a Li-Binol Catalyst[2]



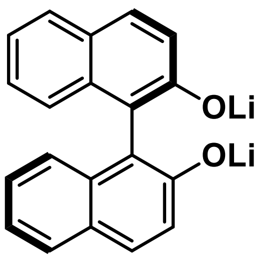
(1) Baeza, A.; Casas, J.; Najera, C.; Sansano, J. M.; Saa, J. M. *Angew. Chem., Int. Ed.* **2003,** *42,* 3143-3146. (2) Hatano, M.; Ikeno, T.; Miyamoto, T.; Ishihara, K. *J. Am. Chem. Soc.* **2005,** *127,* 10776-10777.

4.3. Metal-Ligand Dual Activation: Cyanide Addition

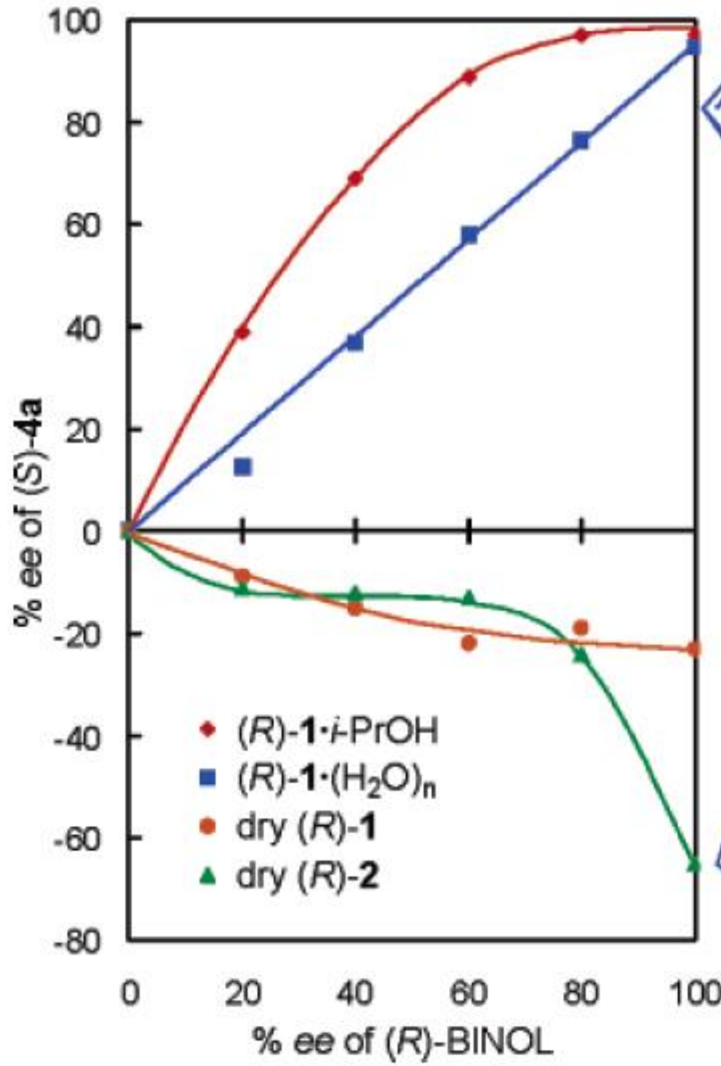
Model for Selectivity: Influence of Additive

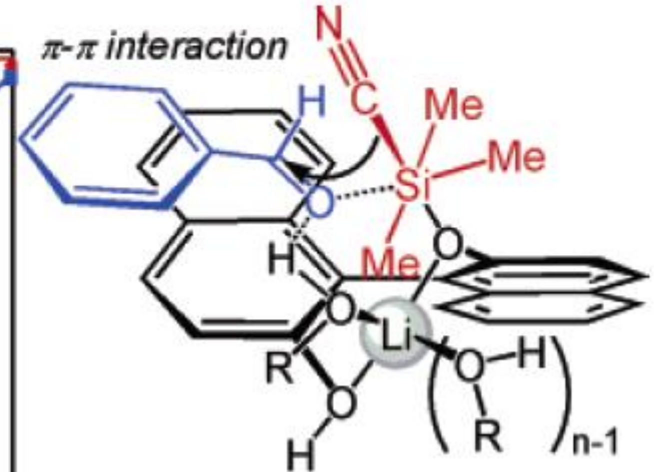


(*R*)-1



(*R*)-2





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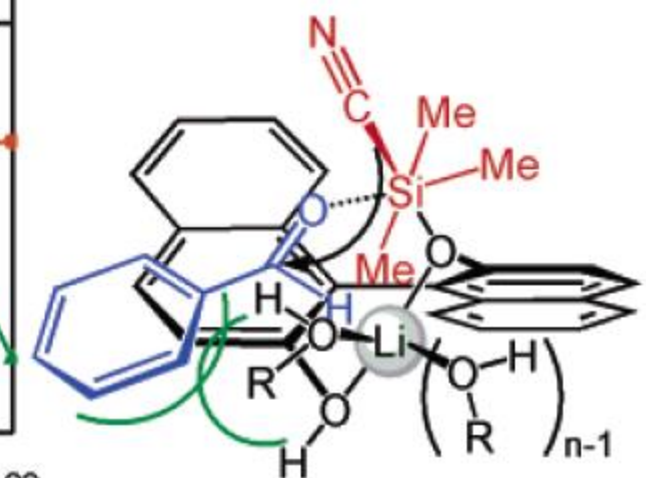
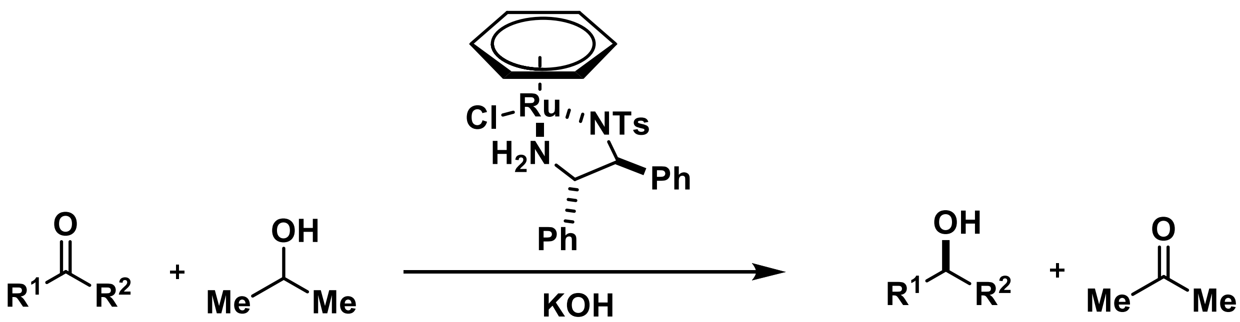


6: *Disfavored*

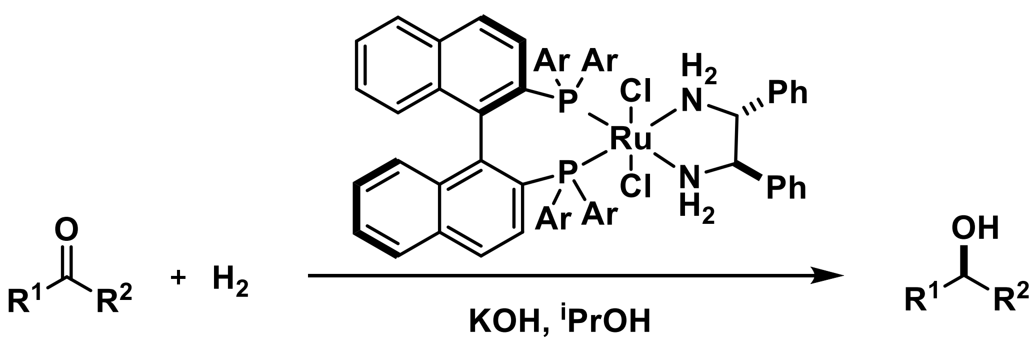
(1) Hatano, M.; Ikeno, T.; Miyamoto, T.; Ishihara, K. *J. Am. Chem. Soc.* **2005,** *127,* 10776-10777.

4.3. Metal-Ligand Dual Activation: Noyori Hydrogenation

Noyori: Transfer Hydrogenation of Ketones with Ru-Diamine Complex[1]



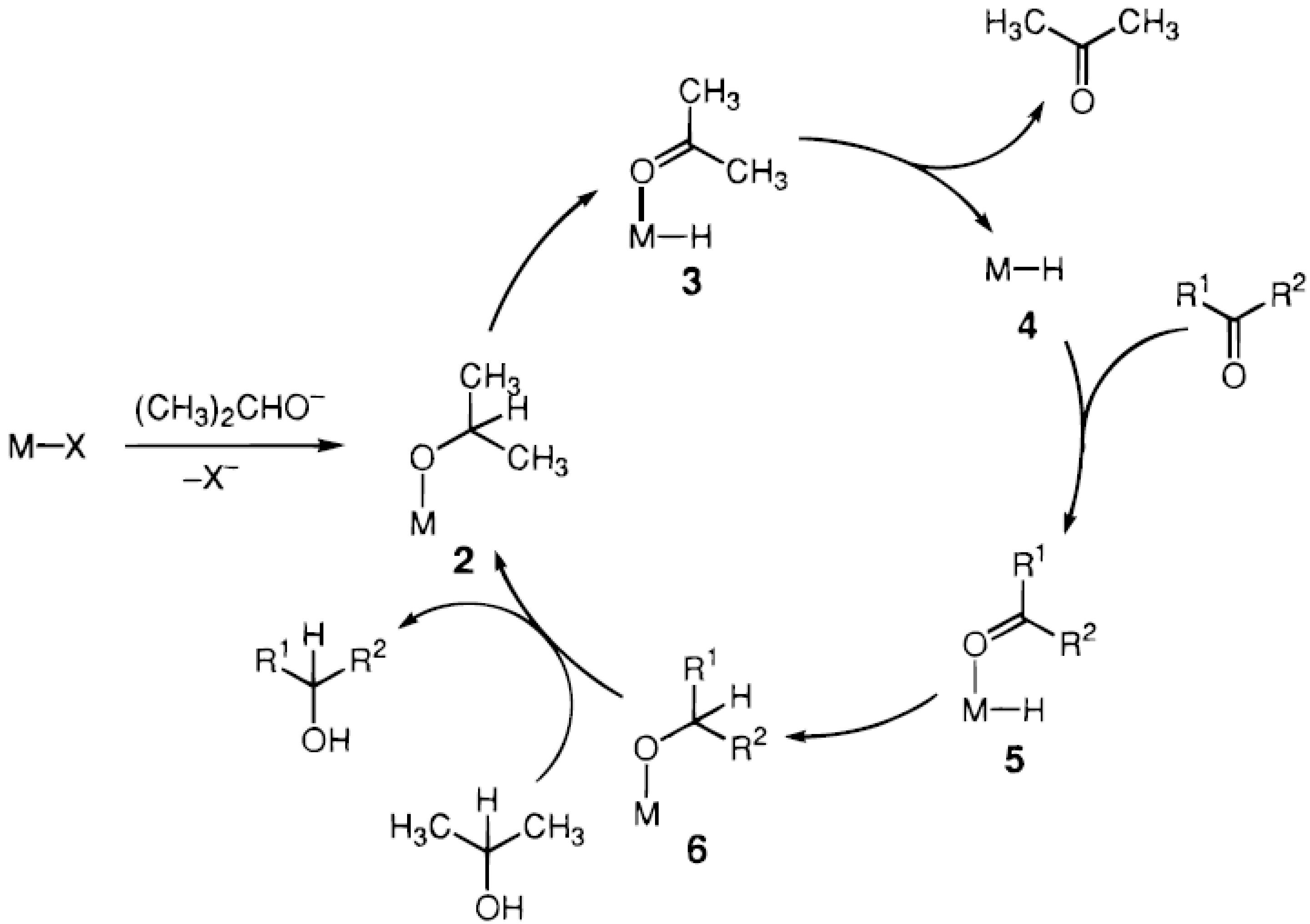
Noyori: Hydrogenation of Ketones with BINAP-Diamine Ru Complex[2]



(1) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000,** *122,* 1466-1478. (2) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001,** *40,* 40-73.

4.3. Metal-Ligand Dual Activation: Noyori Hydrogenation

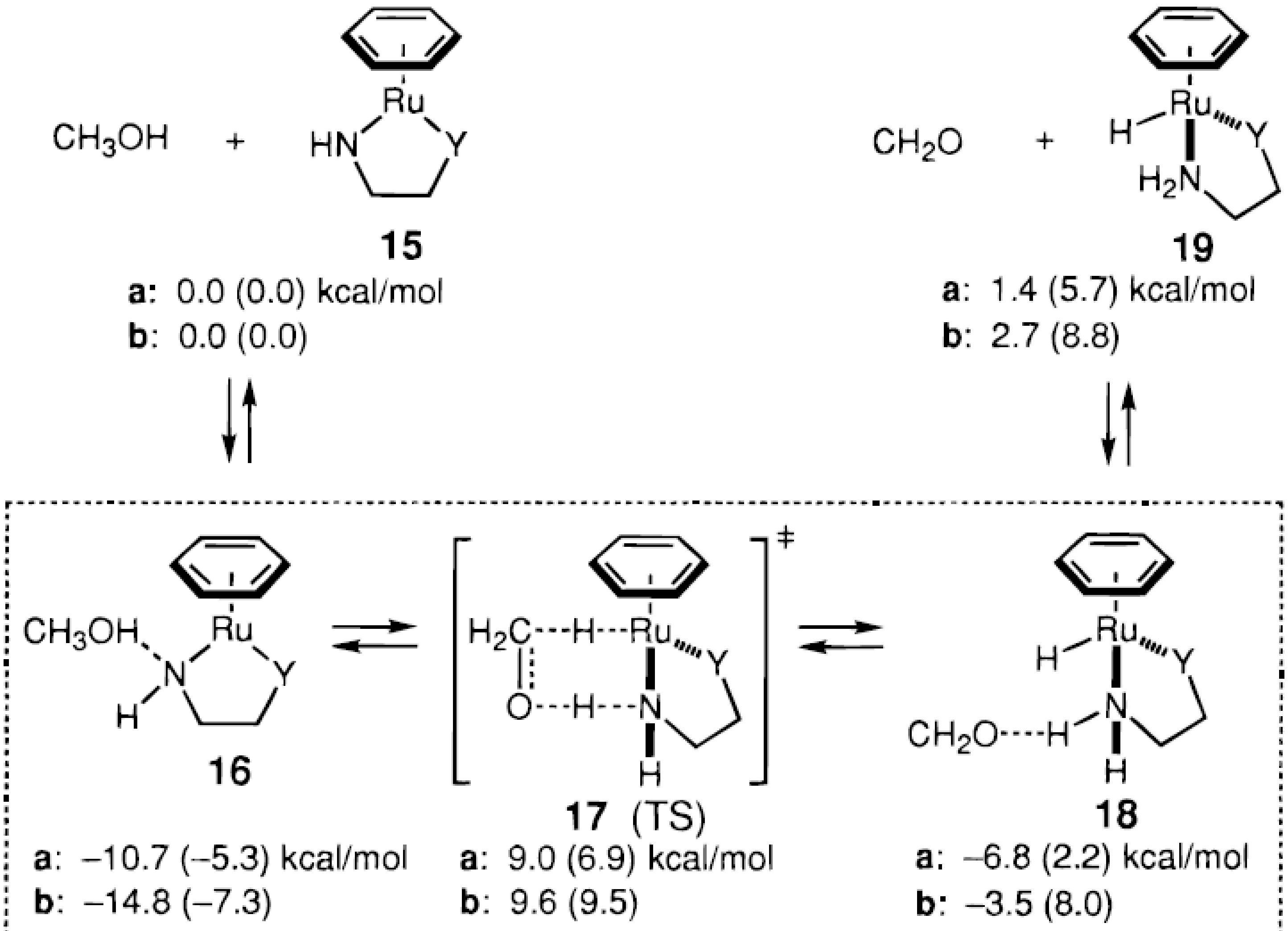
Classical β-Elimination-Insertion Mechanism for Transfer Hydrogenation[1]



(1) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000,** *122,* 1466-1478.

4.3. Metal-Ligand Dual Activation: Noyori Hydrogenation

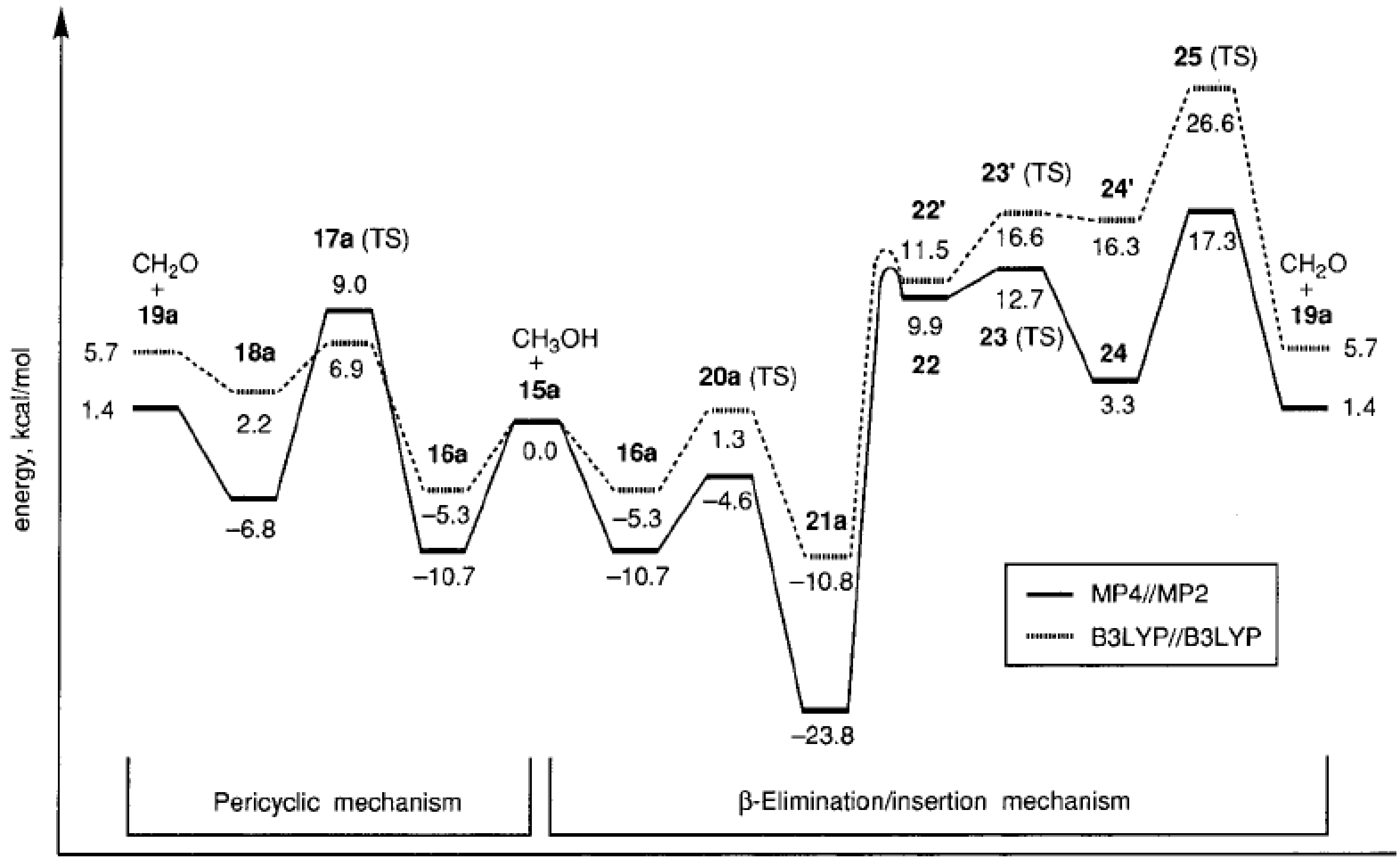
New Pericyclic Mechanism Proposed by Noyori[1]



(1) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000,** *122,* 1466-1478.

4.3. Metal-Ligand Dual Activation: Noyori Hydrogenation

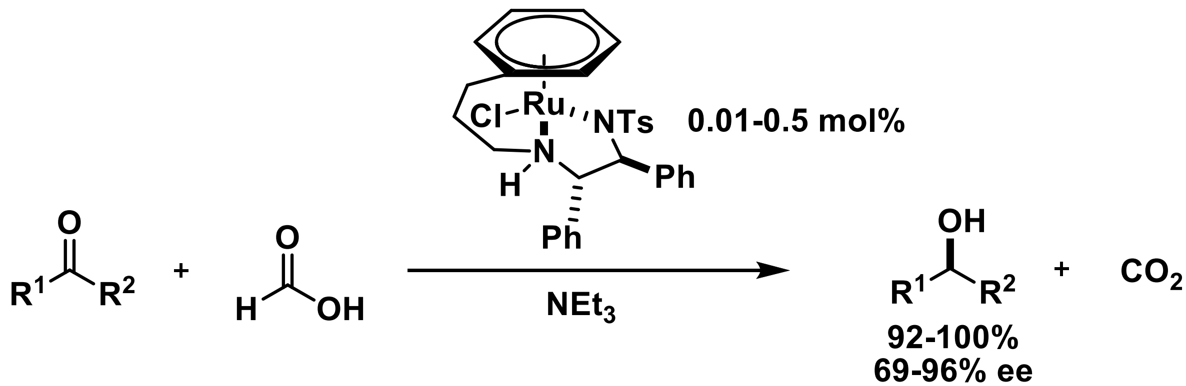
Calculation of the two Possible Mechanisms for Noyori Hydrogenation[1]



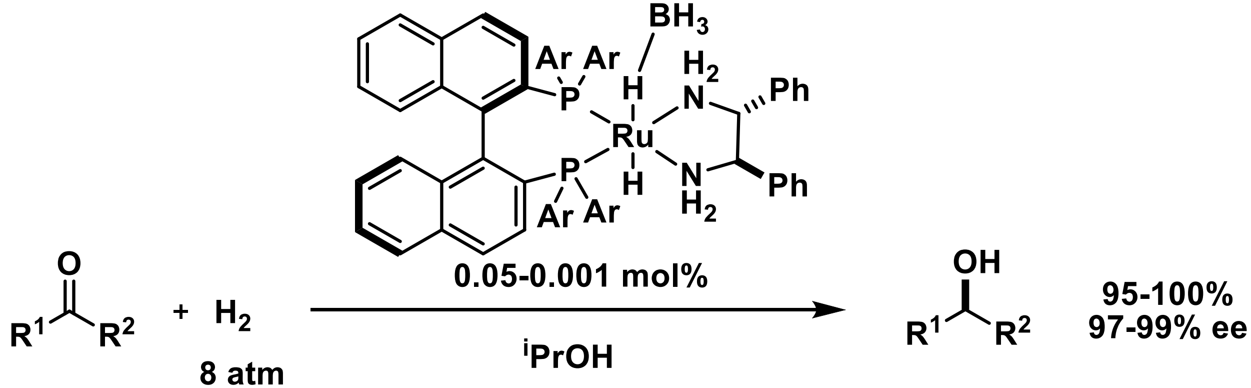
(1) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000,** *122,* 1466-1478.

4.3. Metal-Ligand Dual Activation: Noyori Hydrogenation

Wills: A More Stable Catalyst for Transfer Hydrogenation[1]



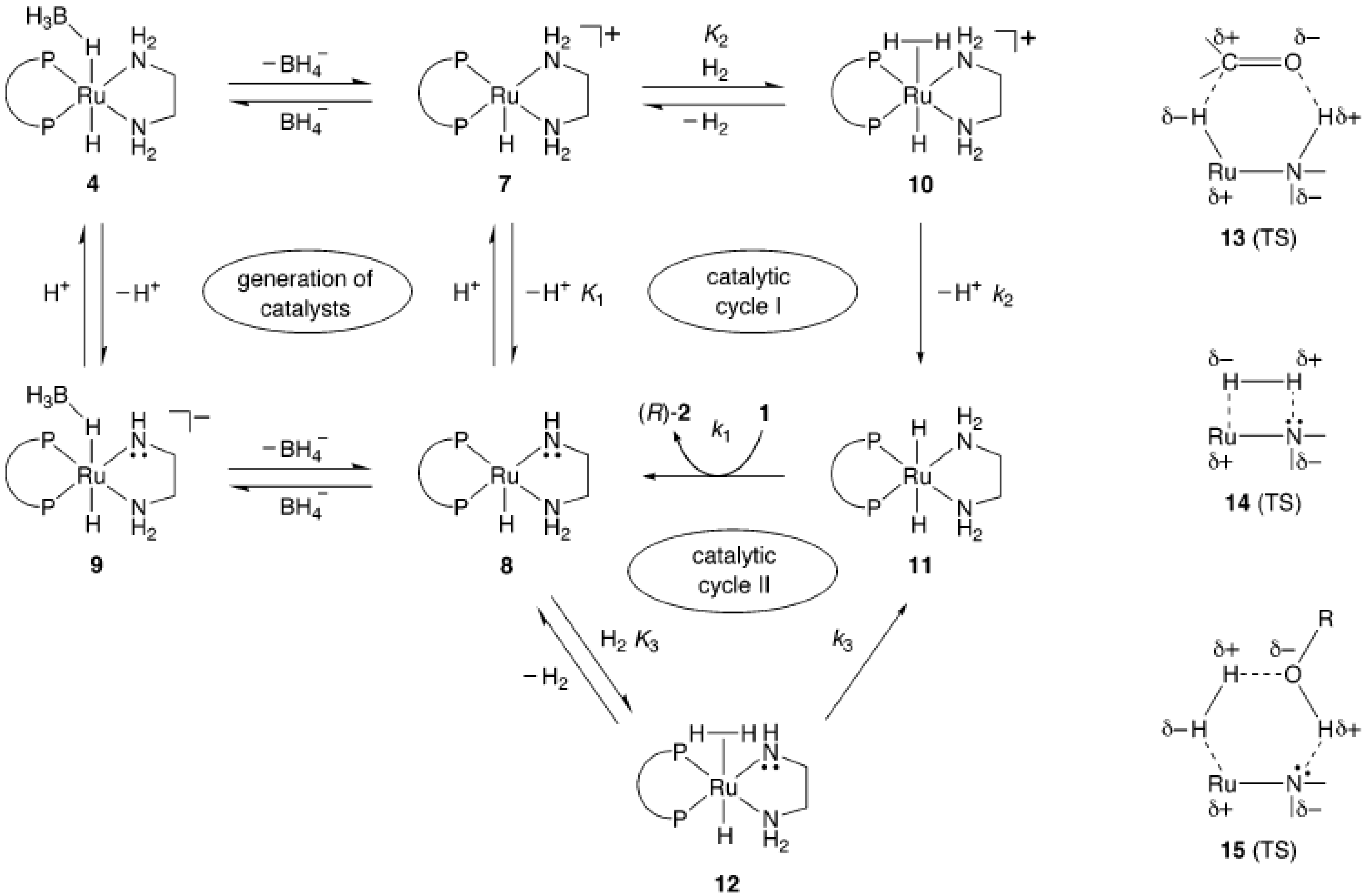
Noyori: A New Catalyst Precursor Allowing a Base-Free Protocole[2]



(1) Hayes, A. M.; Morris, D. J.; Clarkson, G. J.; Wills, M. *J. Am. Chem. Soc.* **2005,** *127,* 7318-7319. (2) Ohkuma, T.; Koizumi, M.; Muniz, K.; Hilt, G.; Kabuto, C.; Noyori, R. *J. Am. Chem. Soc.* **2002,** *124,* 6508-6509.

4.3. Metal-Ligand Dual Activation: Noyori Hydrogenation

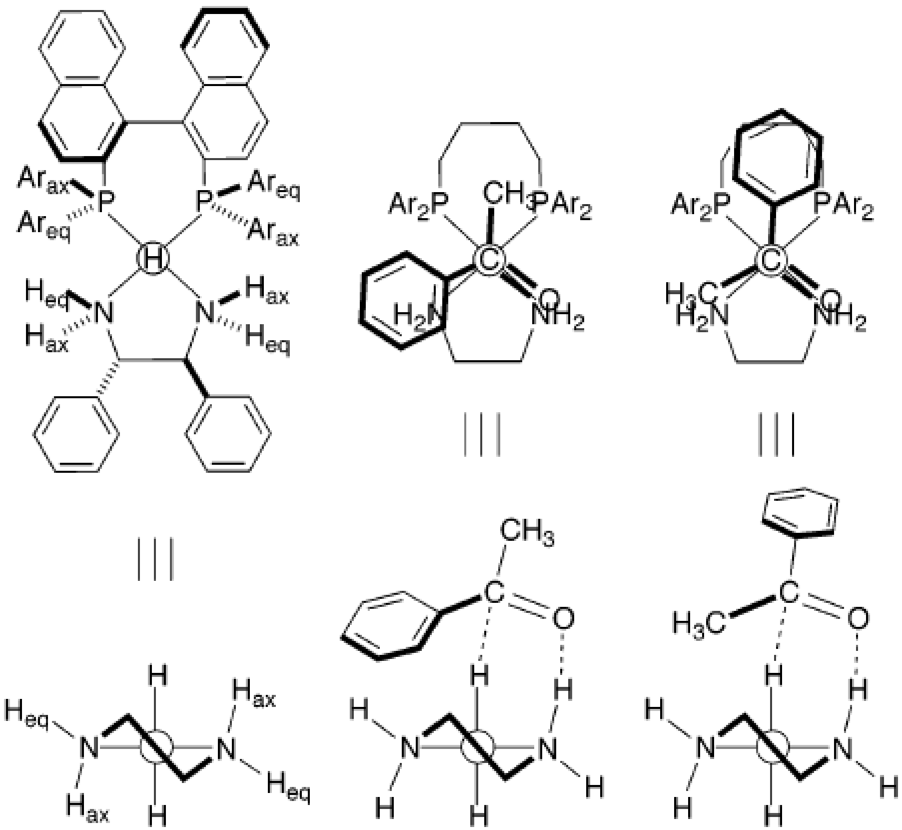
Mechanism for the Noyori Hydrogenation



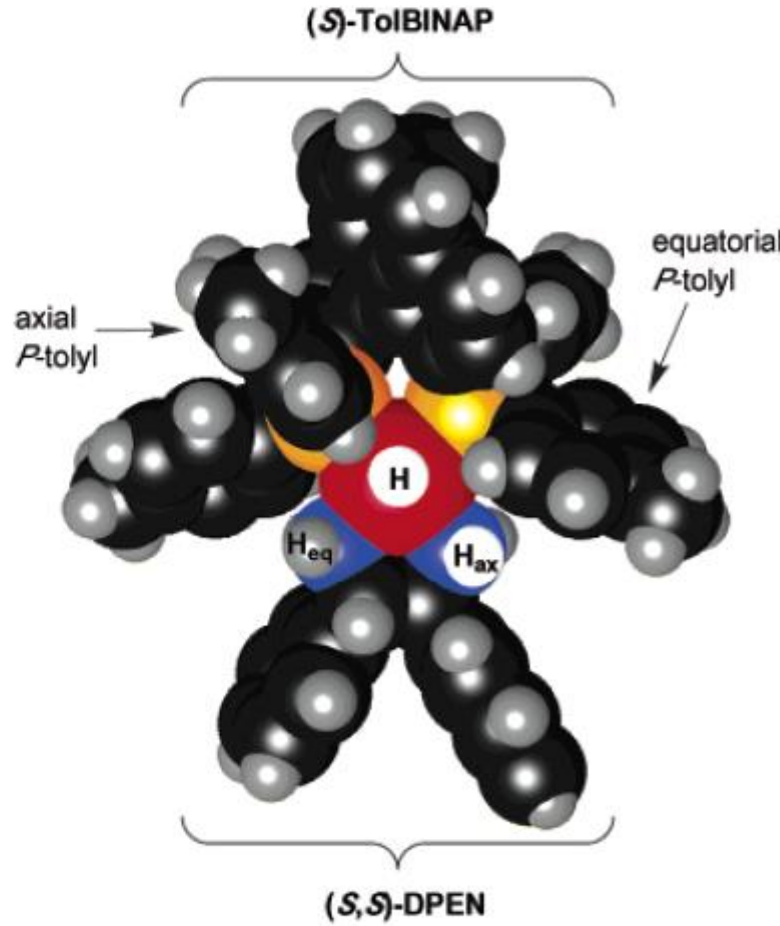
(1) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002,** *124,* 15104. (2) Sandoval, C. A.; Ohkuma, T.; Muniz, K.; Noyori, R. *J. Am. Chem. Soc.* **2003,** *125,* 13490. (3) Dub, P. A.; Henson, N. J.; Martin, R. L.; Gordon, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 3505.

4.3. Metal-Ligand Dual Activation: Noyori Hydrogenation

Model for Enantioselection



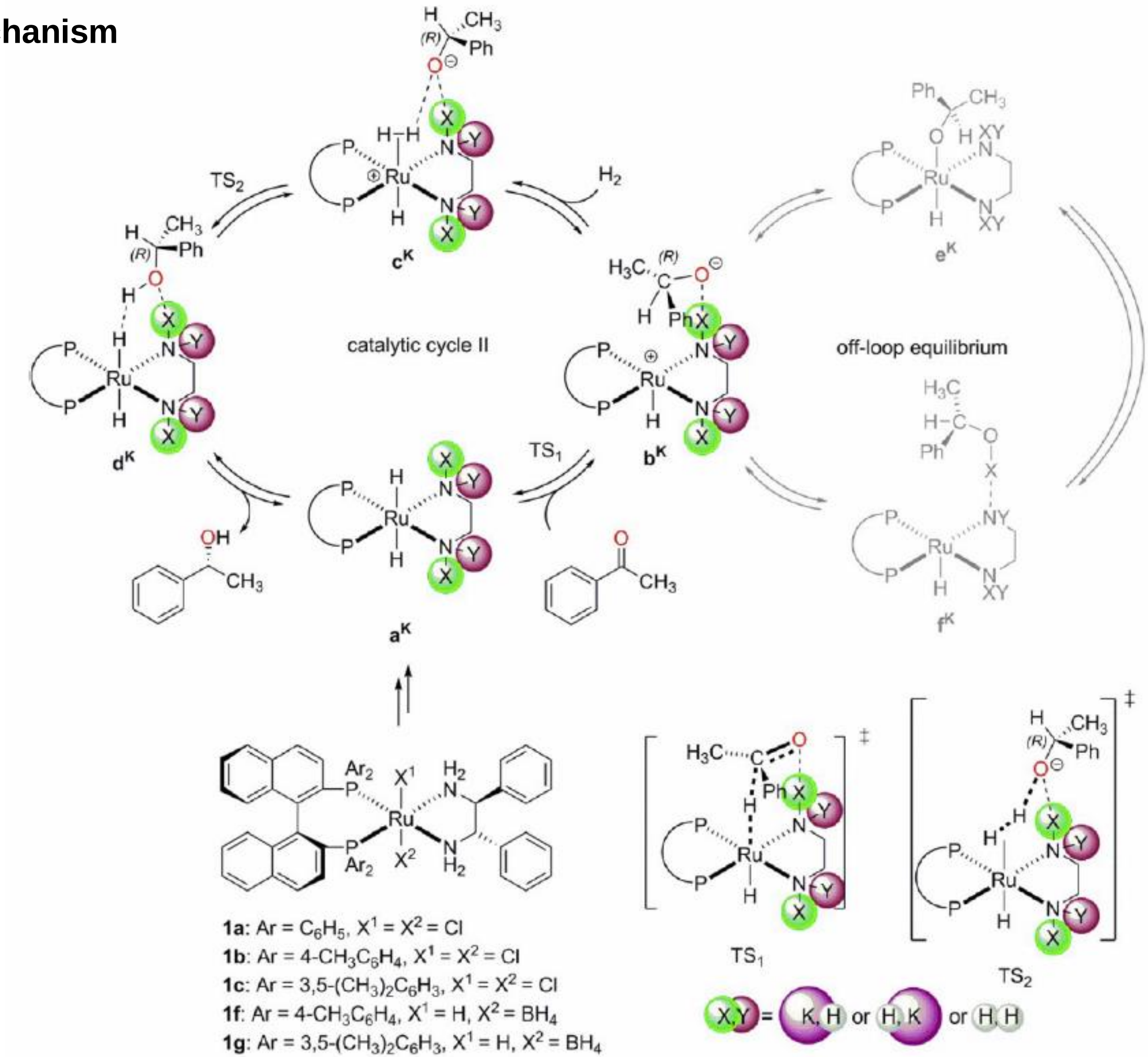
(S,SS)-**11** $\quad$ **17**$_{Si}$ (favored) $\quad$ **17**$_{Re}$ (unfavored)



(1) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002,** *124,* 15104-15118. (2) Sandoval, C. A.; Ohkuma, T.; Muniz, K.; Noyori, R. *J. Am. Chem. Soc.* **2003,** *125,* 13490-13503.

4.3. Metal-Ligand Dual Activation: Noyori Hydrogenation

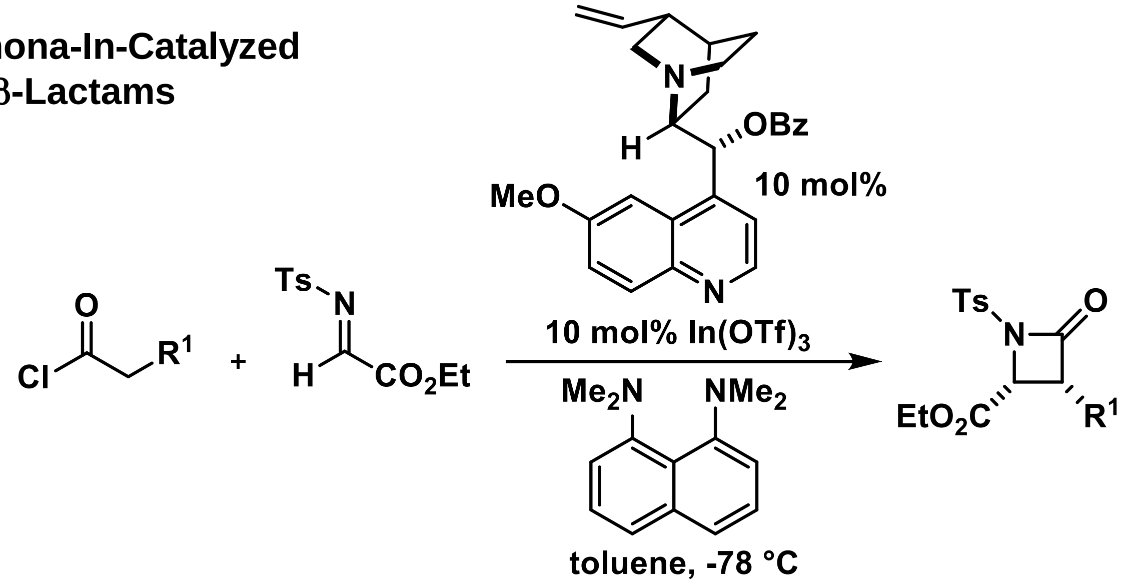
Revised Mechanism



Dub, P. A.; Henson, N. J.; Martin, R. L.; Gordon, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 3505-3521.

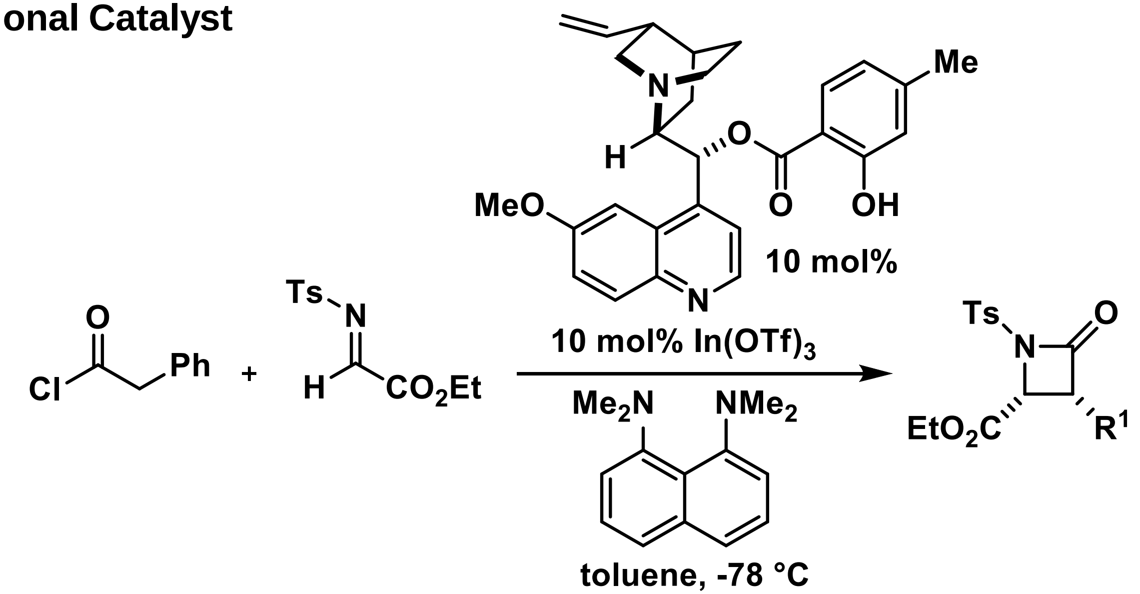
4.3. Metal-Ligand Dual Activation: Ketene Activation

Lectka: Cinchona-In-Catalyzed Synthesis of β-Lactams



91-95 %
96-98% ee
9:1-60:1 dr

A New Bifunctional Catalyst

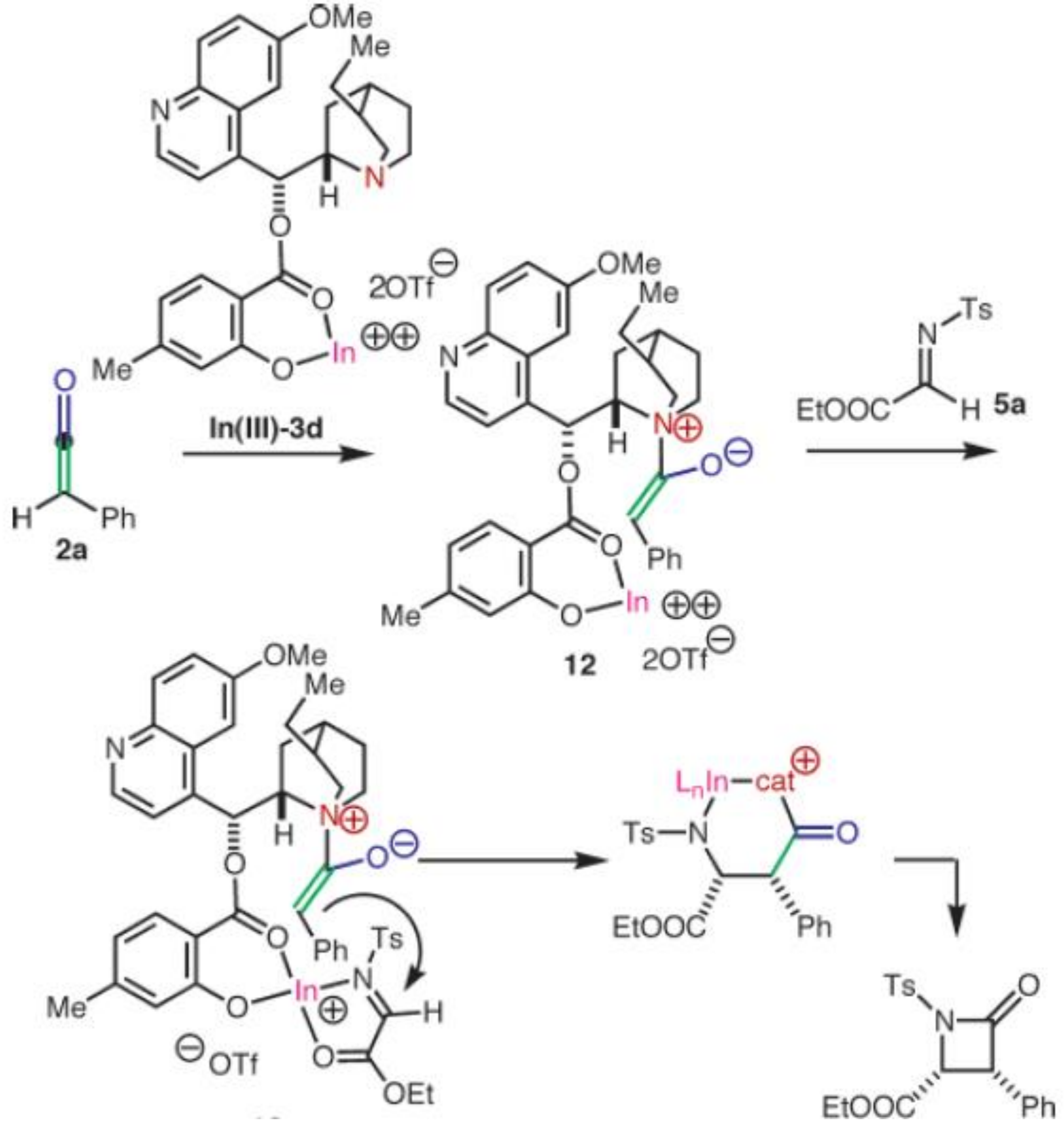


90 %
99% ee
10:1 dr

(1) France, S.; Shah, M. H.; Weatherwax, A.; Wack, H.; Roth, J. P.; Lectka, T. *J. Am. Chem. Soc.* **2005,** *127,* 1206-1215.

4.3. Metal-Ligand Dual Activation: Ketene Activation

Mechanism

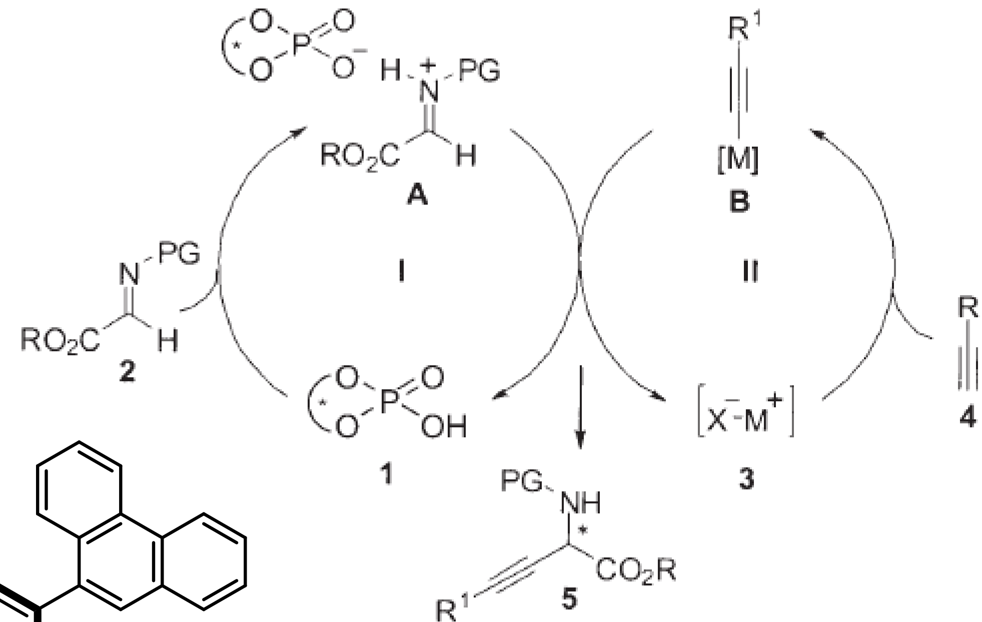


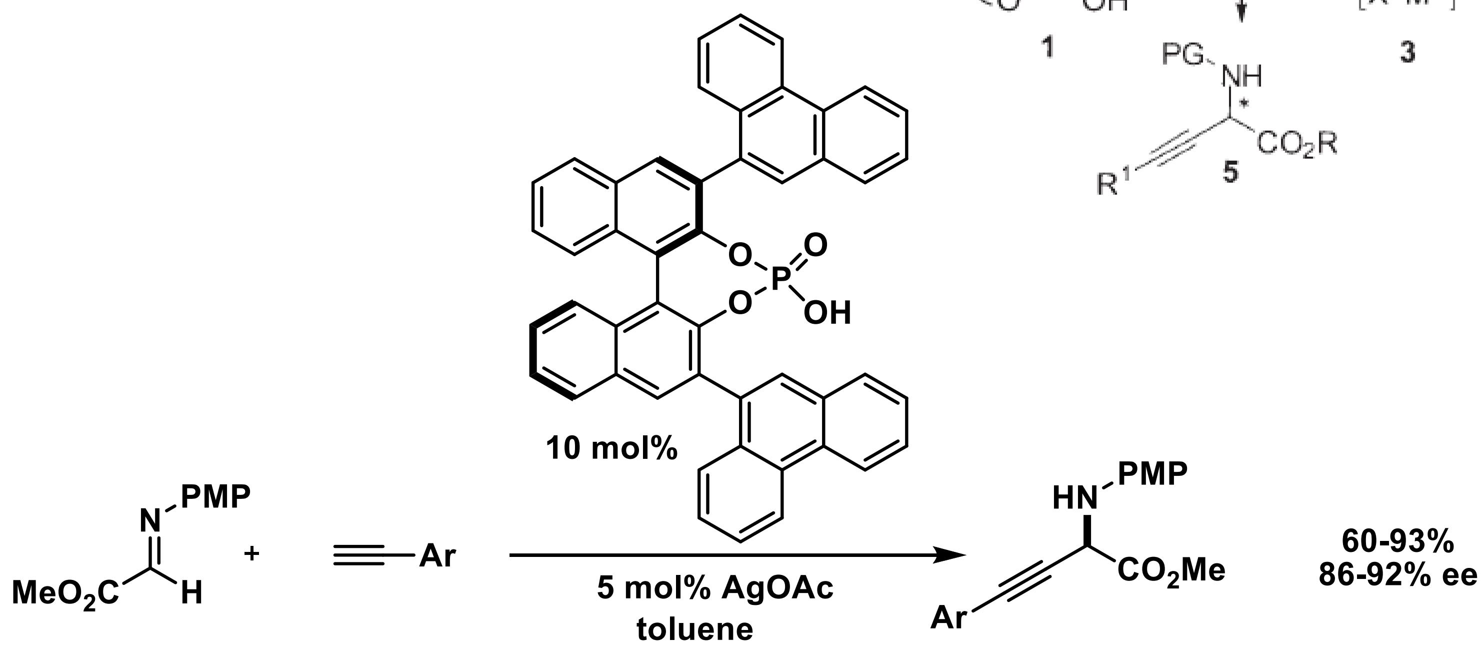
(1) France, S.; Shah, M. H.; Weatherwax, A.; Wack, H.; Roth, J. P.; Lectka, T. *J. Am. Chem. Soc.* **2005,** *127,* 1206-1215.

4.3. Metal-Ligand Dual Activation: Chiral Acid/Metal

Rueping: Silver-Chiral Acid Addition of Alkyne

Mechanism

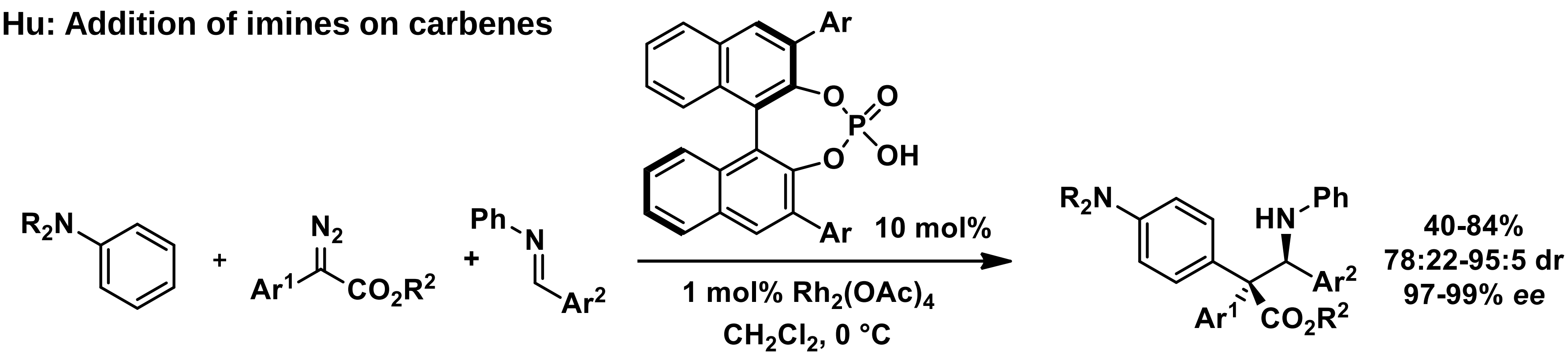


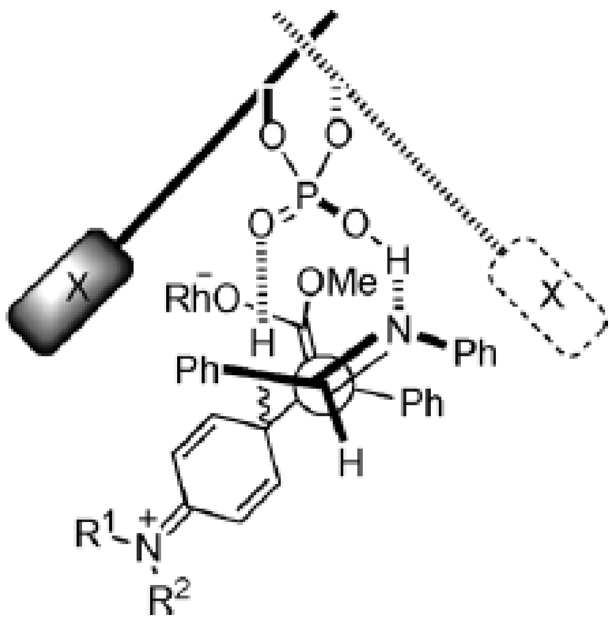


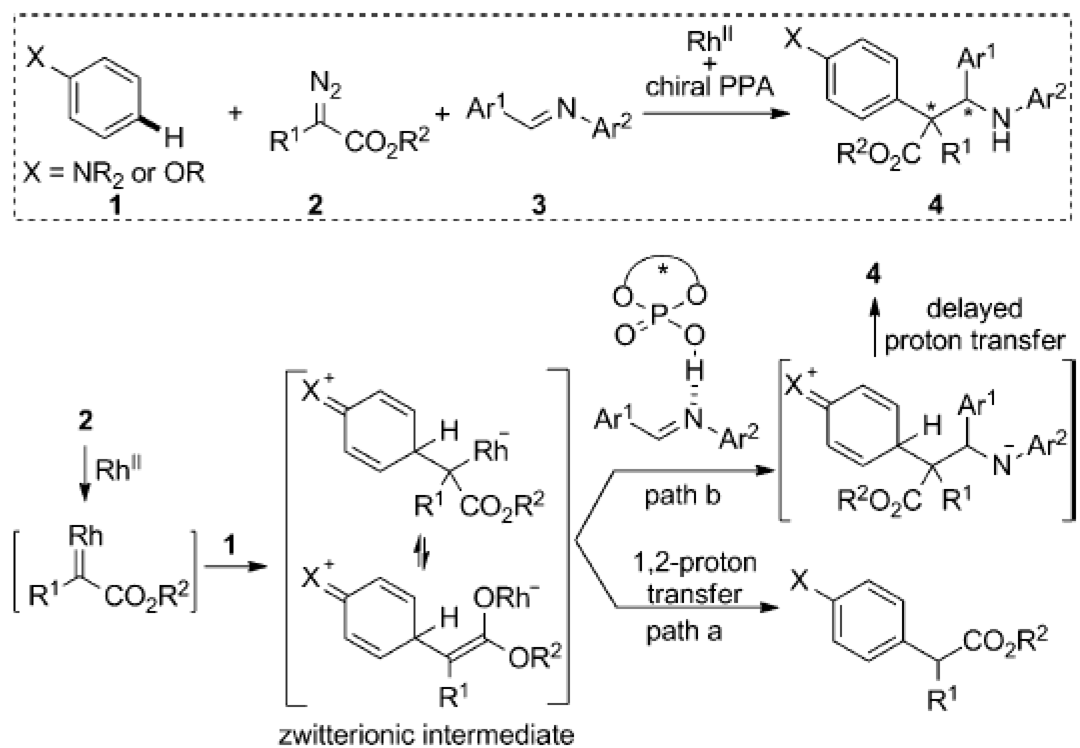
(1) Rueping, M.; Antonchick, A. R.; Brinkmann, C. *Angew. Chem., Int. Ed.* **2007,** *46,* 6903-6906.

4.3. Metal-Ligand Dual Activation: Chiral Acid/Metal

Hu: Addition of imines on carbenes



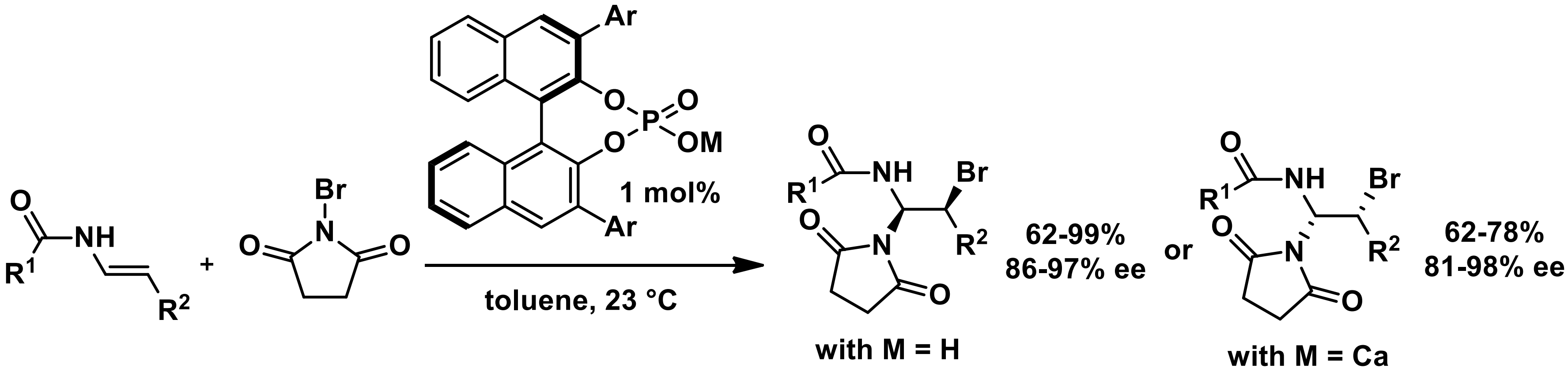


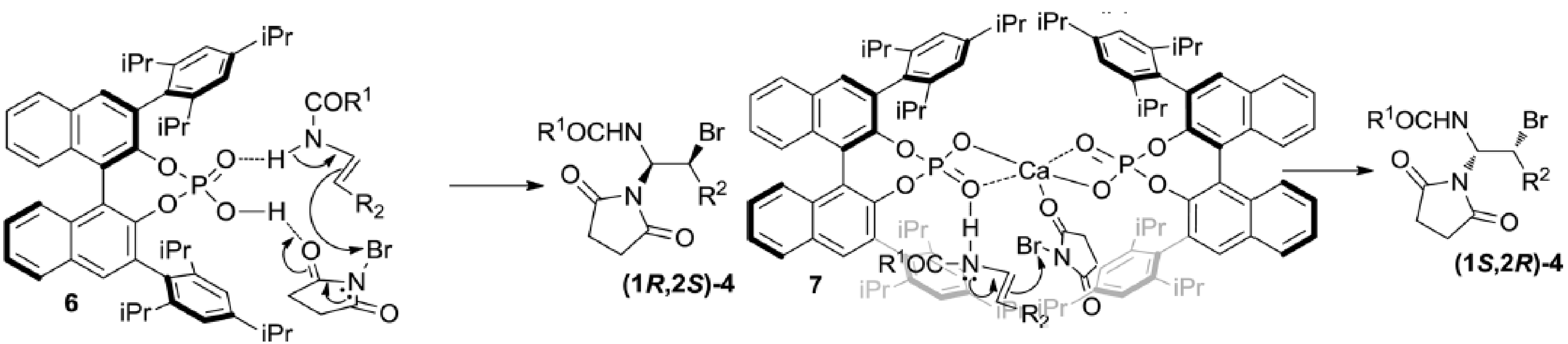


(1) Jia, S.; Xing, D.; Zhang, D.; Hu, W. *Angew. Chem., Int. Ed.* **2014**, *53*, 13098.

4.3. Metal-Ligand Dual Activation: Acid-Metal

Masson: Switching the selectivity with calcium[1]

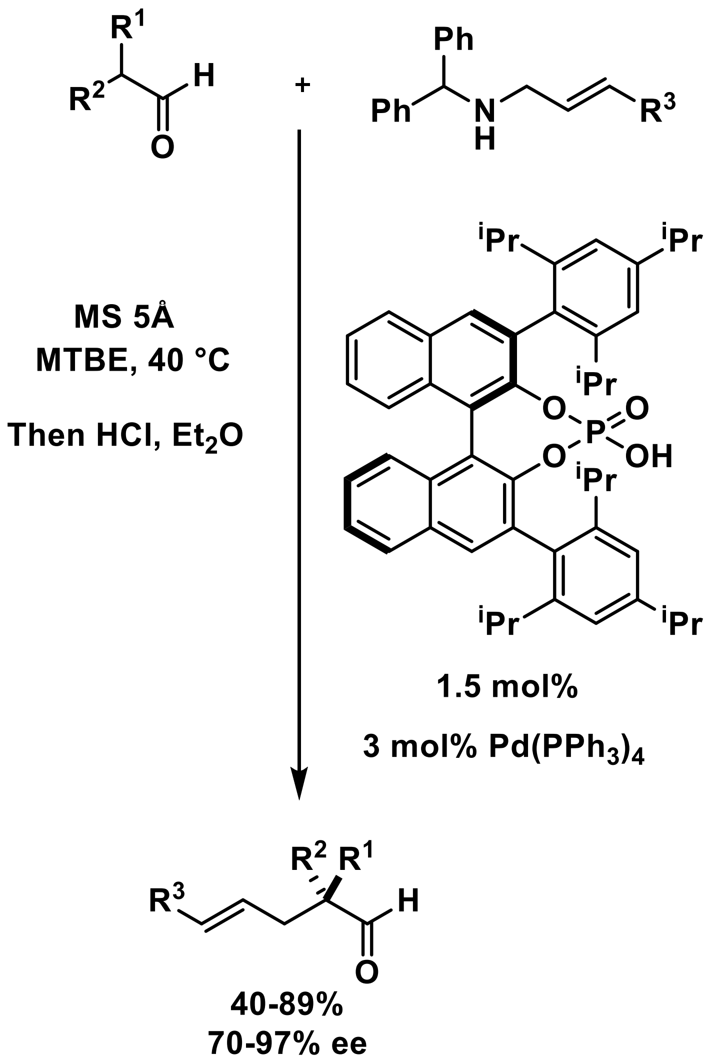




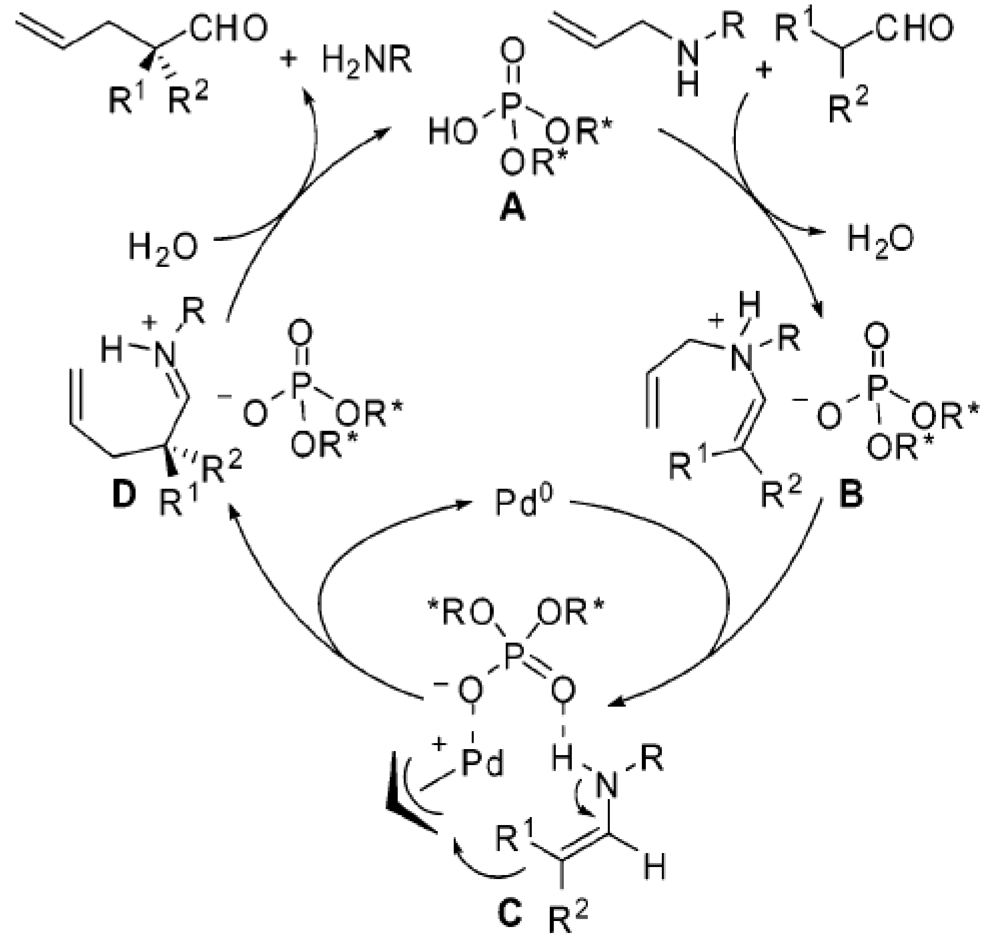
(1) Alix, A.; Lalli, C.; Retailleau, P.; Masson, G. *J. Am. Chem. Soc.* **2012**, *134*, 10389.

4.3. Metal-Ligand Dual Activation: Enamine/Metal

List: Combining Enamine Chemistry and Electrophilic Allylation



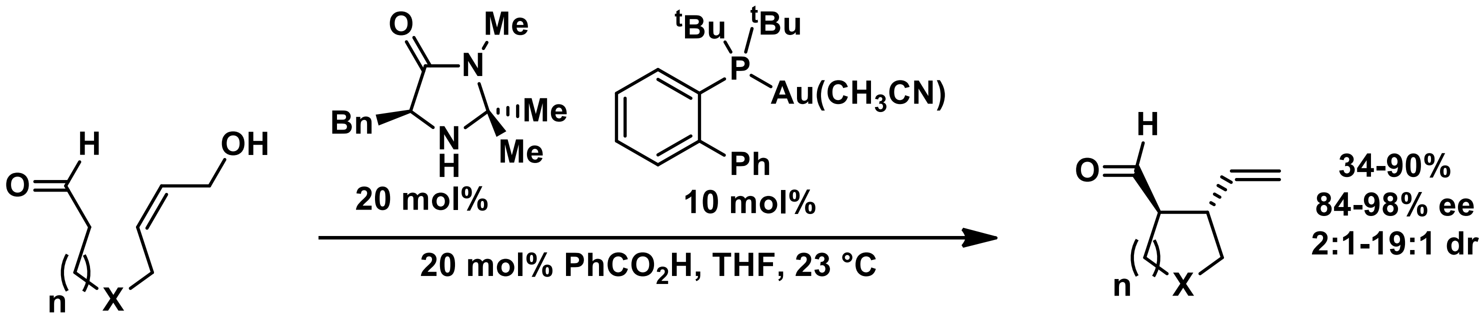
Mechanism



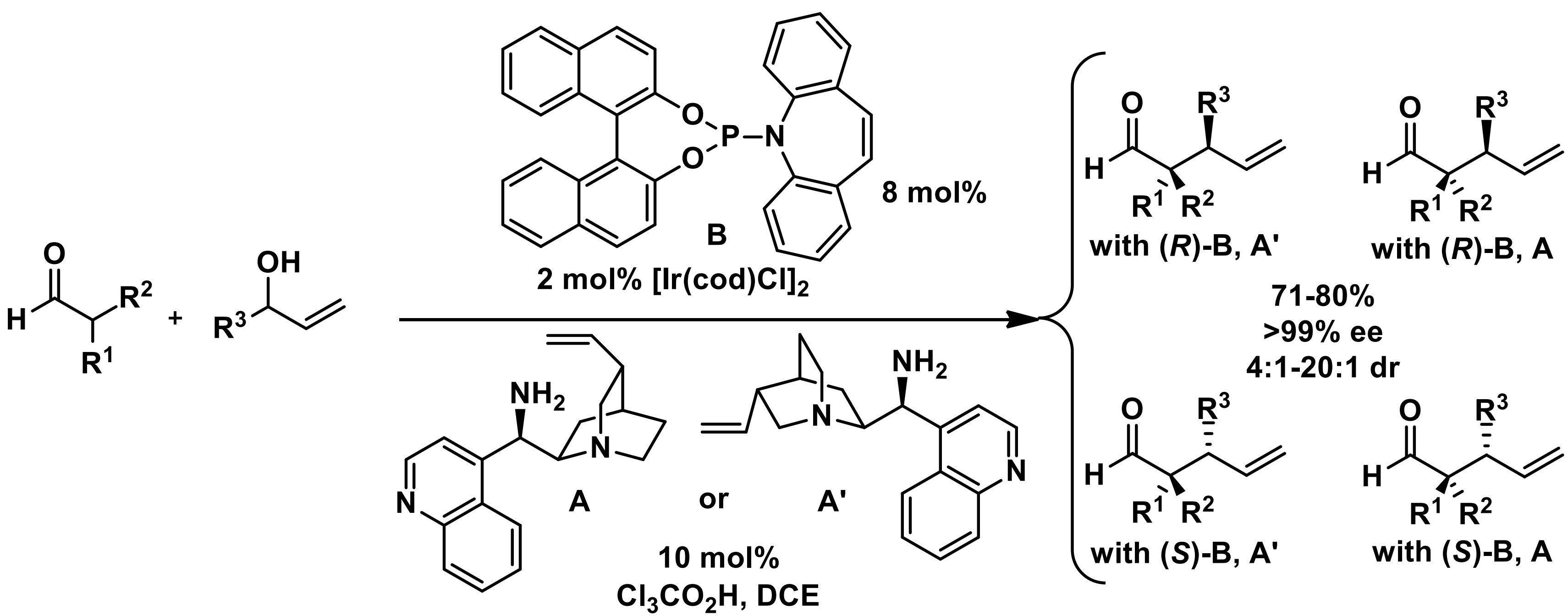
(1) Mukherjee, S.; List, B. *J. Am. Chem. Soc.* **2007,** *129,* 11336-11337.

4.3. Metal-Ligand Dual Activation: Enamine/Metal

Bandini: Combining enamine chemistry and gold catalysis[1]



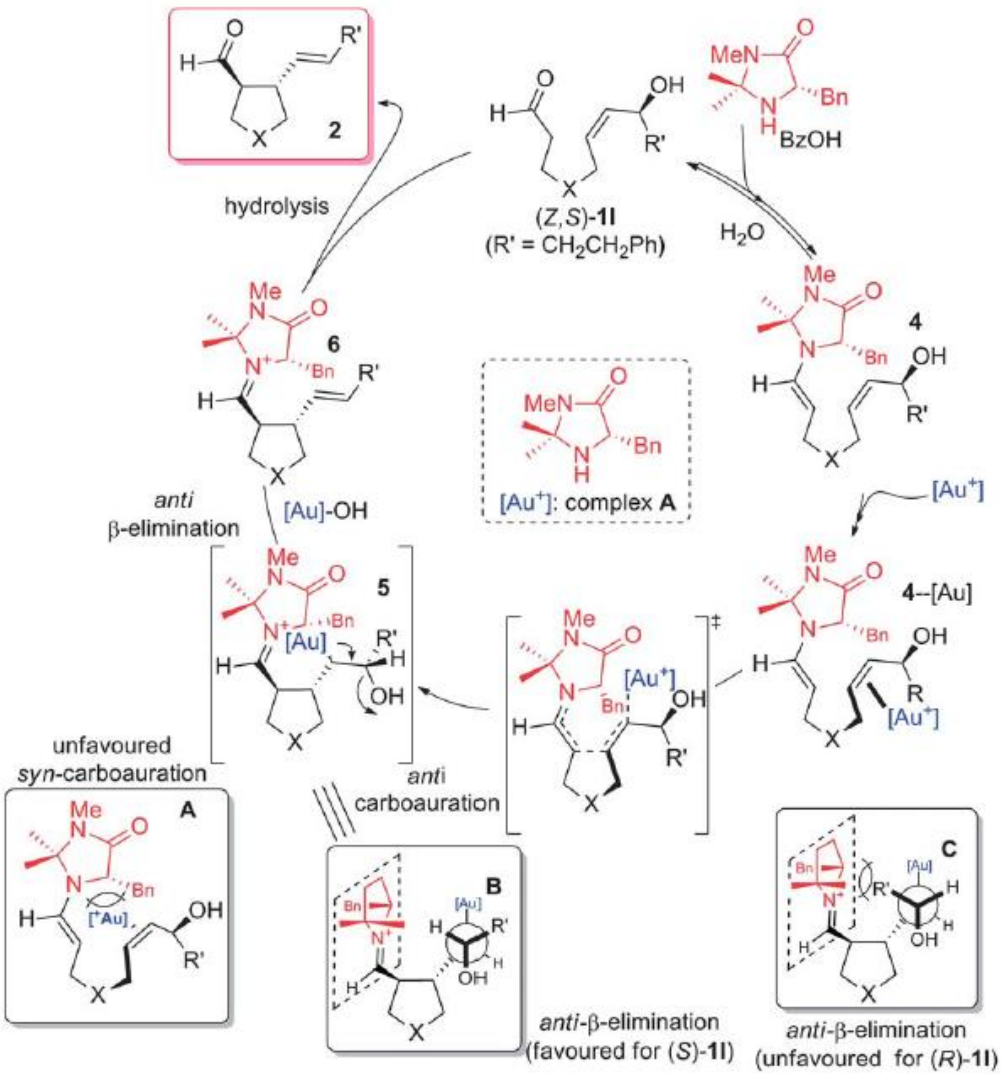
Carreira: Complete control over stereochemistry combining amine and iridium catalysts[2]



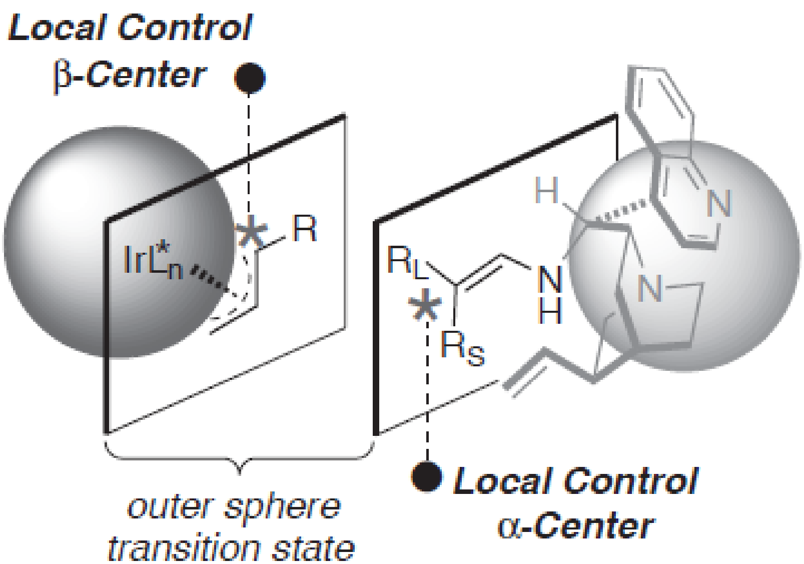
(1) Chiarucci, M.; di Lillo, M.; Romaniello, A.; Cozzi, P. G.; Cera, G.; Bandini, M. *Chemical Science* **2012**, *3*, 2859. (2) Krautwald, S.; Sarlah, D.; Schafroth, M. A.; Carreira, E. M. *Science* **2013**, *340*, 1065.

4.3. Metal-Ligand Dual Activation: Enamine/Metal

Bandini: Enamine-Gold Catalysis[1]



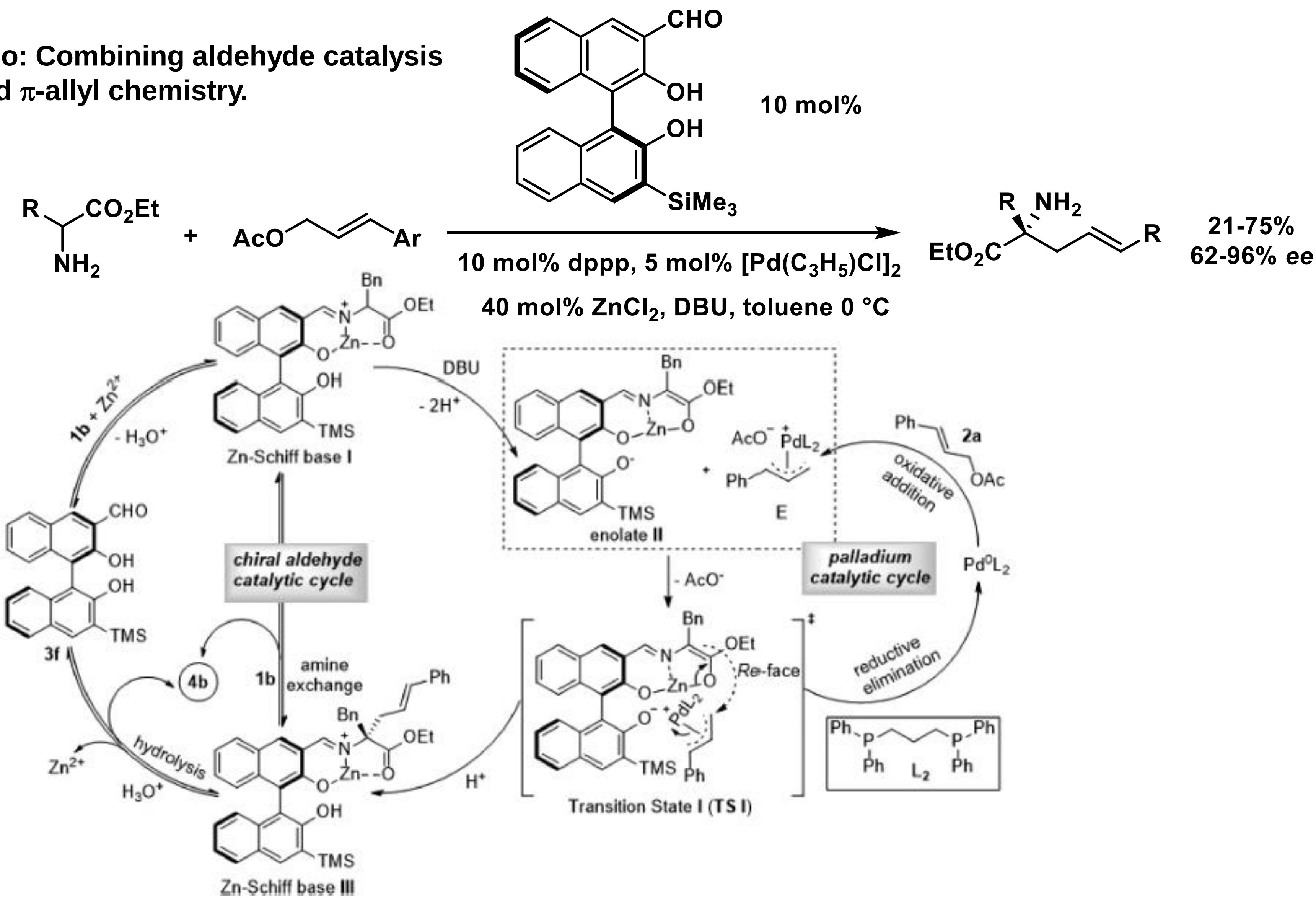
Carreira: Enamine-Iridium Catalysis[2]



(1) Chiarucci, M.; di Lillo, M.; Romaniello, A.; Cozzi, P. G.; Cera, G.; Bandini, M. *Chemical Science* **2012**, *3*, 2859. (2) Krautwald, S.; Sarlah, D.; Schafroth, M. A.; Carreira, E. M. *Science* **2013**, *340*, 1065.

4.3. Metal-Ligand Dual Activation: aldehyde/Pd

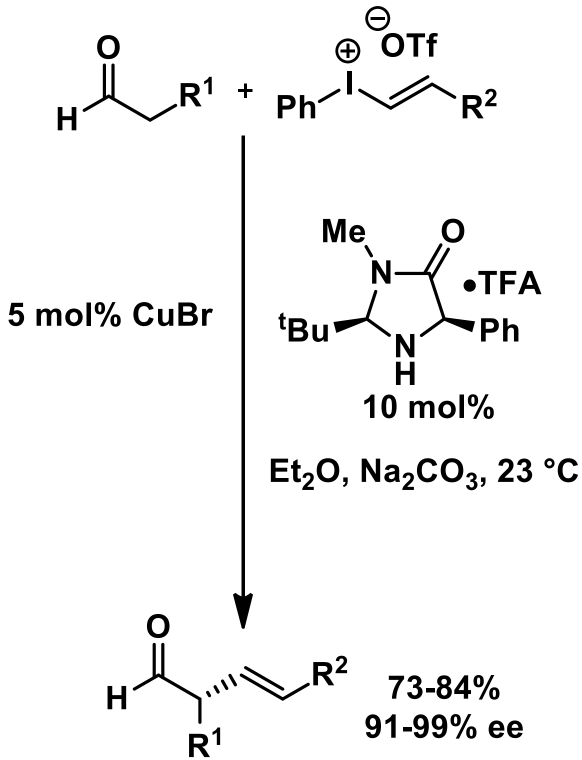
Guo: Combining aldehyde catalysis and π-allyl chemistry.

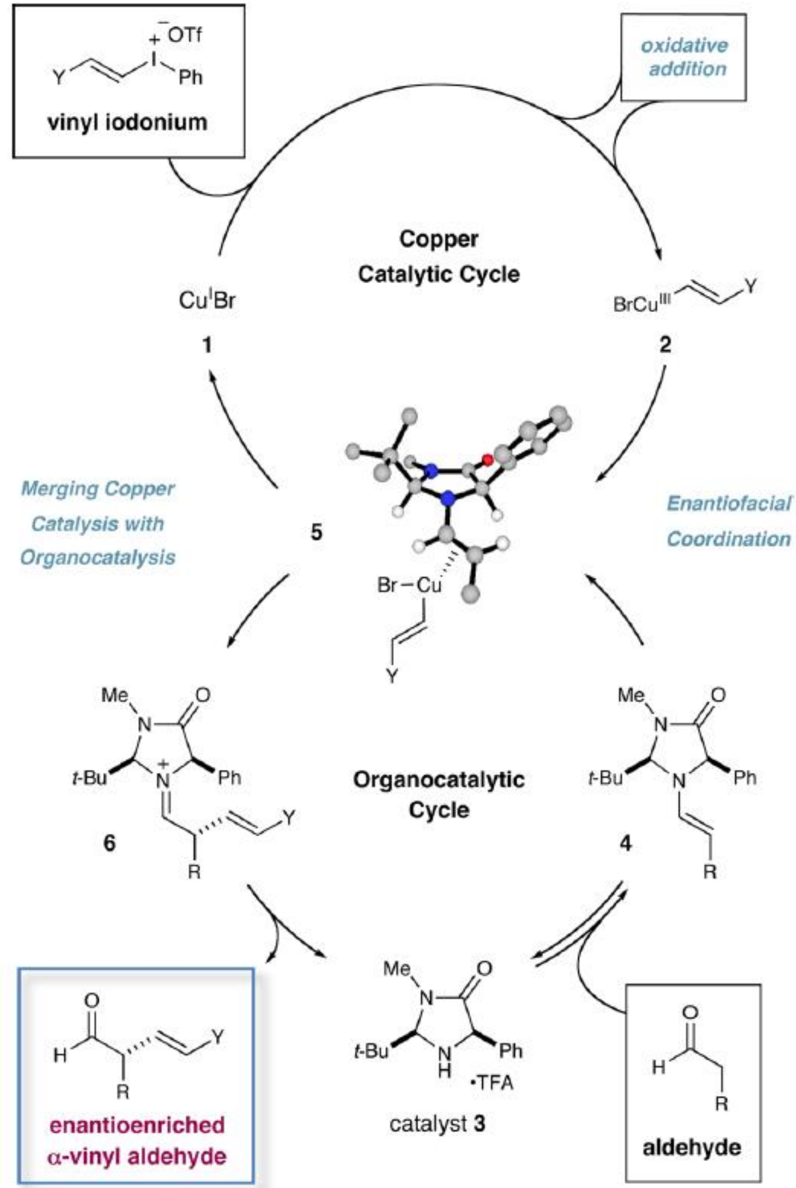


Chen, L.; Luo, M. J.; Zhu, F.; Wen, W.; Guo, Q. X., *J. Am. Chem. Soc.* **2019**, *141*, 5159-5163.

4.3. Metal-Ligand Dual Activation: Enamine/Metal

MacMillan: Vinylation of aldehydes combining enamine and copper catalysis[1]

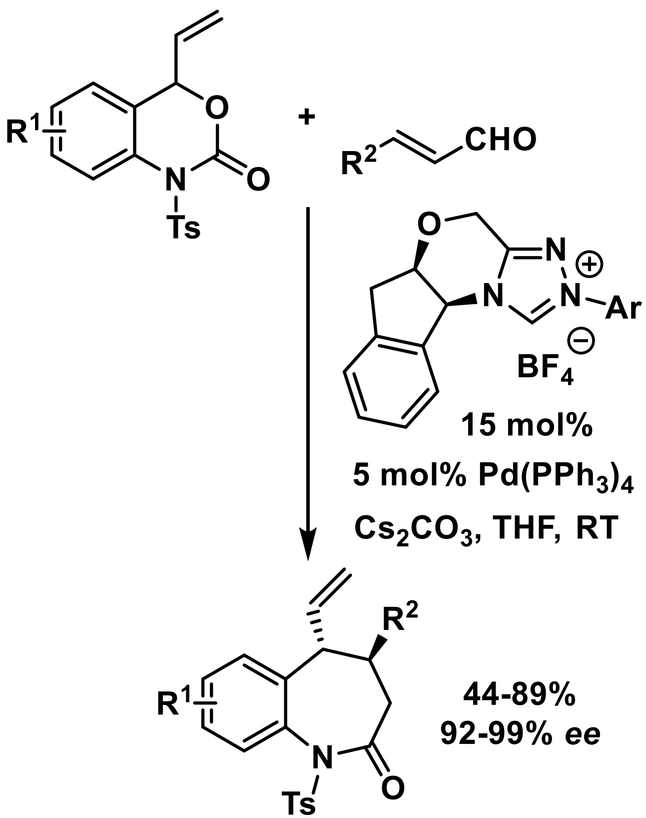


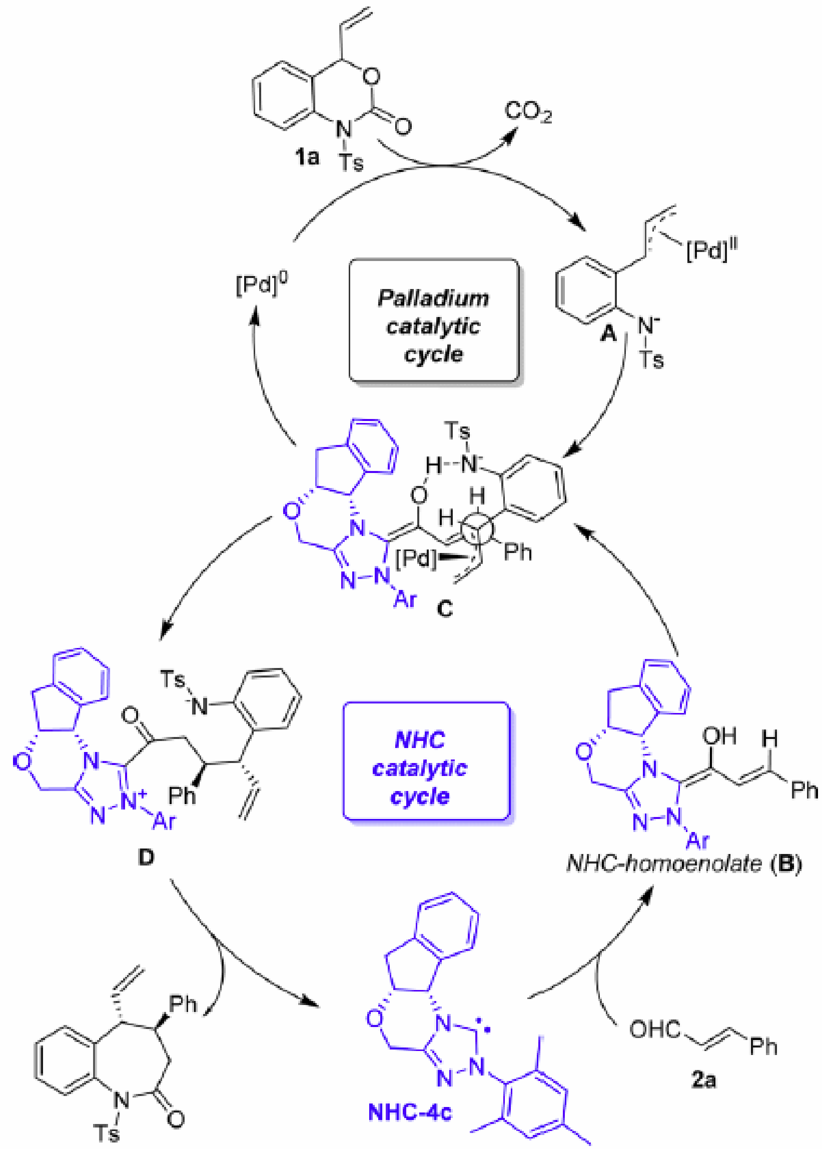


(1) Skucas, E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2012**, *134*, 9090.

4.3. Metal-Ligand Dual Activation: Carbene/Metal

Glorius: NHC-Palladium catalysis

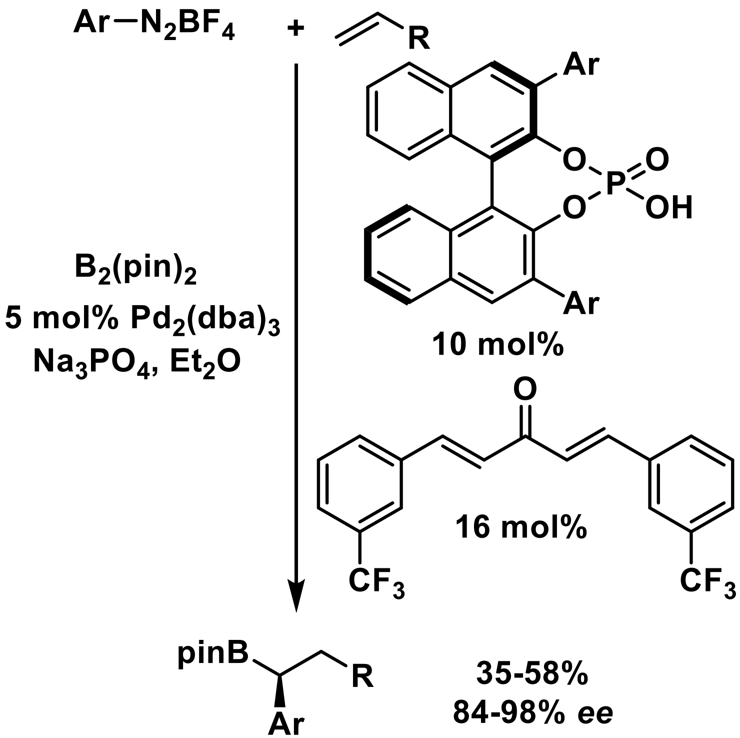


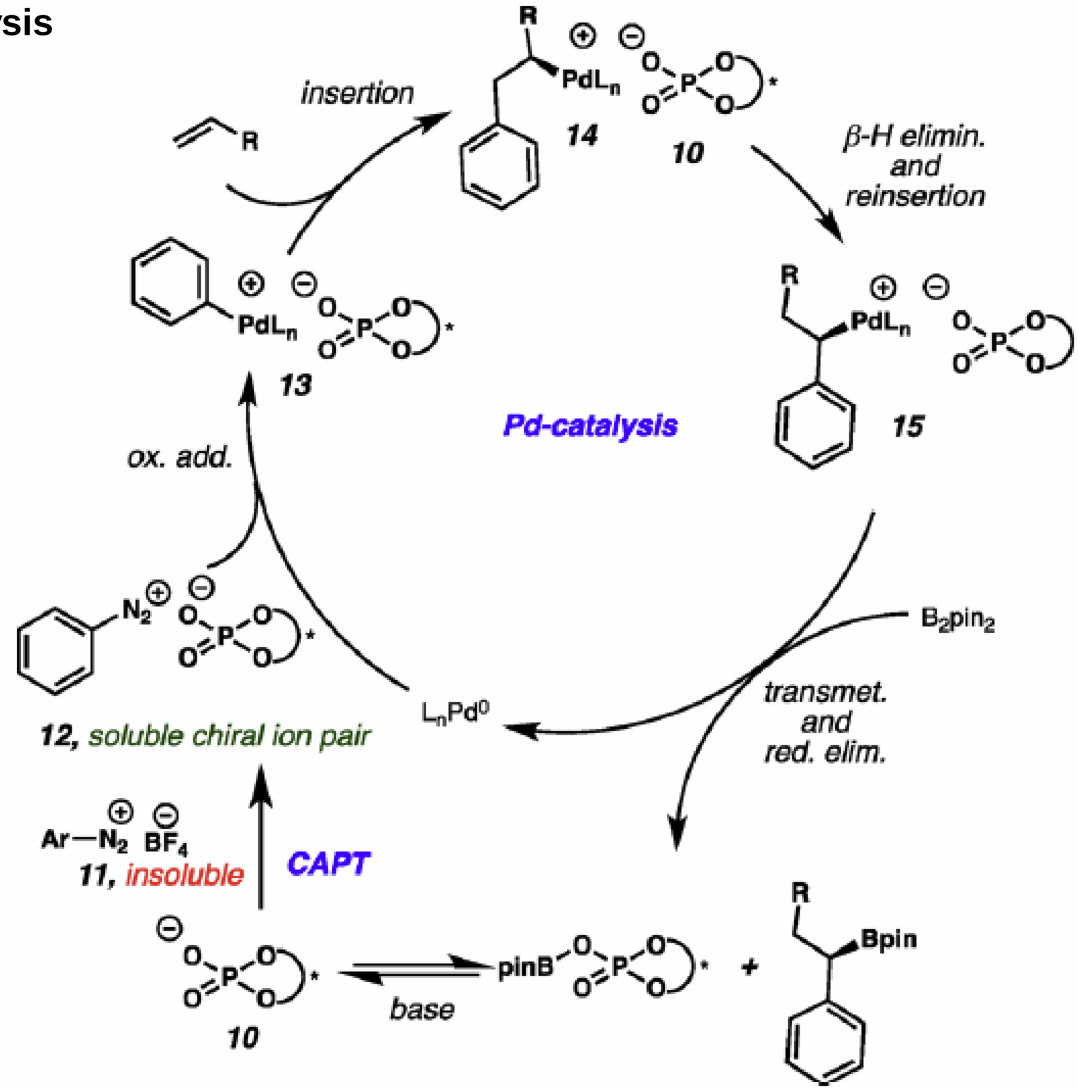


Guo, C.; Fleige, M.; Janssen-Muller, D.; Daniliuc, C. G.; Glorius, F. *J. Am. Chem. Soc.* **2016**, *138*, 7840-7843.

4.3. Metal-Ligand Dual Activation: Palladium/PTC

Toste: Palladium and phase transfer catalysis

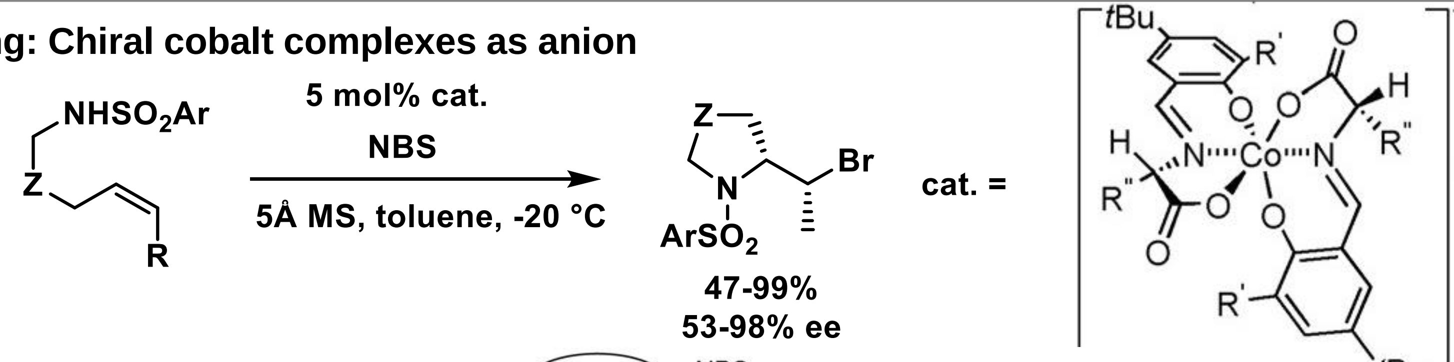


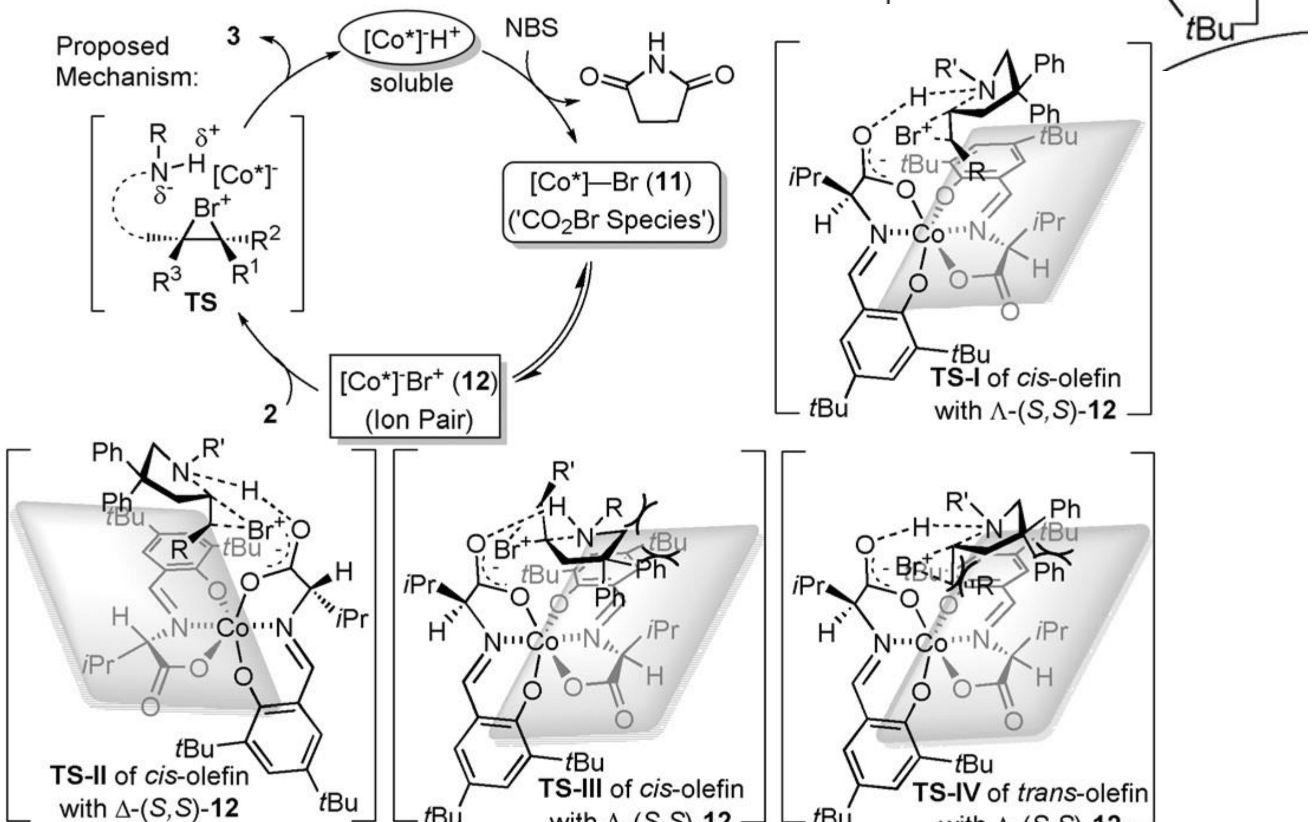


Nelson, H. M.; Williams, B. D.; Miro, J.; Toste, F. D. *J. Am. Chem. Soc.* **2015**, *137*, 3213-3216.

4.3. Metal-Ligand Dual Activation: Bromonium/PTC

Gong: Chiral cobalt complexes as anion

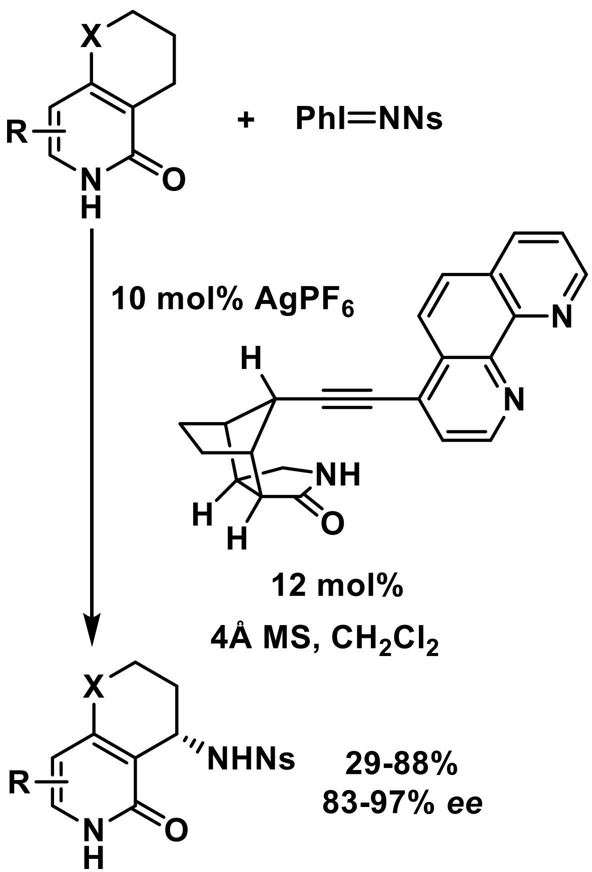


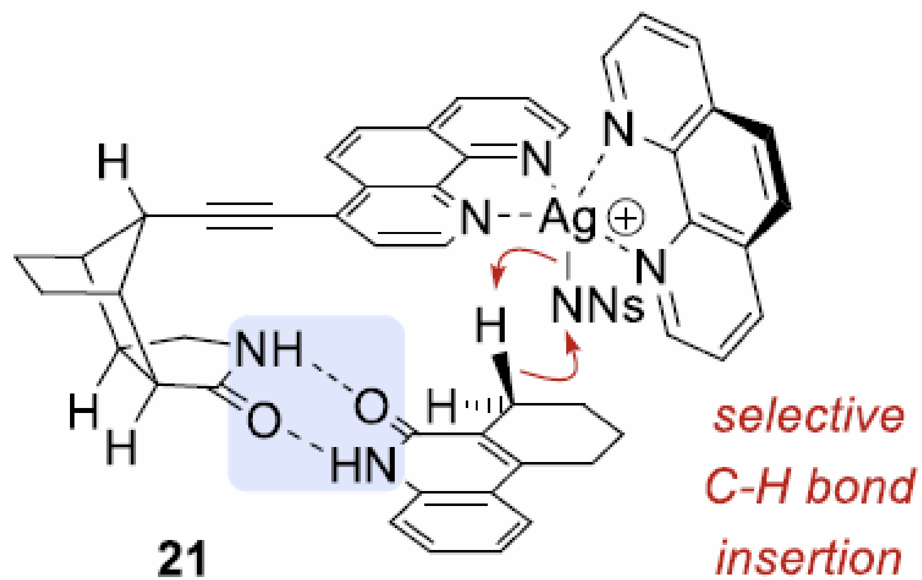


Jiang, H. J.; Liu, K.; Yu, J.; Zhang, L.; Gong, L. Z. *Angew. Chem., Int. Ed.* **2017**, *56*, 11931-11935.

4.3. Metal-Ligand Dual Activation: Nitrene/H bonding

Bach: H-bonding directed nitrene insertion





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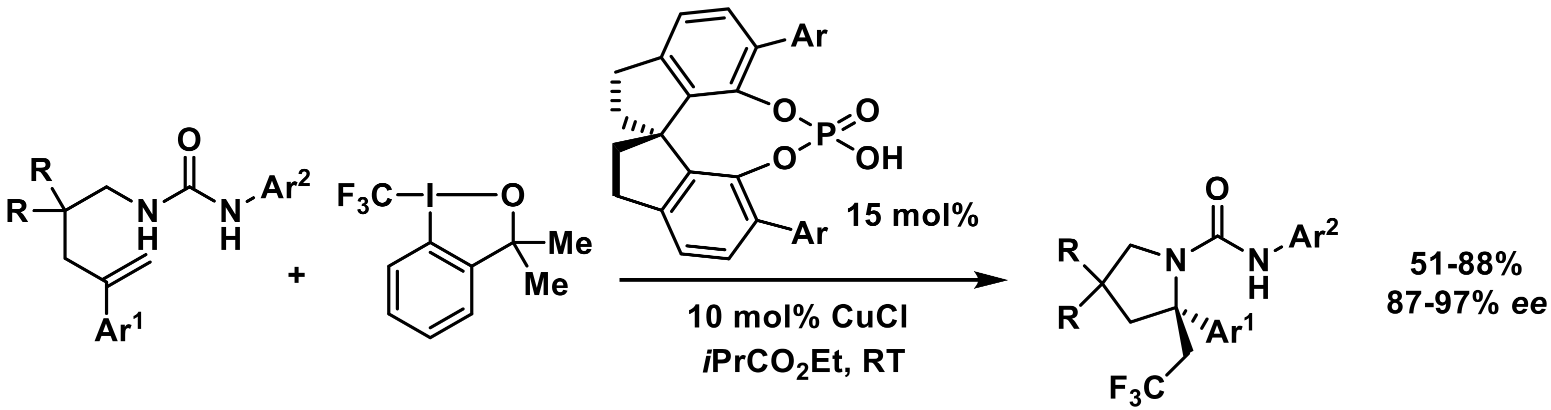
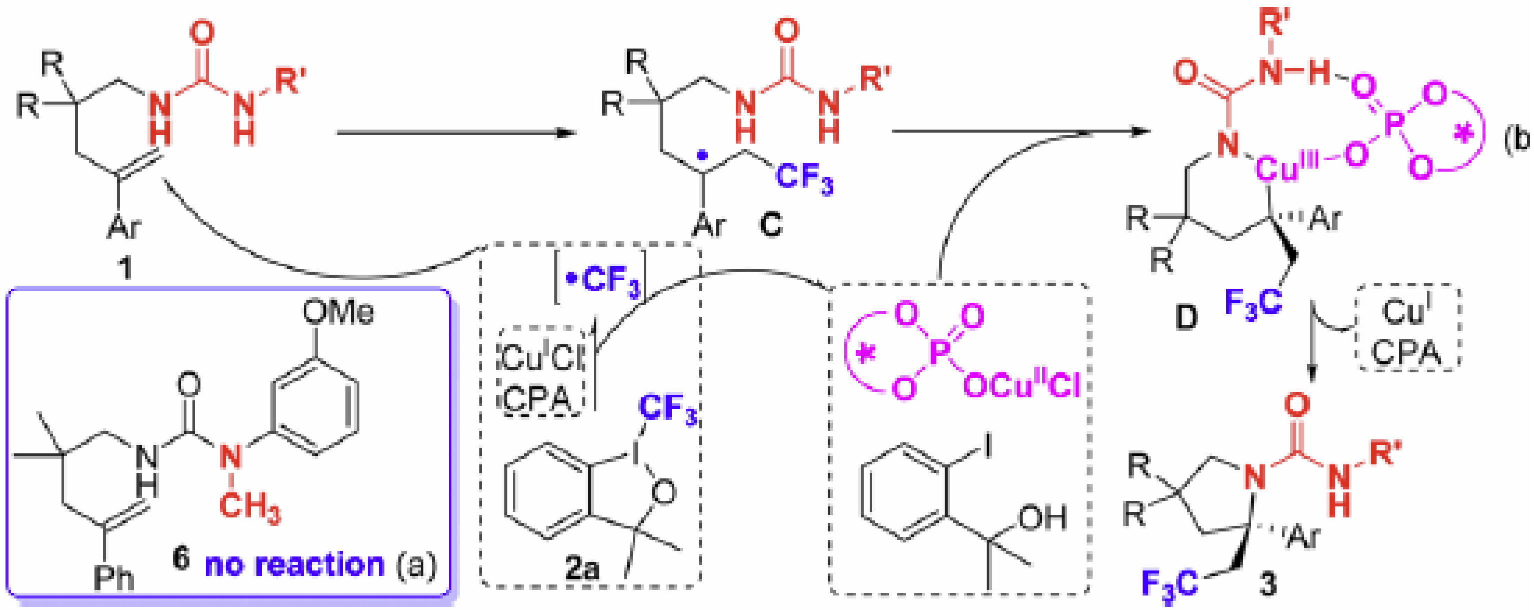
Annapureddy, R. R.; Jandl, C.; Bach, T. *J. Am. Chem. Soc.* **2020,** *142*, 7374-7378.

4.3. Metal-Ligand Dual Activation: Radicals

Liu: Combining radical chemistry, copper catalysis and chiral phosphates





Lin, J. S.; Dong, X. Y.; Li, T. T.; Jiang, N. C.; Tan, B.; Liu, X. Y. *J. Am. Chem. Soc.* **2016**, *138*, 9357-9360.

4.4 Dual Activation on Two Metal Centers

4.4.1 Aldol and Mannich Reactions

4.4.2 Addition of Metal Alkyl Reagents

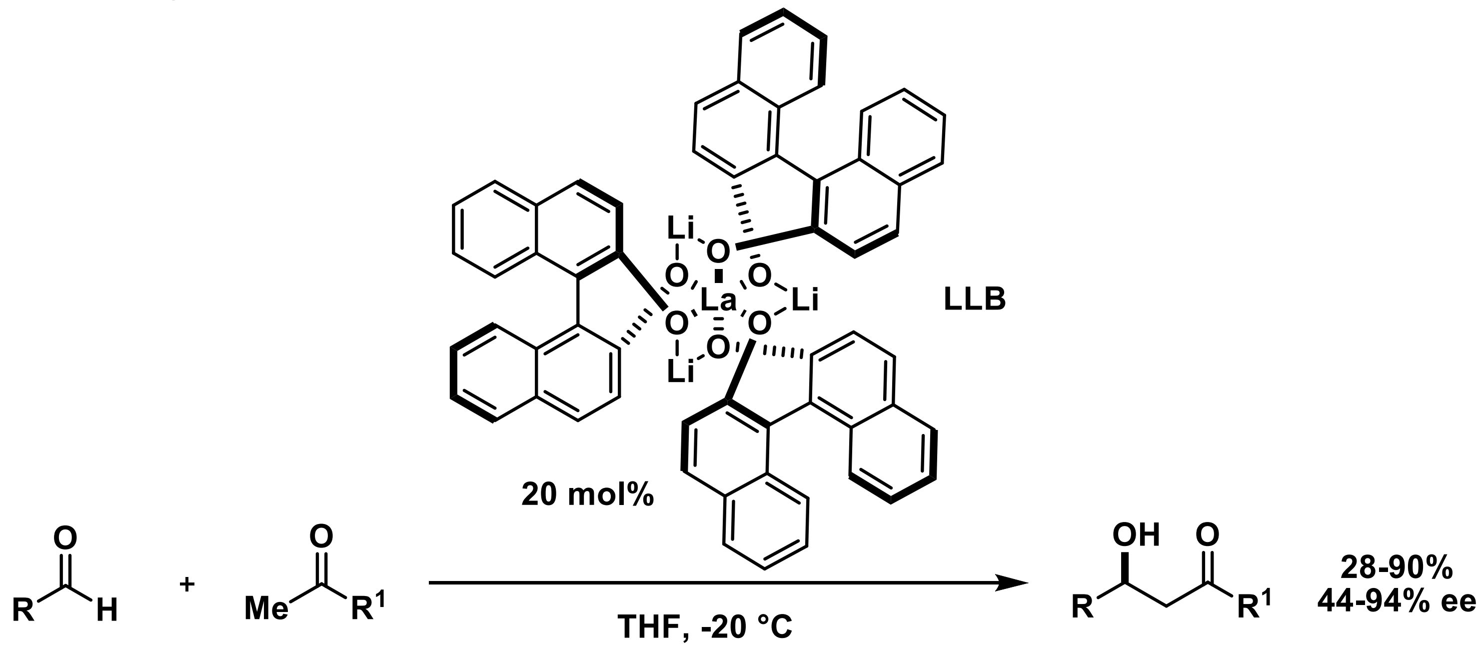
4.4.3 Other Additions to Carbonyl and Imines

4.4.4 Conjugate Addition

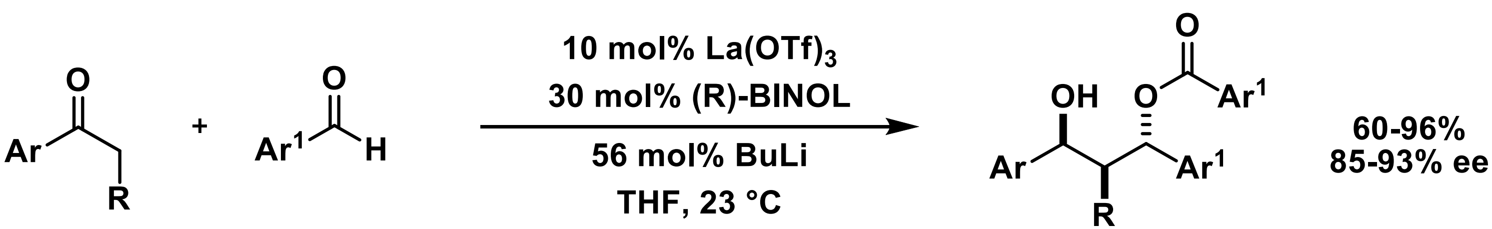
4.4.5 Other Reactions

4.4.1 Aldol and Mannich Reactions: Shibasaki

Shibasaki: LLB Catalyst for the Direct Aldol Reaction[1]



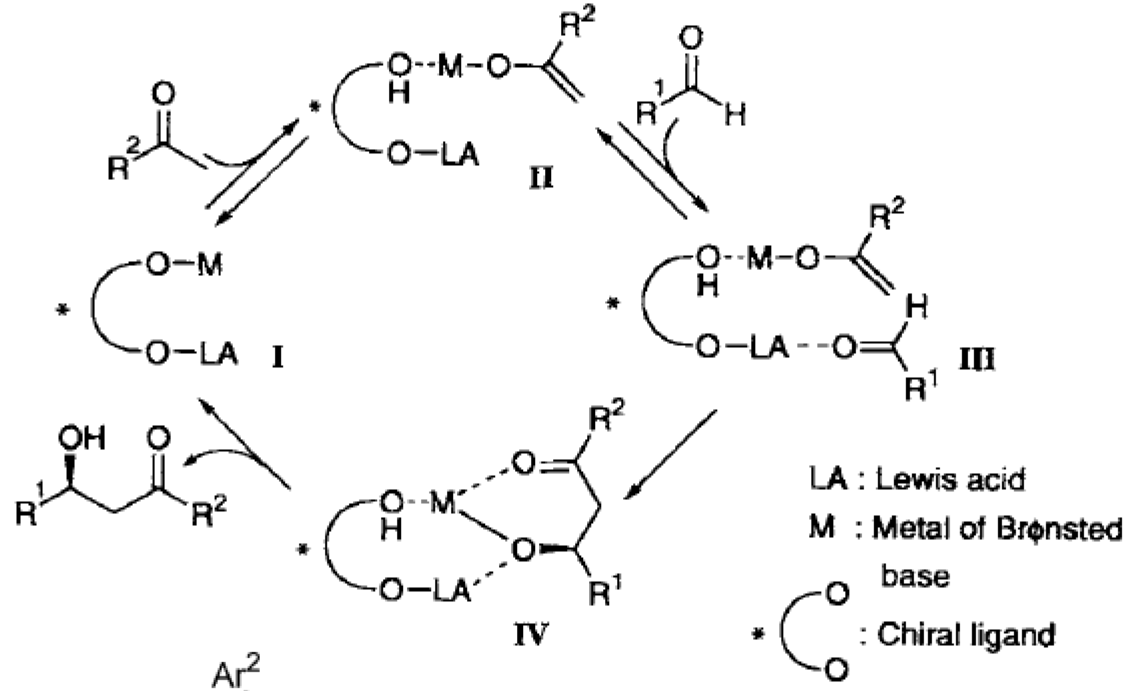
Shibasaki: Aldol-Tischenko Reaction[2]



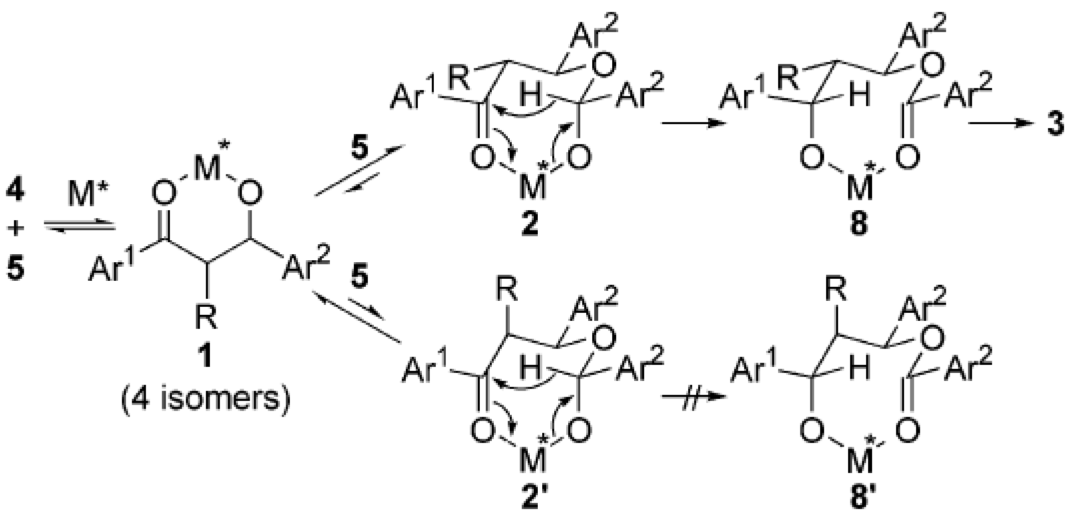
(1) Yamada, Y. M. A.; Yoshikawa, N.; Sasai, H.; Shibasaki, M. *Angew. Chem., Int. Ed. Engl.* **1997,** *36,* 1871-1873. (2) Gnanadesikan, V.; Horiuchi, Y.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2004,** *126,* 7782-7783.

4.4.1 Aldol and Mannich Reactions: Shibasaki

General Mechanism for the Aldol Reaction[1]



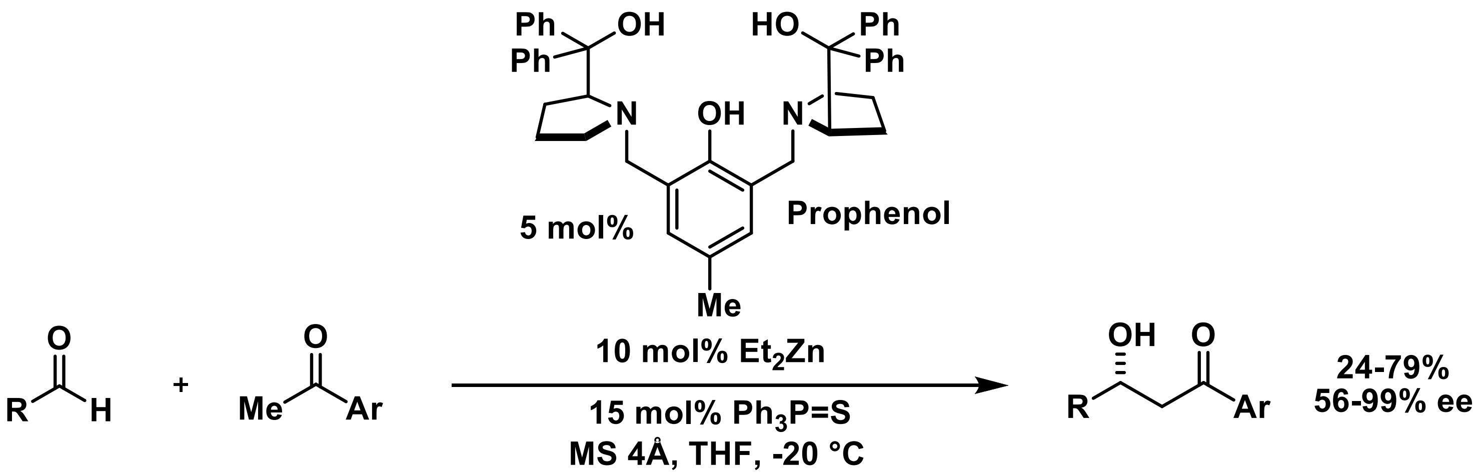
Mechanism for the Tischenko Reaction[2]

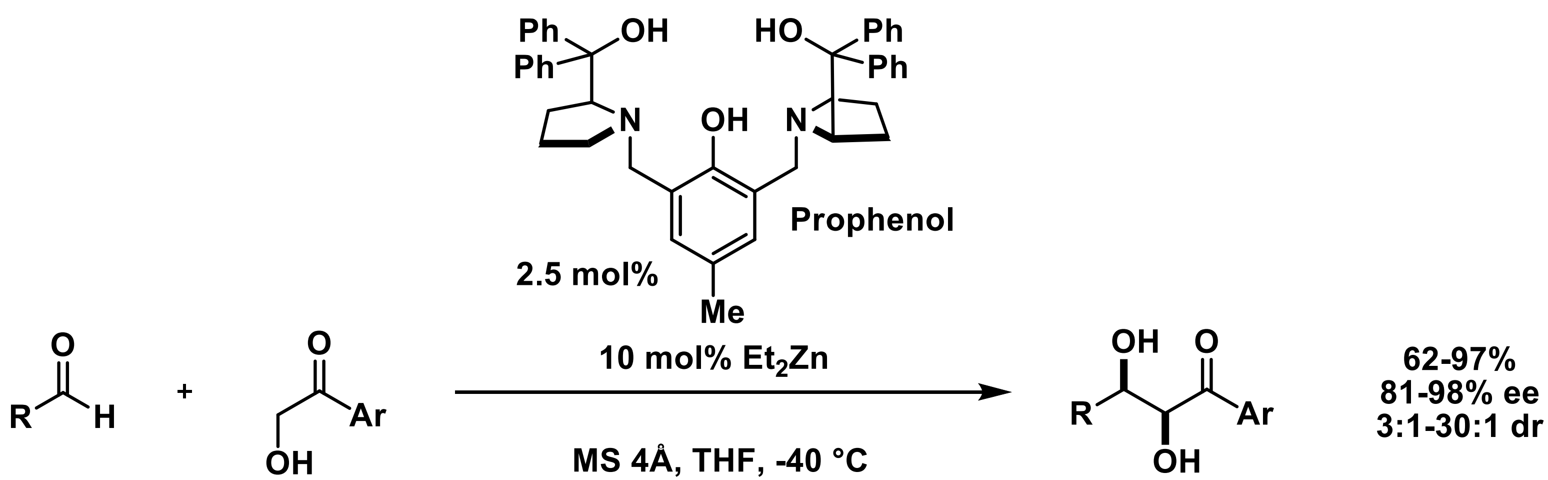


(1) Yamada, Y. M. A.; Yoshikawa, N.; Sasai, H.; Shibasaki, M. *Angew. Chem., Int. Ed. Engl.* **1997,** *36,* 1871-1873. (2) Gnanadesikan, V.; Horiuchi, Y.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2004,** *126,* 7782-7783.

4.4.1 Aldol and Mannich Reactions: Trost

Trost: Direct Aldol Reaction with Bis-Zn Catalysts

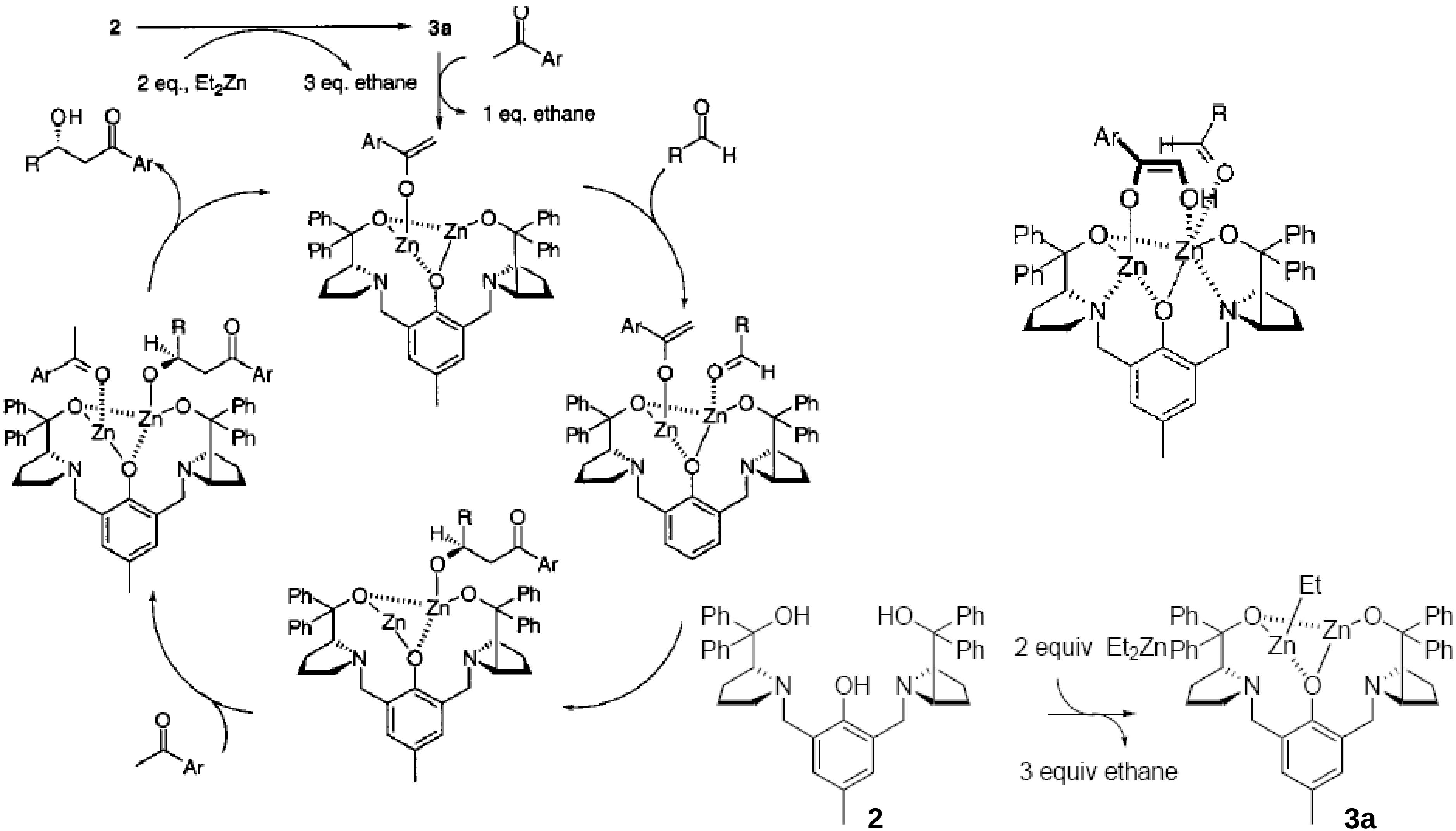




(1) Trost, B. M.; Ito, H. *J. Am. Chem. Soc.* **2000,** *122,* 12003-12004. (2) Trost, B. M.; Ito, H.; Silcoff, E. R. *J. Am. Chem. Soc.* **2001,** *123,* 3367-3368.

4.4.1 Aldol and Mannich Reactions: Trost

Mechanism

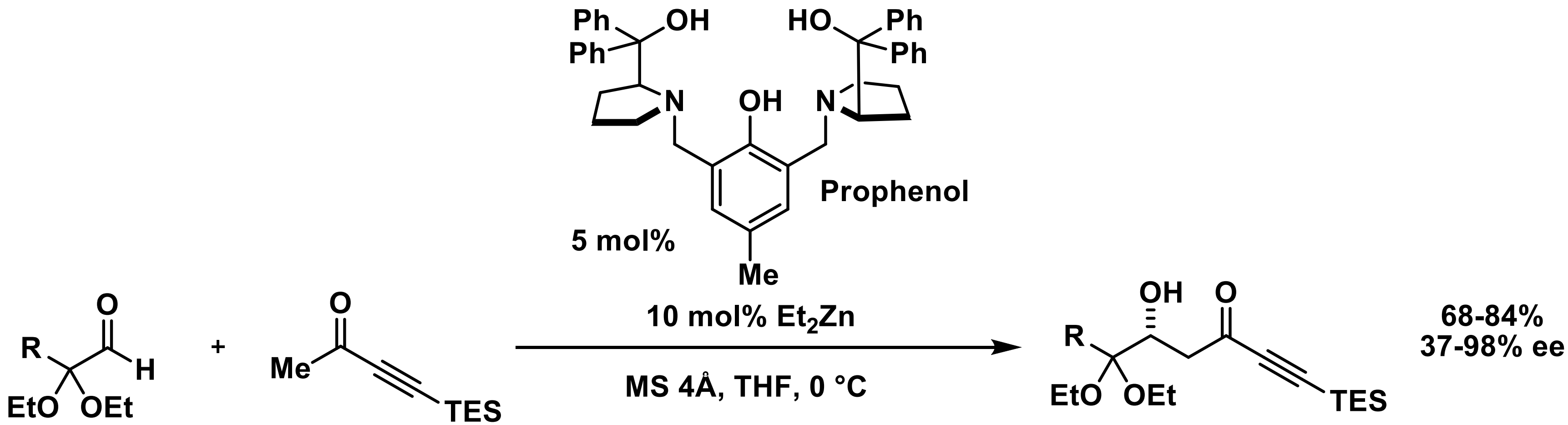


2 **3a**

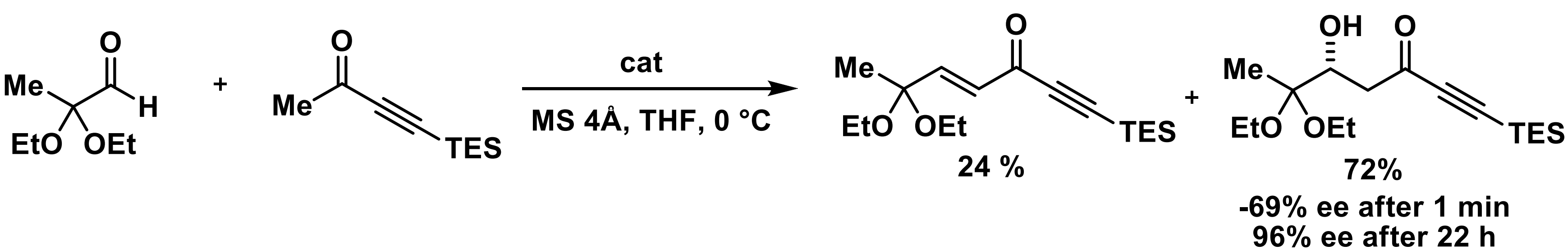
(1) Trost, B. M.; Ito, H. *J. Am. Chem. Soc.* **2000,** *122,* 12003-12004. (2) Trost, B. M.; Ito, H.; Silcoff, E. R. *J. Am. Chem. Soc.* **2001,** *123,* 3367-3368.

4.4.1 Aldol and Mannich Reactions: Trost

Trost: Aldol Using Alkynone as Nucleophiles



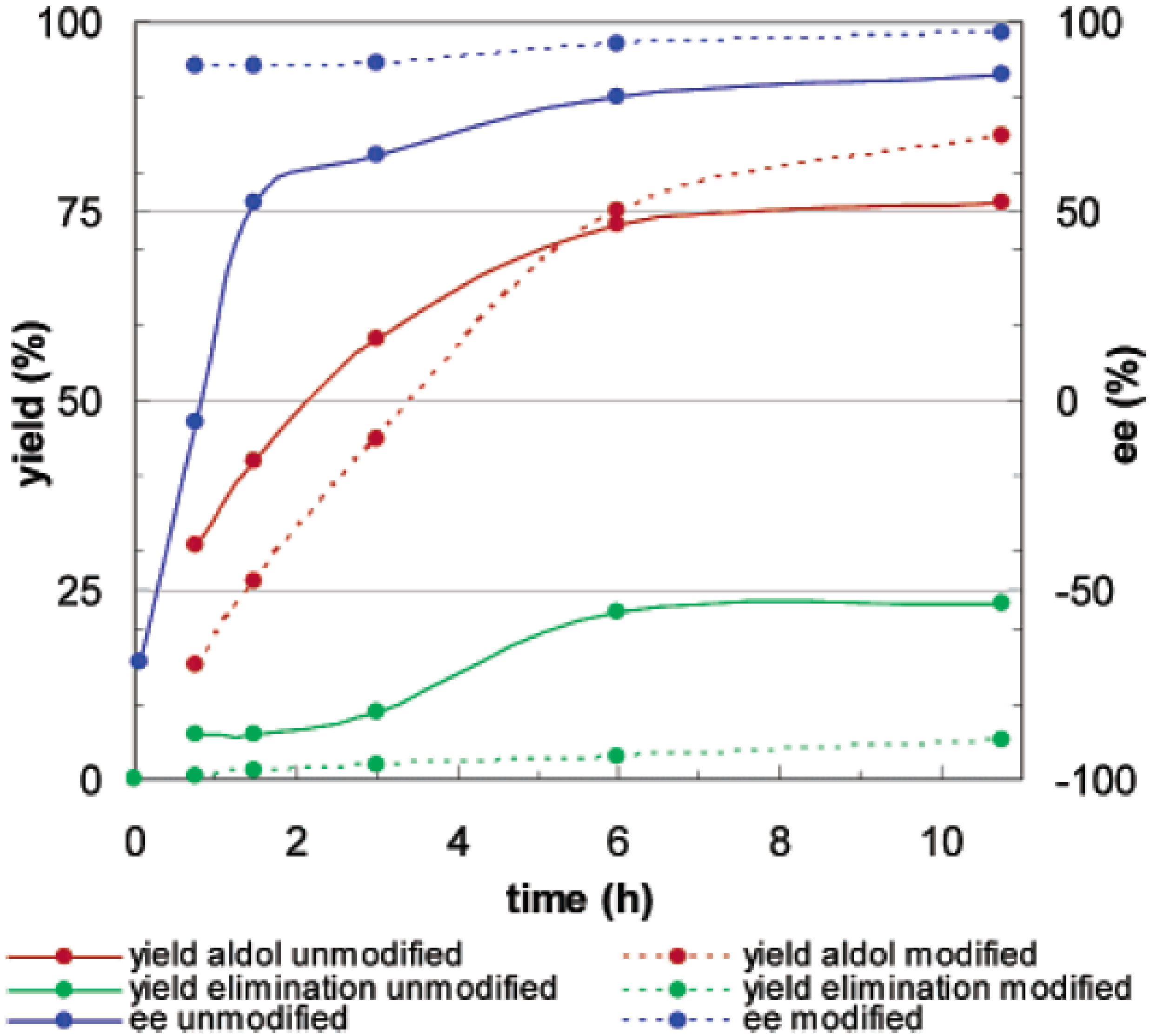
Inversion of the ee During the Reaction!



(1) Trost, B. M.; Fettes, A.; Shireman, B. T. *J. Am. Chem. Soc.* **2004,** *126,* 2660-2661.

4.4.1 Aldol and Mannich Reactions: Trost

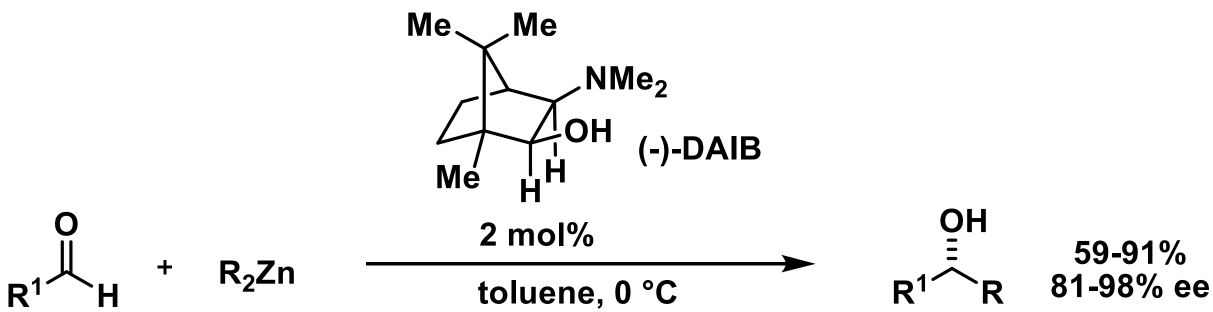
Effect of Adding the Product to the Catalyst Prior to Reaction



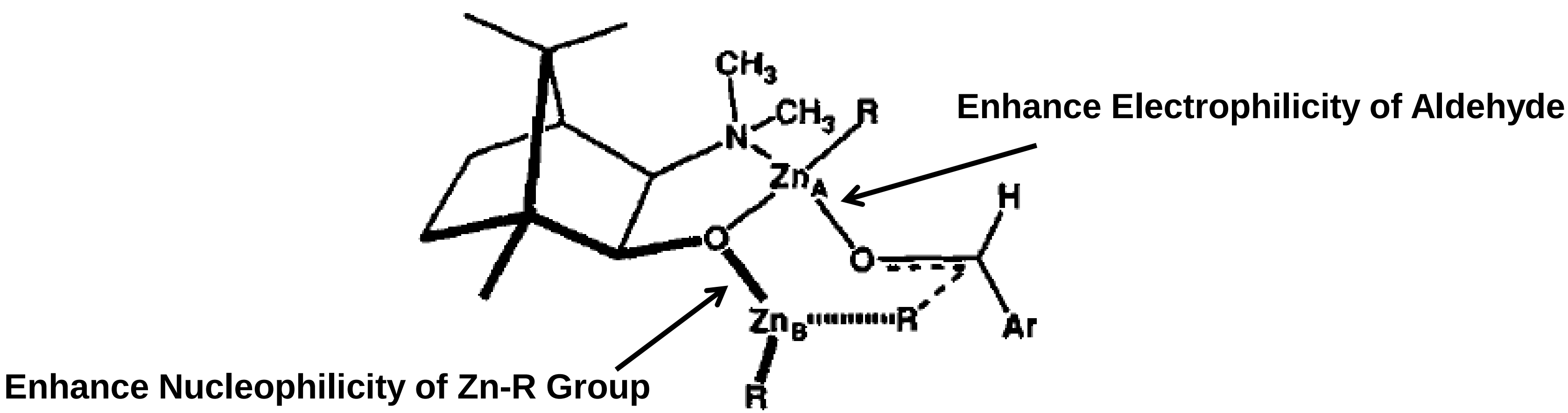
(1) Trost, B. M.; Fettes, A.; Shireman, B. T. *J. Am. Chem. Soc.* **2004,** *126,* 2660-2661.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-Zn Activation

Noyori Seminal Discovery: Addition of Alkyl Zinc to Aldehydes Catalyzed by Amino Alcohols



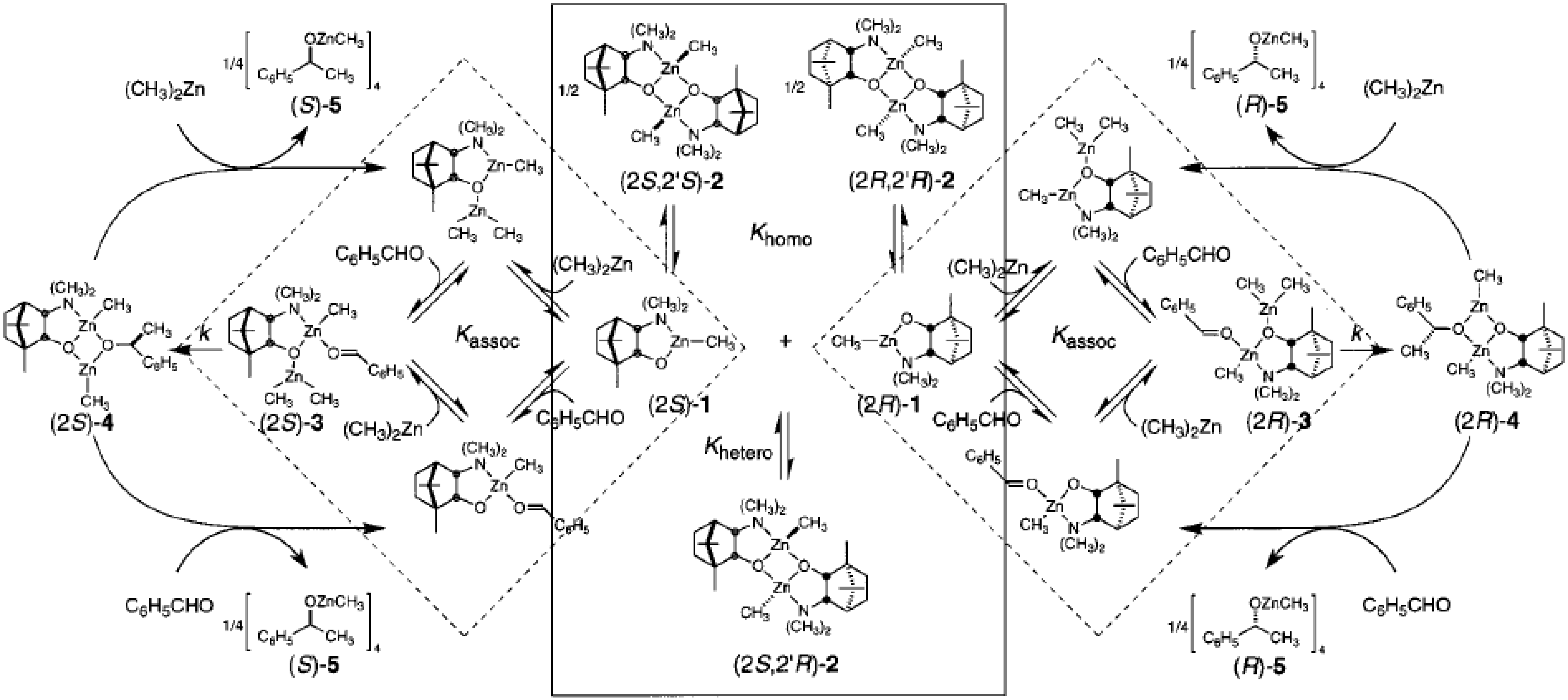
The Principle of Dual Activation with two Zn Centers



(1) Kitamura, M.; Suga, S.; Kawai, K.; Noyori, R. *J. Am. Chem. Soc.* **1986,** *108,* 6071-6072. (2) Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 49-69.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-Zn Activation

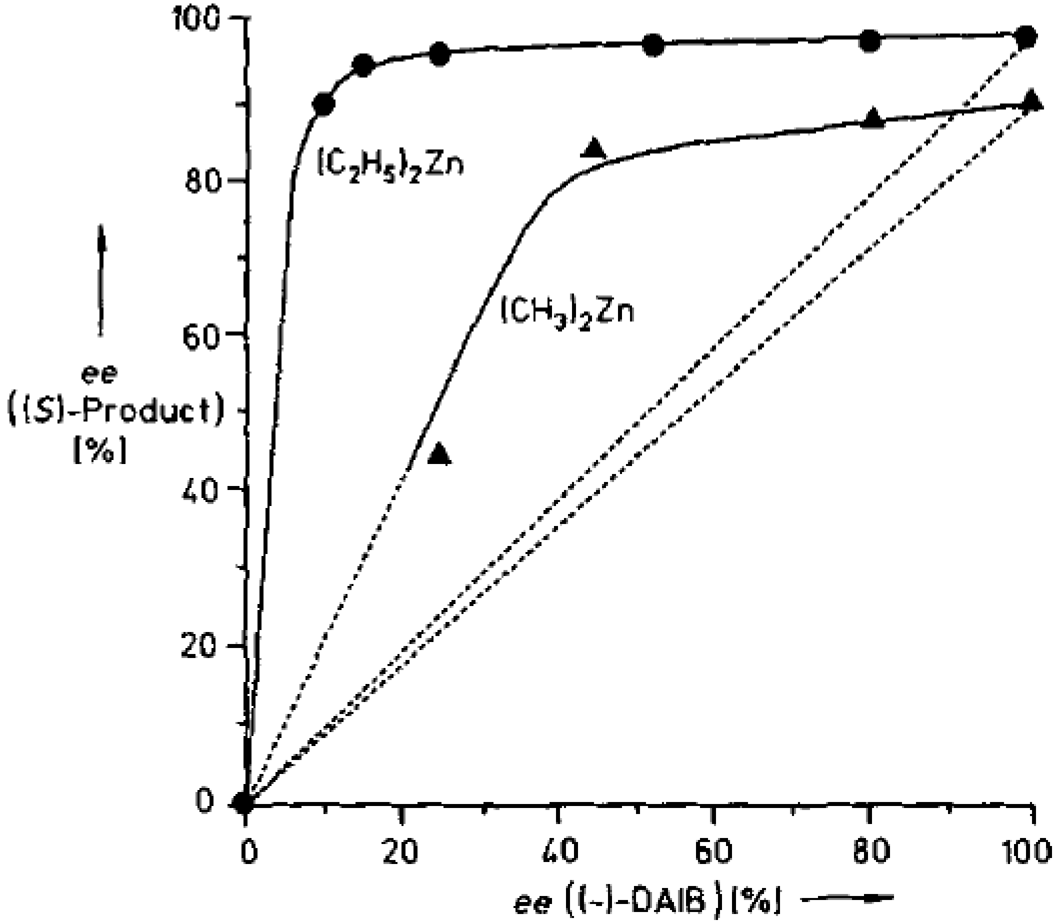
Detailed Mechanism

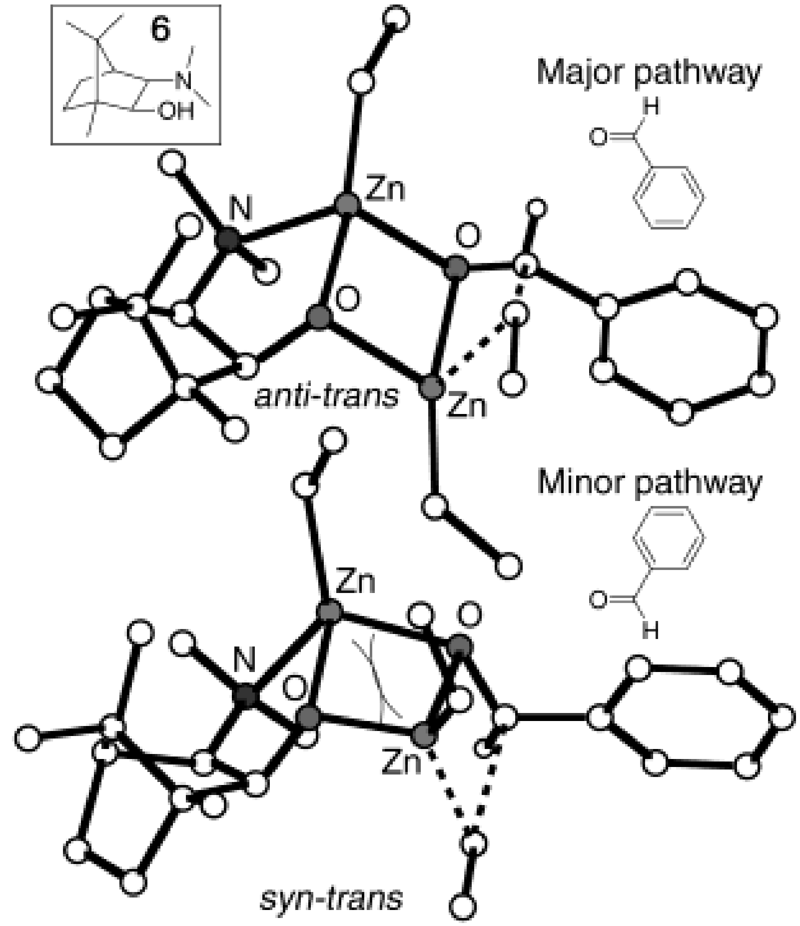


(1) Kitamura, M.; Suga, S.; Oka, H.; Noyori, R. *J. Am. Chem. Soc.* **1998,** *120,* 9800-9809.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-Zn Activation

Non-Linear Effect and Transitions State

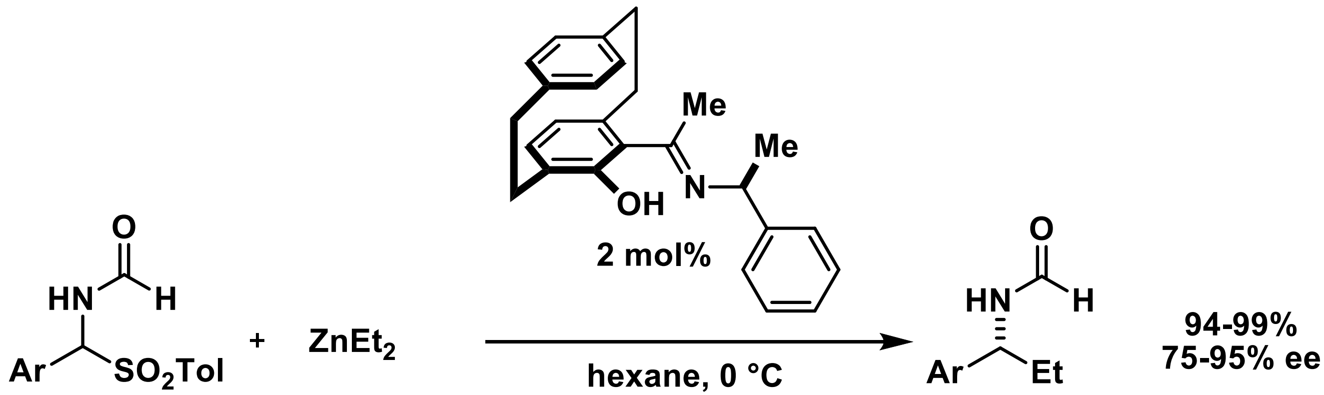




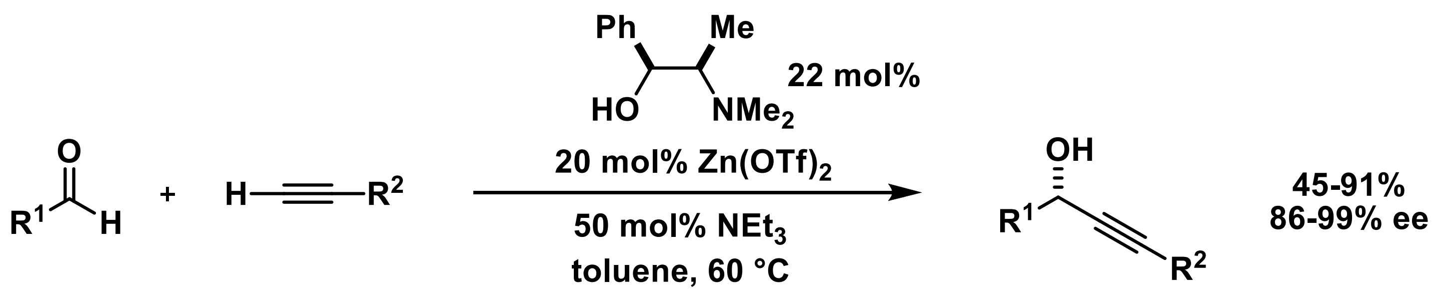
(1) Kitamura, M.; Suga, S.; Oka, H.; Noyori, R. *J. Am. Chem. Soc.* **1998,** *120,* 9800-9809. (2) Rasmussen, T.; Norrby, P. O. *J. Am. Chem. Soc.* **2003,** *125,* 5130-5138.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-Zn Activation

Bräse: Cyclophane Catalyst for Addition of Diethyl Zinc to Imines[1]



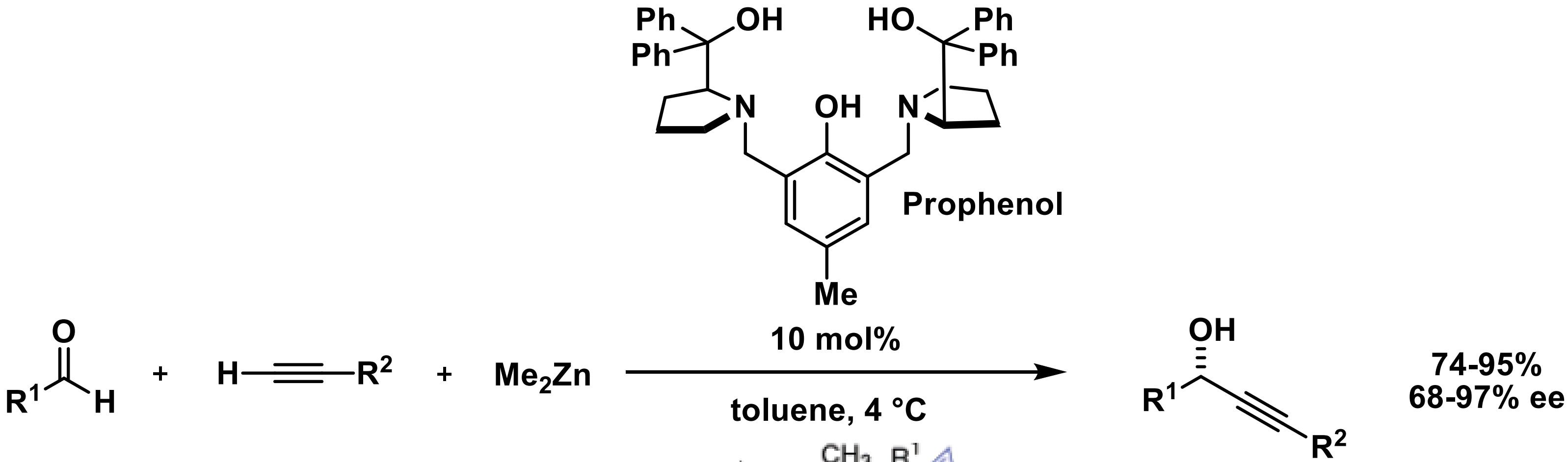
Carreira: In-Situ Formation and Asymmetric Addition of Zn Acetylides[2,3]



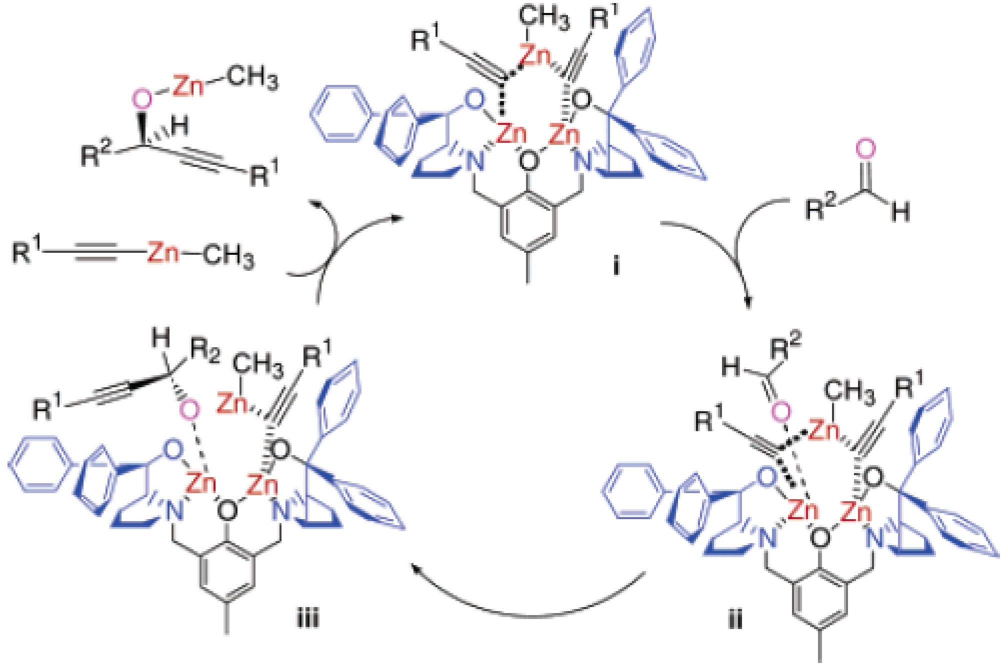
(1) Dahmen, S.; Brase, S. *J. Am. Chem. Soc.* **2002,** *124,* 5940-5941. (2) Frantz, D. E.; Fassler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **2000,** *122,* 1806-1807. (3) Anand, N. K.; Carreira, E. M. *J. Am. Chem. Soc.* **2001,** *123,* 9687-9688.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-Zn Activation

Trost: Addition of Zn-Acetylide Catalyzed by Prophenol Ligand



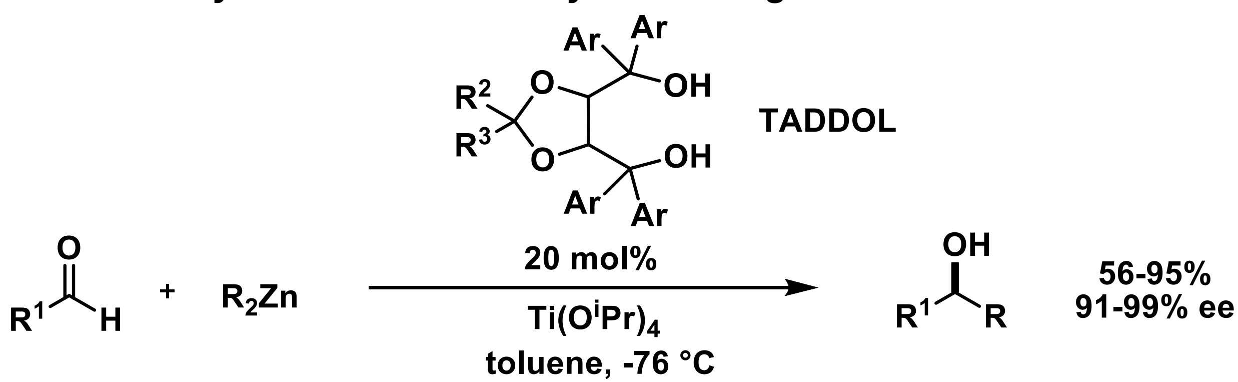
Mechanism



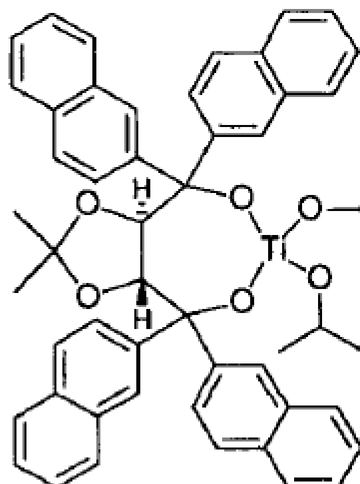
(1) Trost, B. M.; Weiss, A. H.; von Wangelin, A. J. *J. Am. Chem. Soc.* **2006,** *128,* 8-9.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-LA Activation

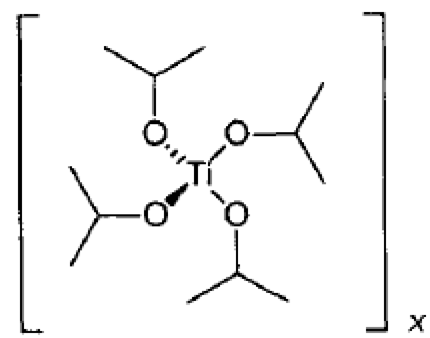
Seebach: Ti-TADDOL-Catalyzed Addition of Alkyl Zinc Reagents



Ligand Accelerating Effect of TADDOL



11



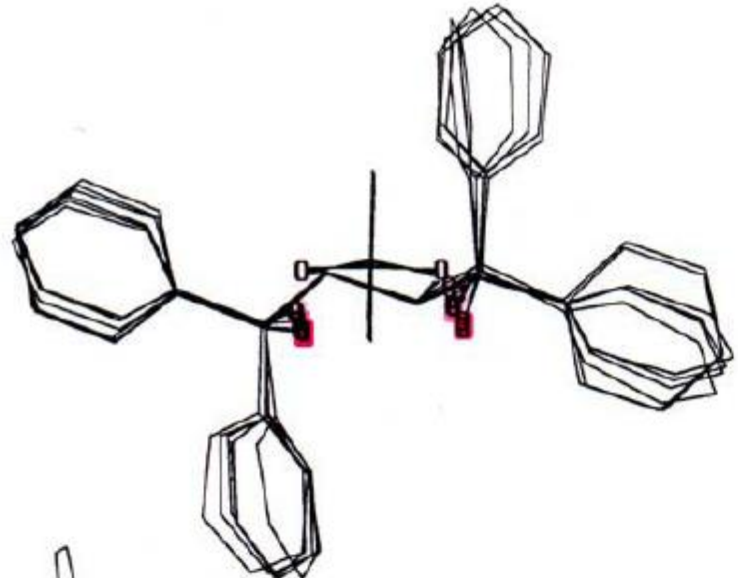
- steric hindrance to coordination
- fast dynamics of ligand exchange

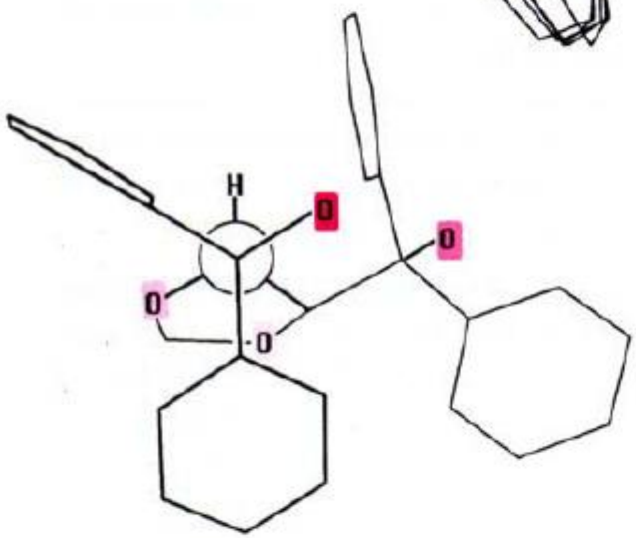
- aggregates or solvated, higher coordinated Ti
- slow ligand exchange

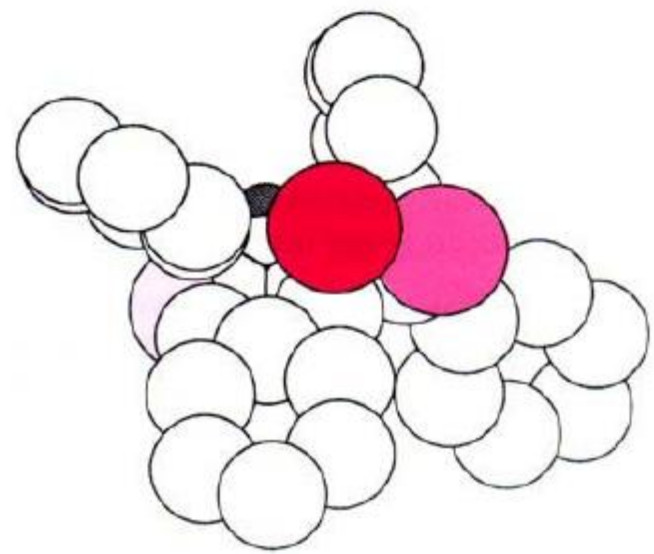
(1) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 1321-1323. (2) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 99-101. (3) Seebach, D.; Beck, A. K.; Heckel, A. *Angew. Chem., Int. Ed.* **2001,** *40,* 92-138.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-LA Activation

Structure of TADDOL



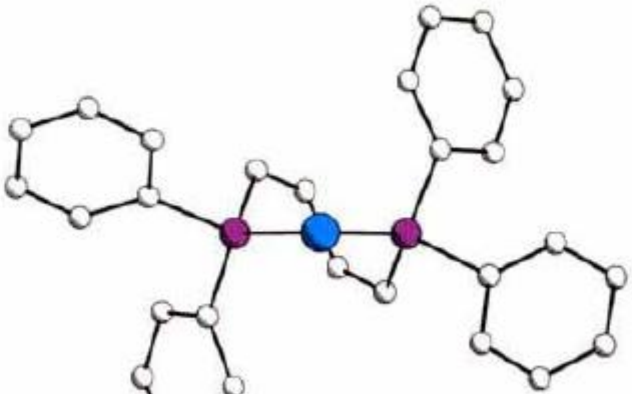




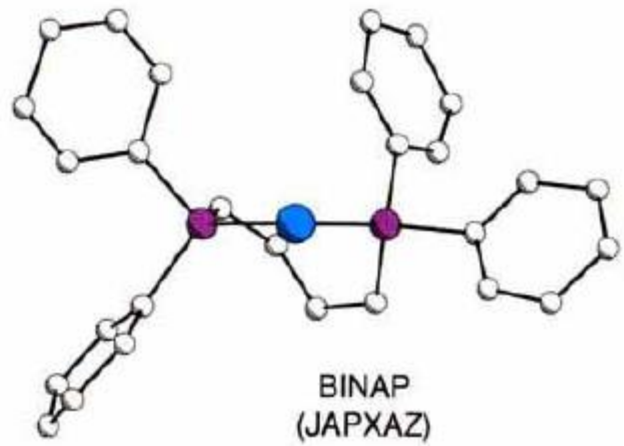
(1) Seebach, D.; Plattner, D. A.; Beck, A. K.; Wang, Y. M.; Hunziker, D.; Petter, W. *Helv. Chim. Acta* **1992,** *75,* 2171-2209.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-LA Activation

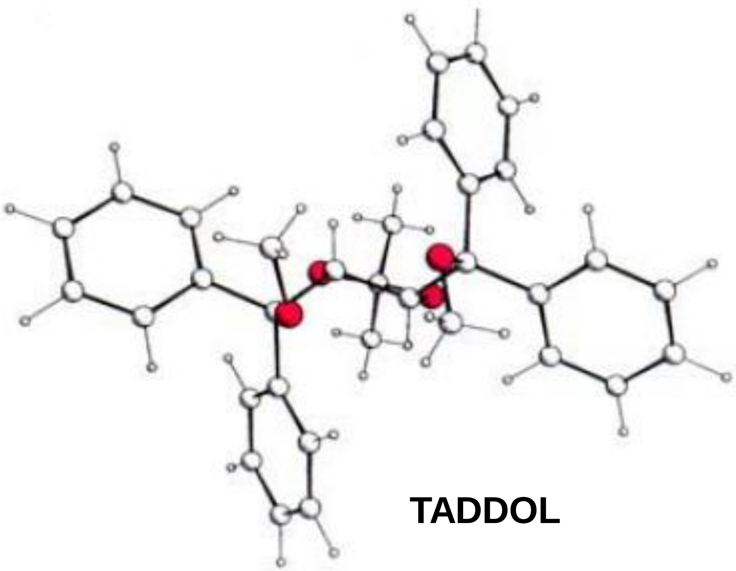
Structure of TADDOL: Comparison with BINAP



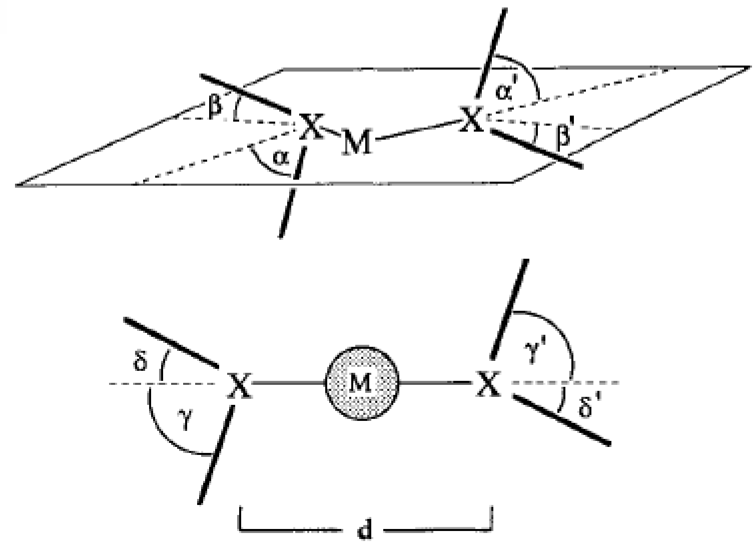
BINAP
(FUXSUM)



BINAP
(JAPXAZ)



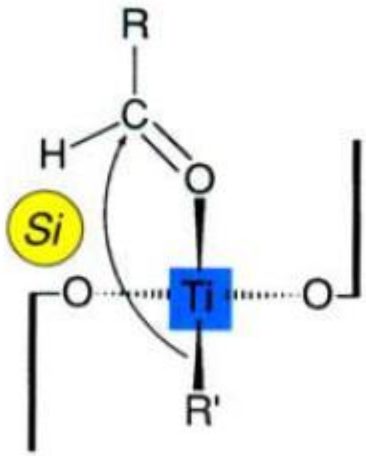
TADDOL



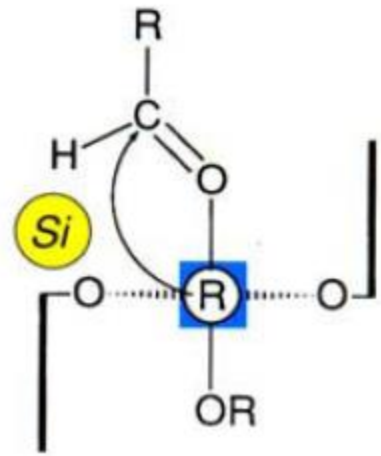
(1) Seebach, D.; Plattner, D. A.; Beck, A. K.; Wang, Y. M.; Hunziker, D.; Petter, W. *Helv. Chim. Acta* **1992,** *75,* 2171-2209.

4.4.2 Addition of Metal-Alkyl Reagents: Zn-LA Activation

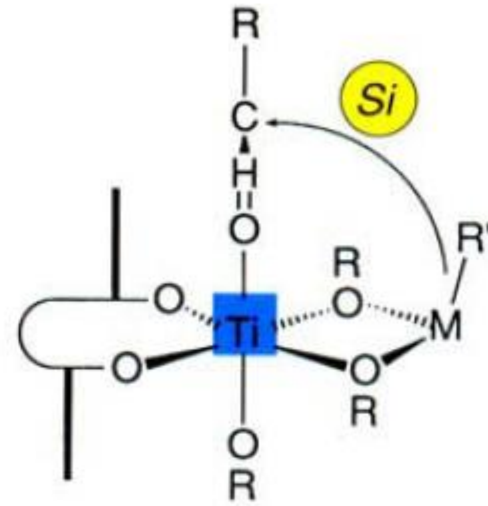
Different Models for Selectivity



tetrahedral

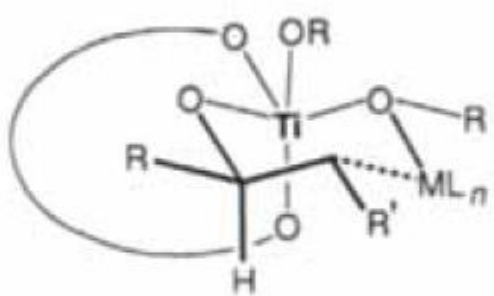


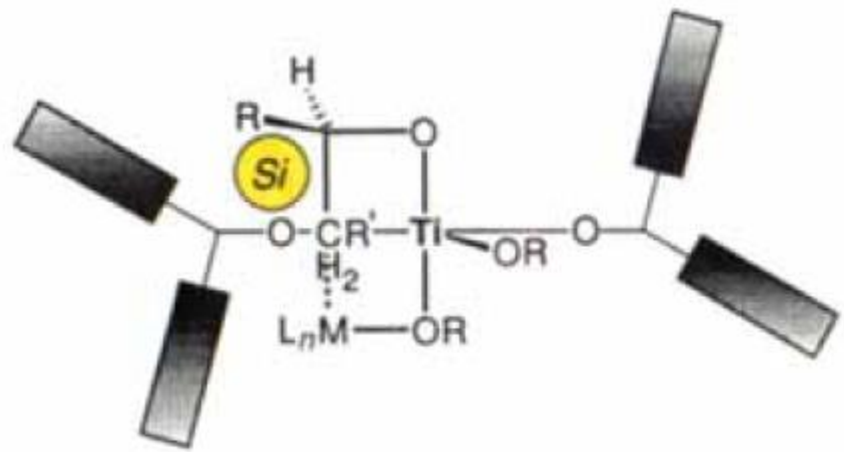
trigonal bipyramidal



octahedral
(bimetallic)

Pentacoordinated Bimetallic

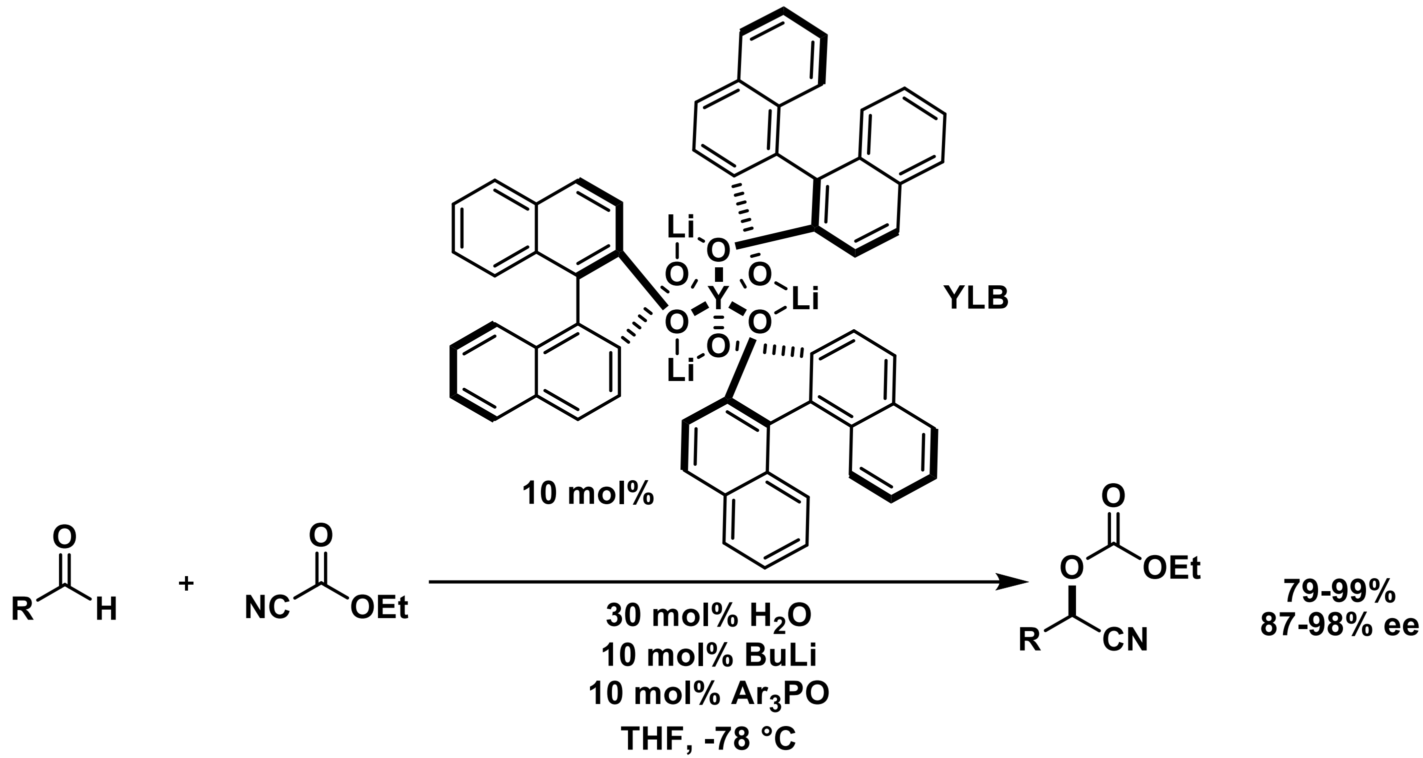




(1) Seebach, D.; Plattner, D. A.; Beck, A. K.; Wang, Y. M.; Hunziker, D.; Petter, W. *Helv. Chim. Acta* **1992,** *75,* 2171-2209.

4.4.3 Other Additions to Carbonyl and Imine: Cyanide

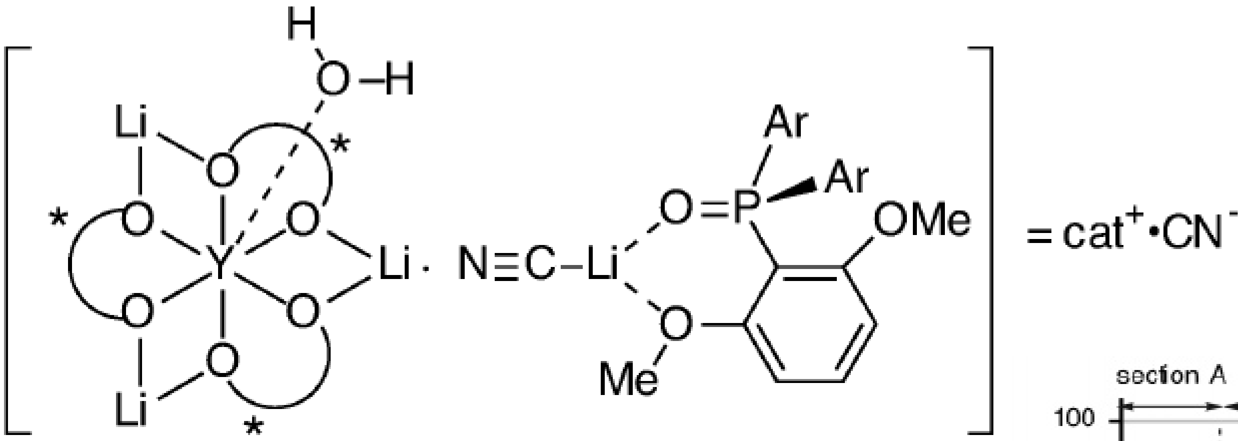
Shibasaki: YLB Catalyst for the Cyanation of Aldehydes



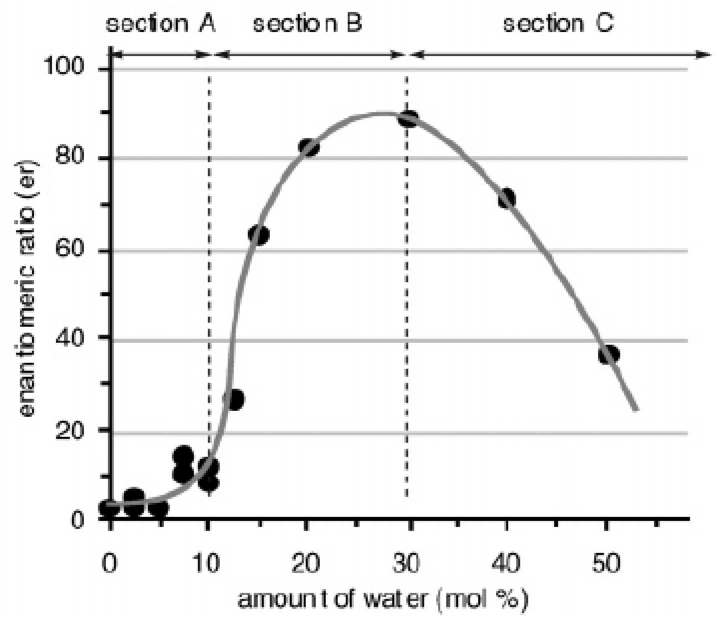
(1) Tian, J.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2002,** *41,* 3636-3638. (2) Yamagiwa, N.; Tian, J.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2005,** *127,* 3413-3422.

4.4.3 Other Additions to Carbonyl and Imine: Cyanide

Postulated Active Catalyst



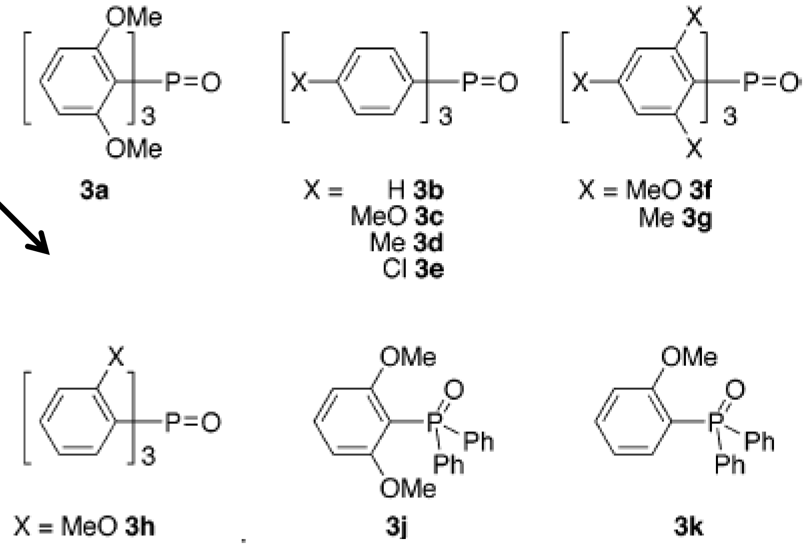
Effect of Water

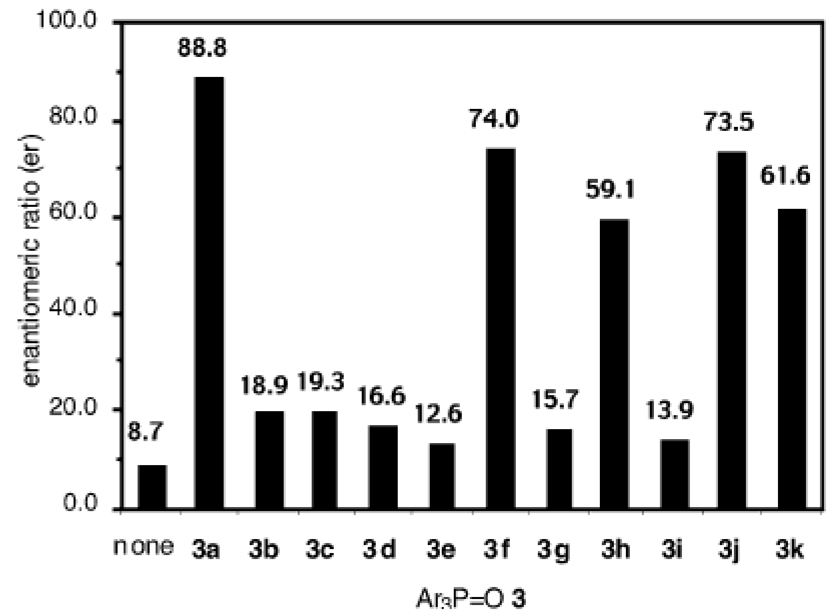


(1) Tian, J.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2002,** *41,* 3636-3638. (2) Yamagiwa, N.; Tian, J.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2005,** *127,* 3413-3422.

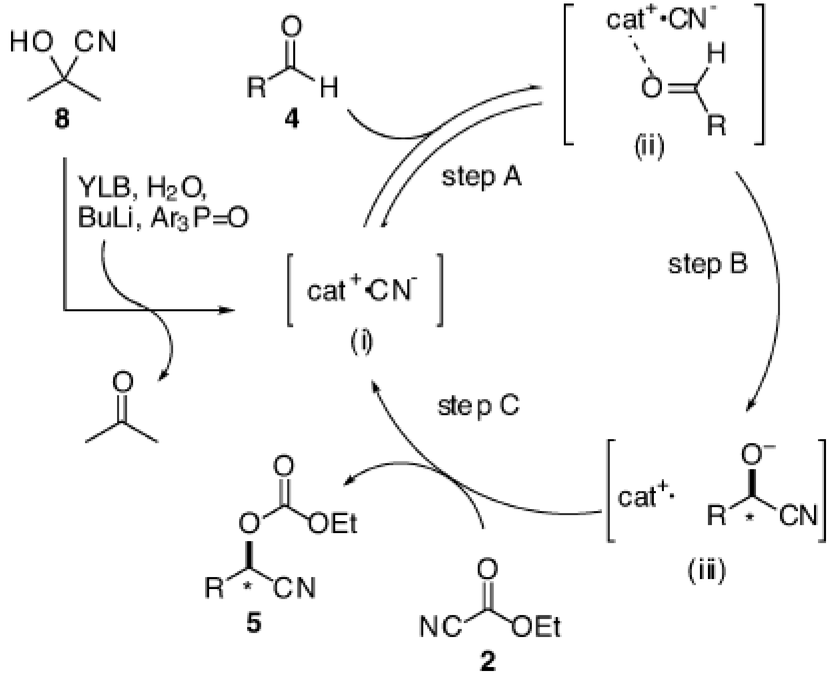
4.4.3 Other Additions to Carbonyl and Imine: Cyanide

Phosphine Oxide Effect





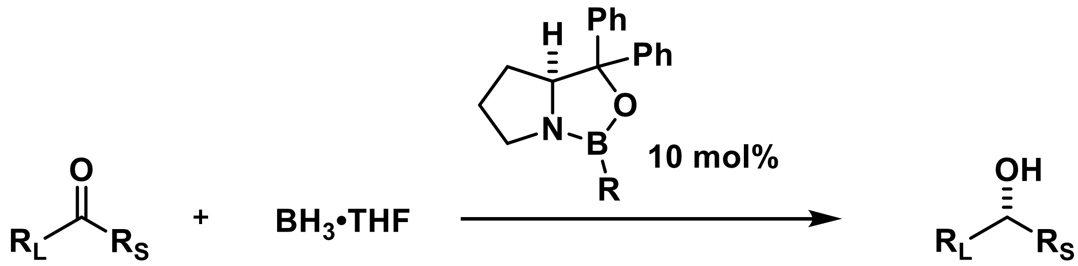
Catalytic Cycle



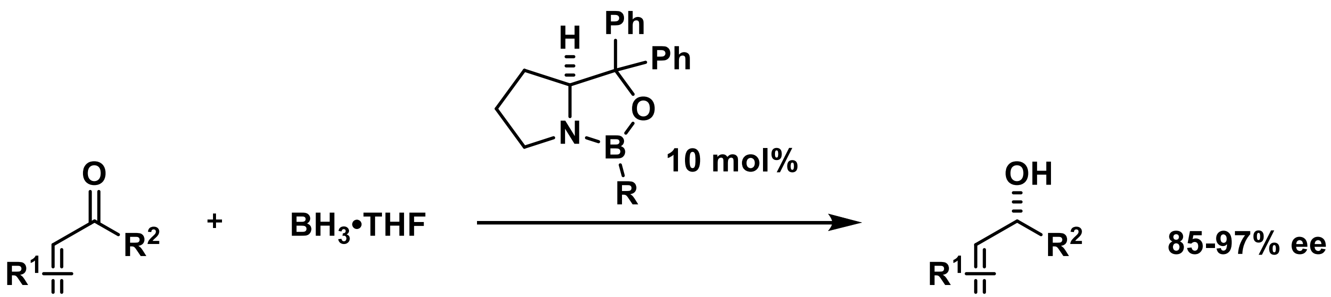
(1) Tian, J.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2002,** *41,* 3636-3638. (2) Yamagiwa, N.; Tian, J.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2005,** *127,* 3413-3422.

4.4.3 Other Additions to Carbonyl and Imine: Reduction

Corey-Bakshi-Shibata Reduction (CBS Reduction)



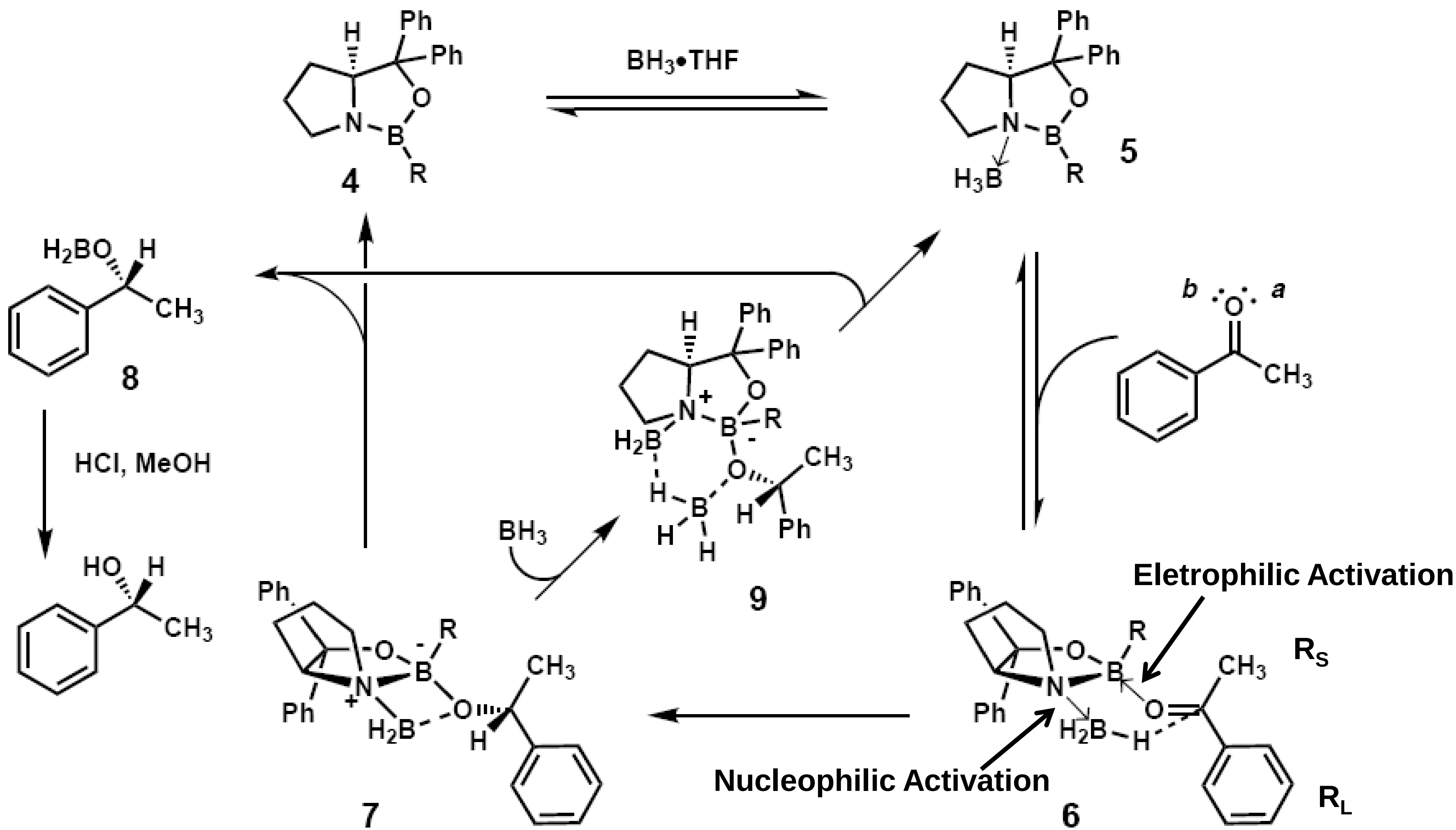
Specially Interesting: Highly Selective Reduction of Acrylates



(1) Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C. P.; Singh, V. K. *J. Am. Chem. Soc.* **1987,** *109,* 7925-7926. (2) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998,** *37,* 1987-2012.

4.4.3 Other Additions to Carbonyl and Imine: Reduction

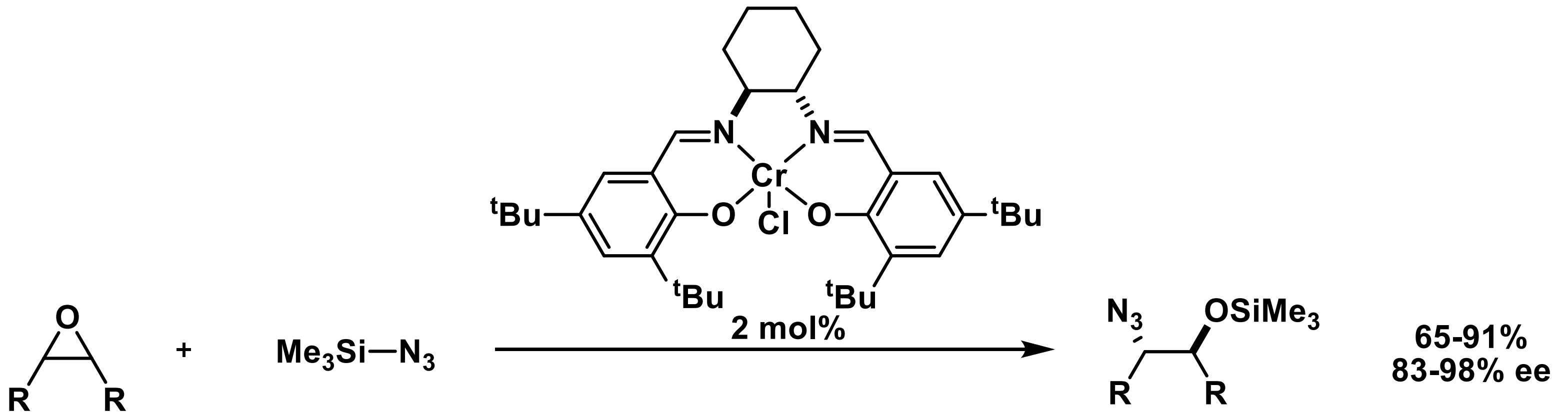
Mechanism and Model for Selectivity



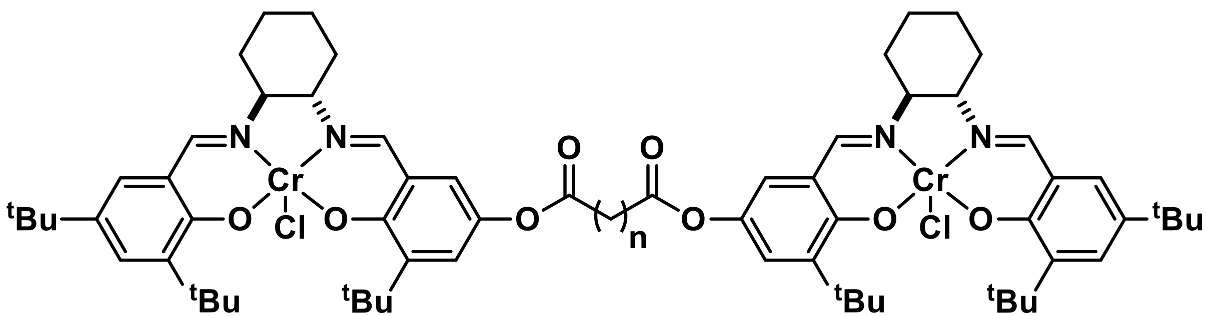
(1) Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C. P.; Singh, V. K. *J. Am. Chem. Soc.* **1987,** *109,* 7925-7926. (2) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998,** *37,* 1987-2012.

4.4.5 Other Reactions: Epoxide Opening

Jacobsen: Asymmetric Opening of Meso-Epoxides with Azides



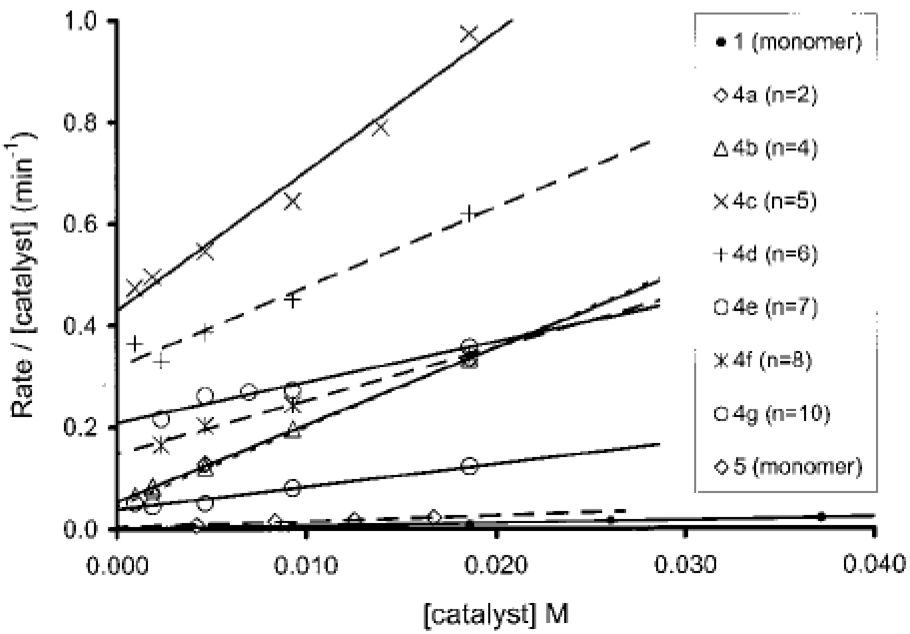
Jacobsen: A Dimeric Catalyst for Probing the Reaction Mechanism

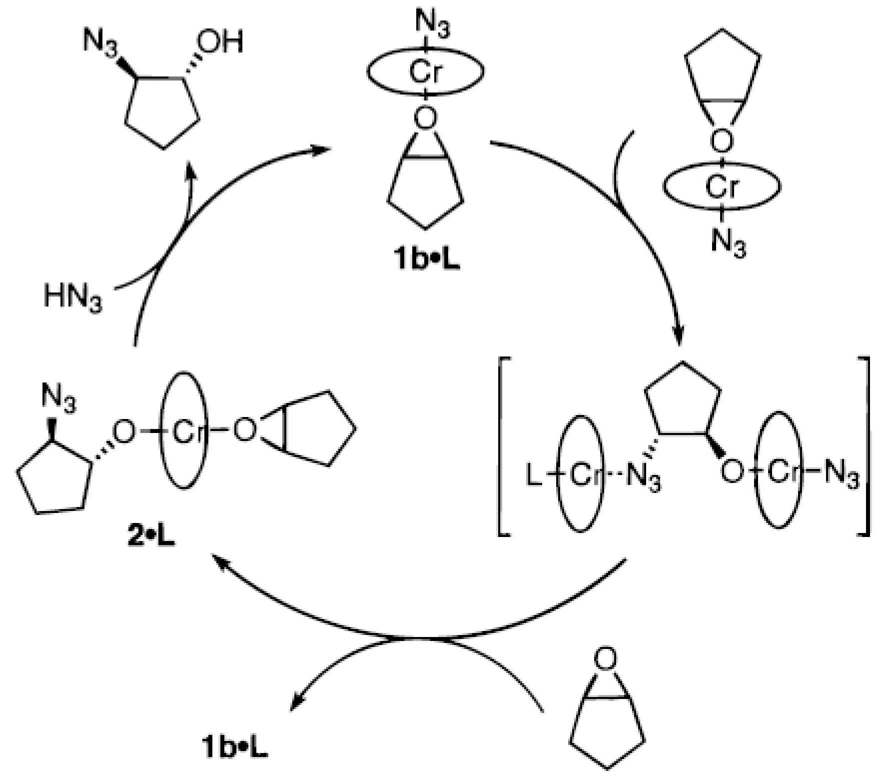


(1) Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995,** *117,* 5897-5898. (2) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996,** *118,* 10924-10925. (3) Konsler, R. G.; Karl, J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998,** *120,* 10780-10781.

4.4.5 Other Reactions: Epoxide Opening

Mechanism and Results with Dimeric Catalysts

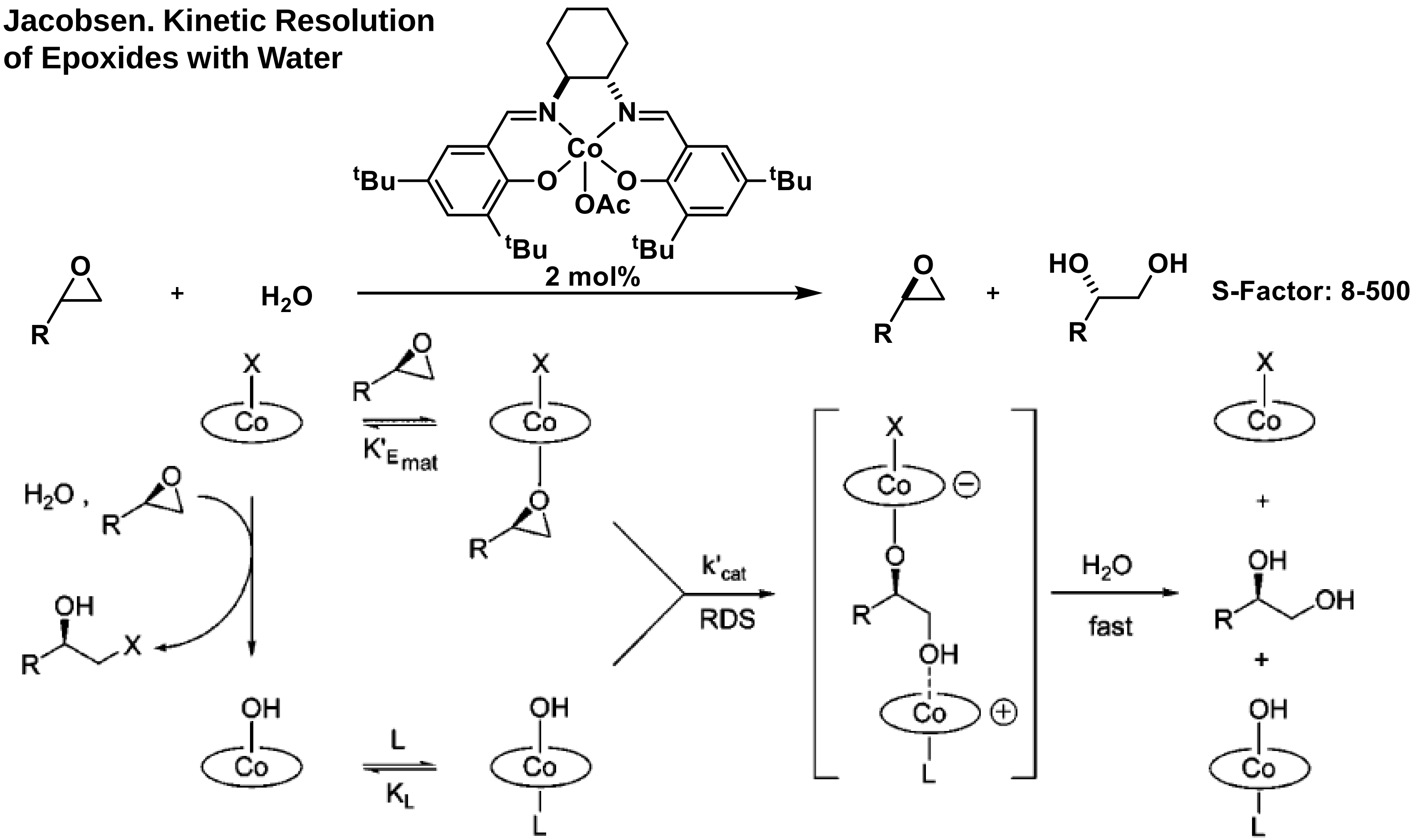




(1) Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995,** *117,* 5897-5898. (2) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996,** *118,* 10924-10925. (3) Konsler, R. G.; Karl, J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998,** *120,* 10780-10781.

4.4.5 Other Reactions: Epoxide Opening

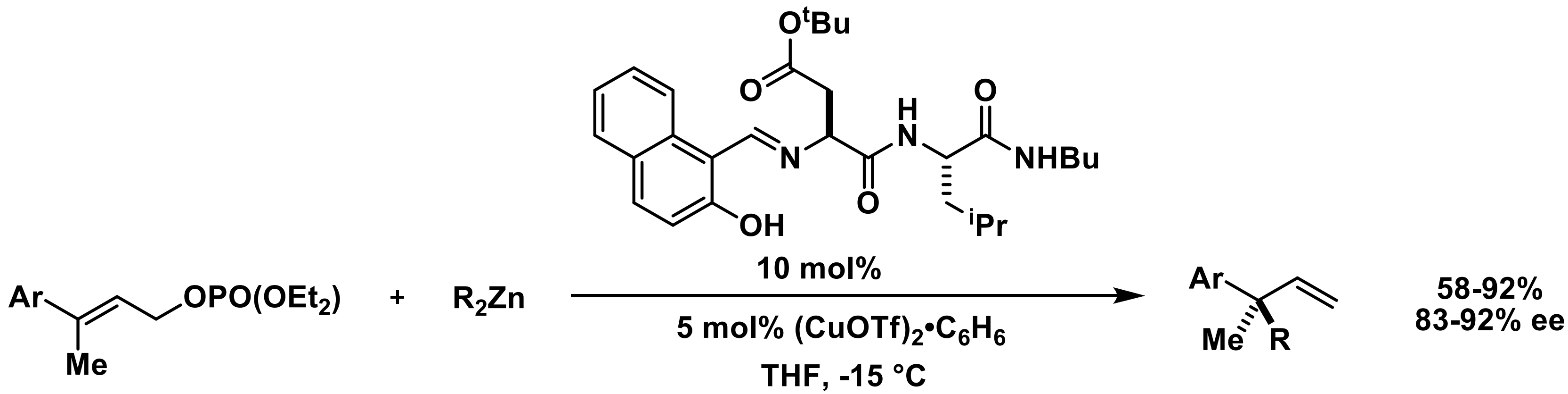
Jacobsen. Kinetic Resolution of Epoxides with Water



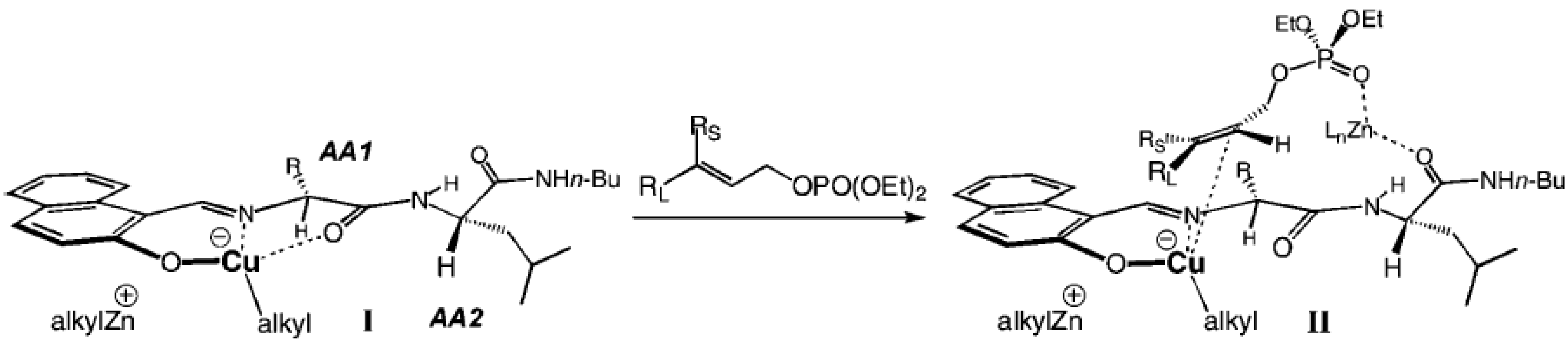
(1) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997,** *277,* 936-938. (2) Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* ***2002,*** **124,** *1307-1315.* (3) Nielsen, L. P. C.; Stevenson, C. P.; Blackmond, D. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004,** *126,* 1360-1362. (4) Ford, D. D.; Nielsen, L. P. C.; Zuend, S. J.; Musgrave, C. B.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2013**, *135*, 15595.

4.4.5 Other Reactions: Asymmetric Allylation

Hoveyda: Cu-Catalyzed Allylation of Organozinc Reagents



Proposed Model



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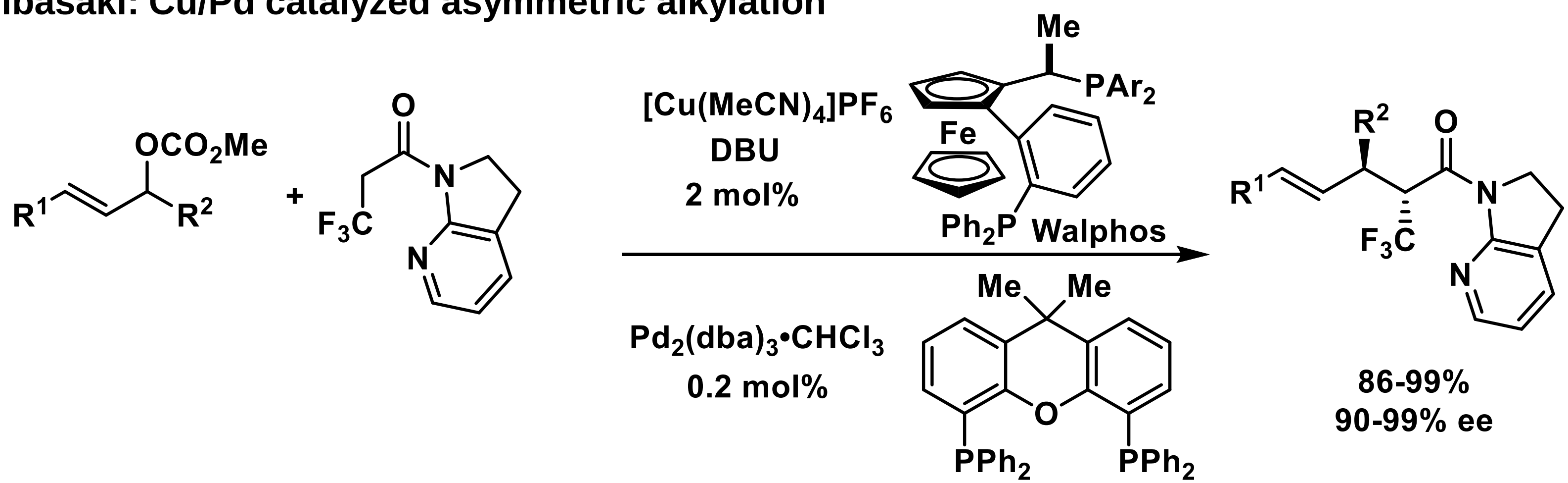
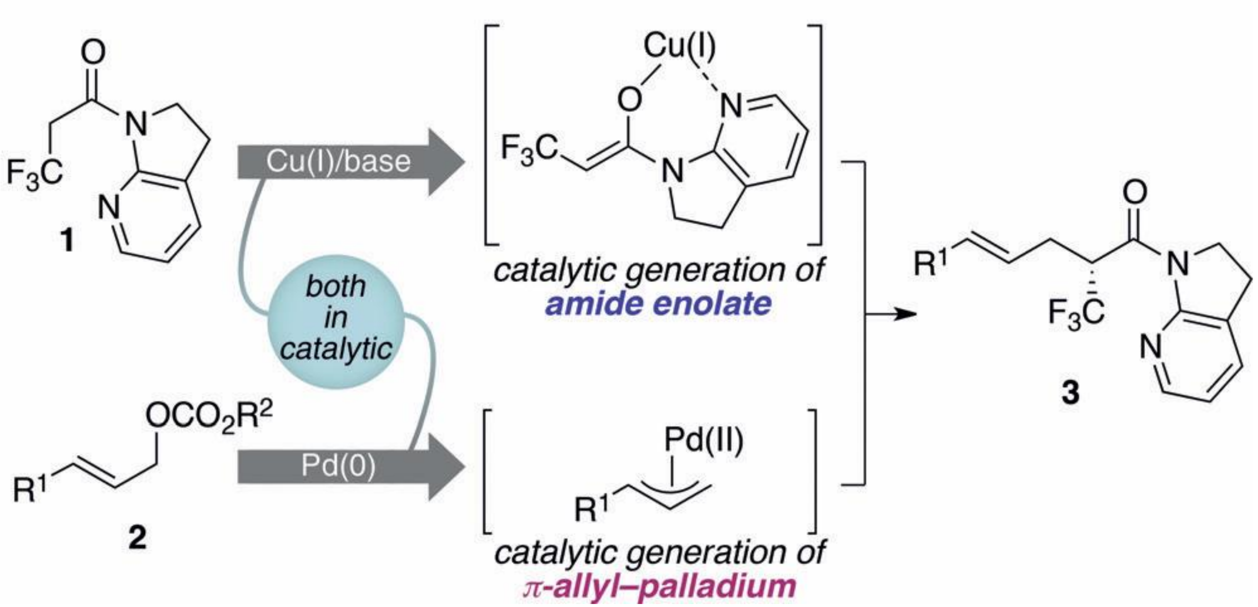
4.4.5 Other Reactions: Asymmetric Allylation

Shibasaki: Cu/Pd catalyzed asymmetric alkylation

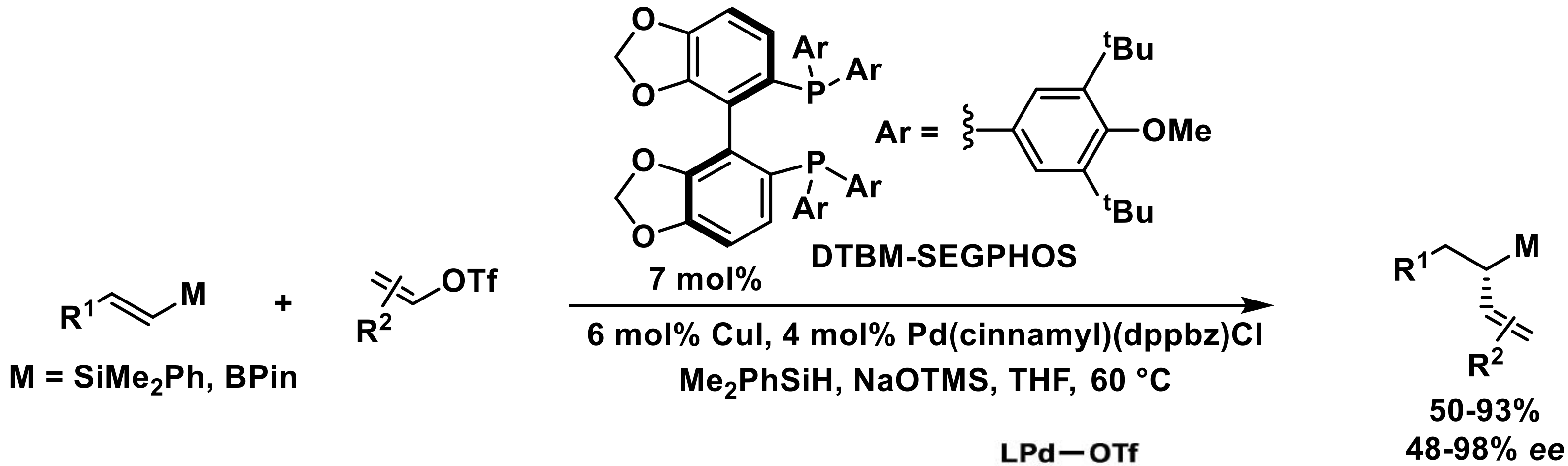


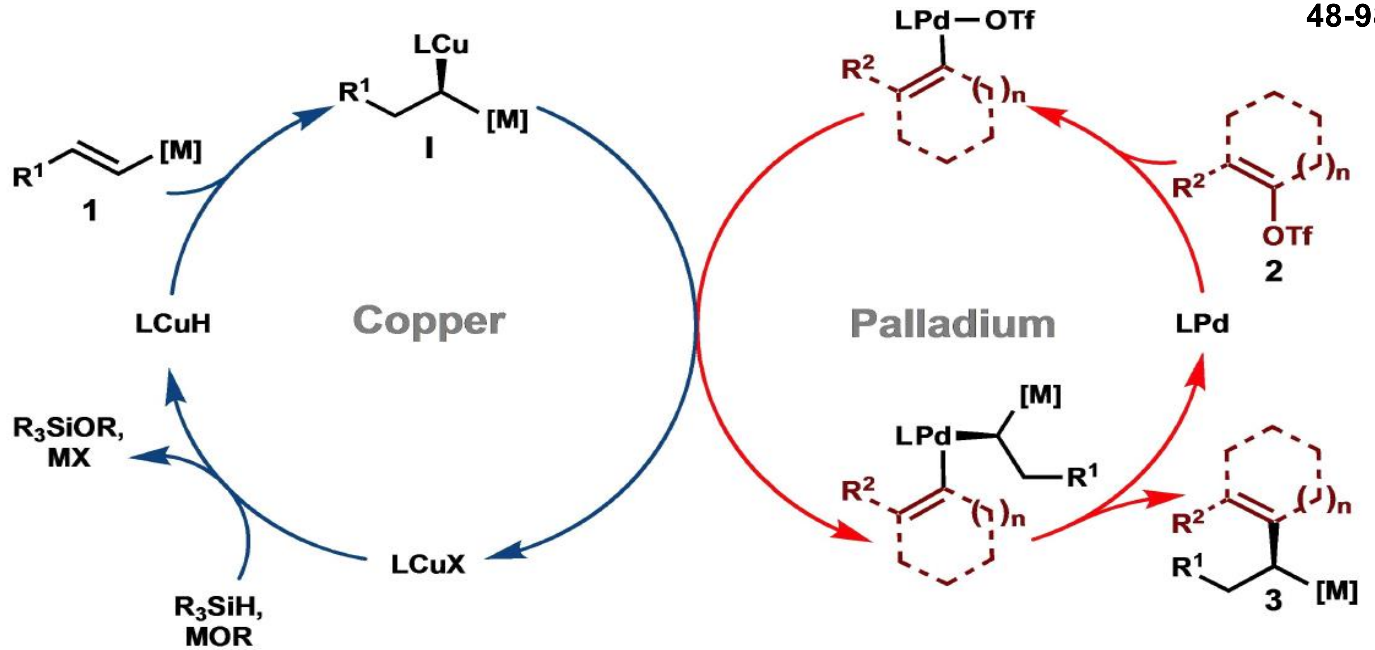


Saito, A.; Kumagai, N.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2017**, *56*, 5551-5555.

4.4.5 Other Reactions: Alkene Vinylation

Buchwald: Cu/Pd catalyzed olefin alkenylation

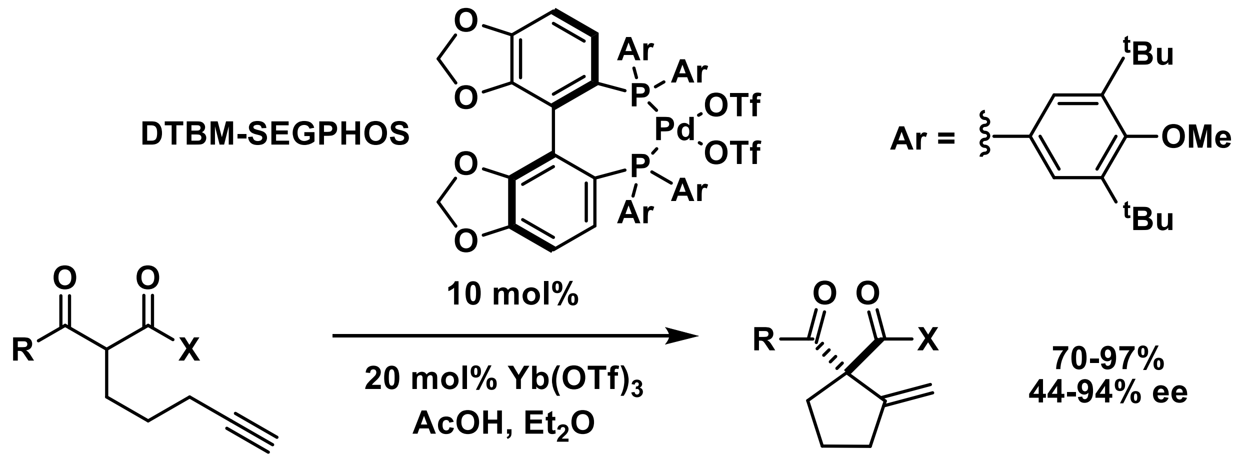




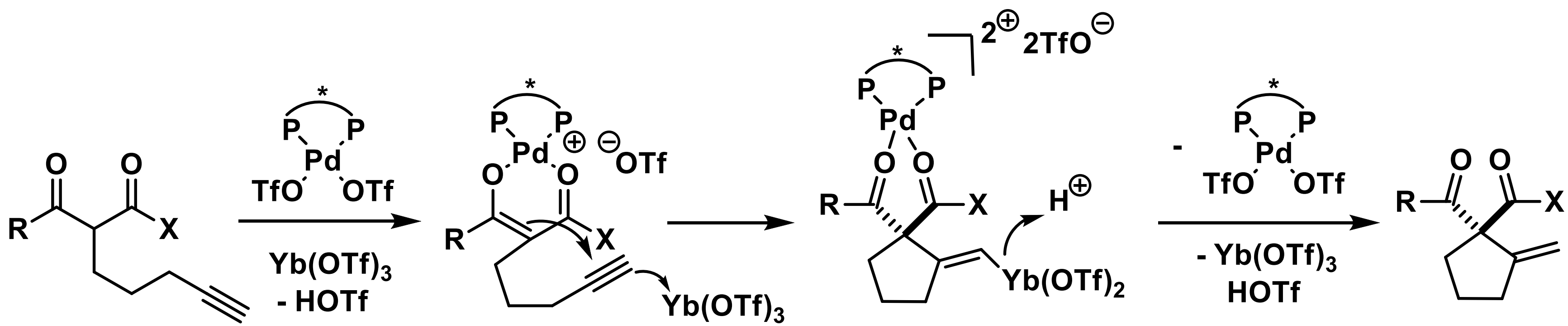
Levi Knippel, J.; Ni, A. Z.; Schuppe, A. W.; Buchwald, S. L. *Angew., Chem., Int. Ed.* **2022**, *61*, e202212630.

4.4.5 Other Reactions: Conia-Ene Reaction

Toste: Asymmetric Conia-Ene Reaction



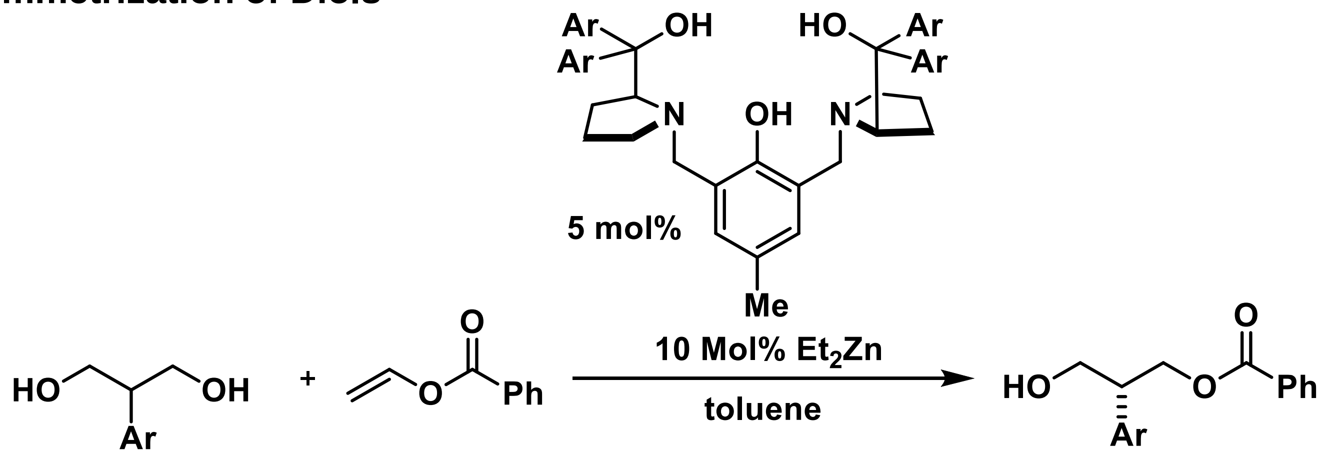
Proposed Mechanism



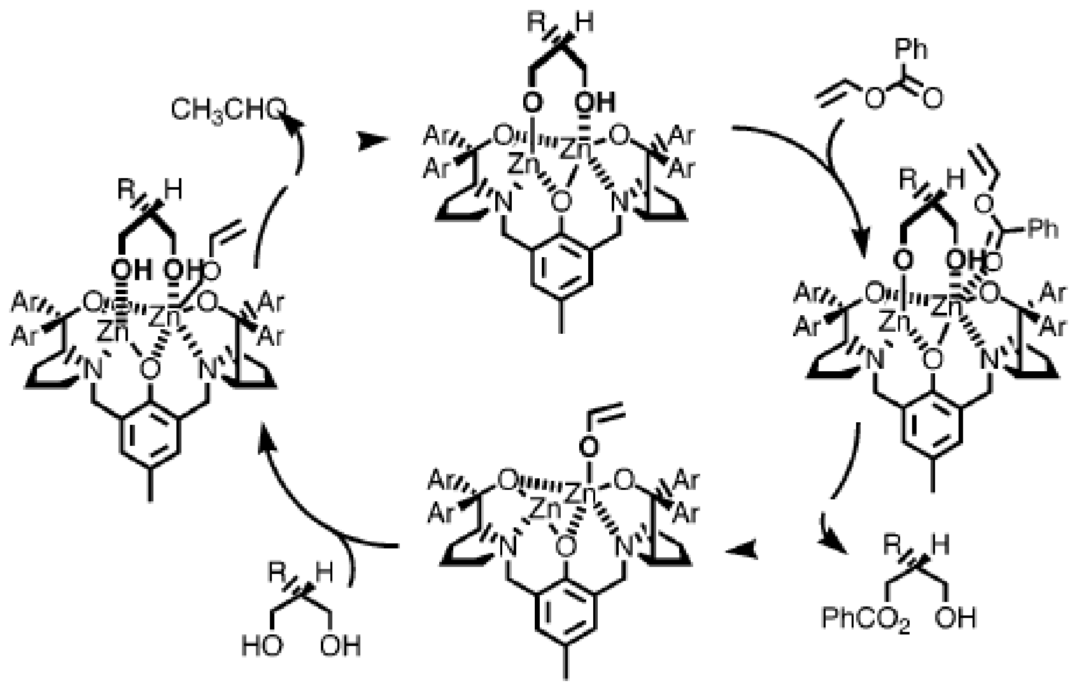
(1) Corkey, B. K.; Toste, F. D. *J. Am. Chem. Soc*. **2005,** *127,* 17168-17169.

4.4.5 Other Reactions: Desymmetrization

Trost: Desymmetrization of Diols



Proposed Mechanism



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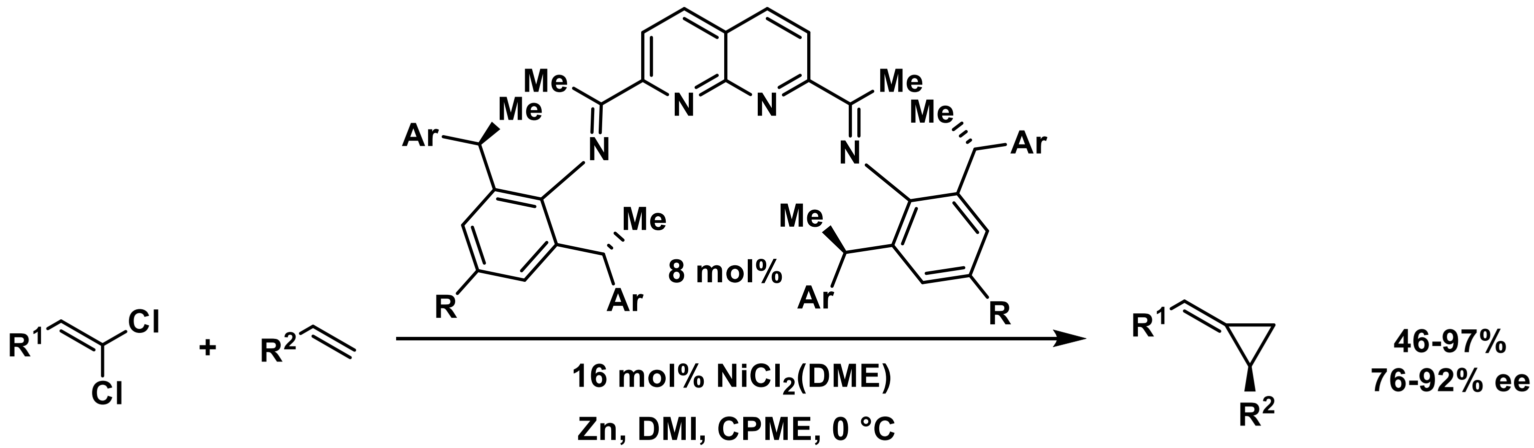
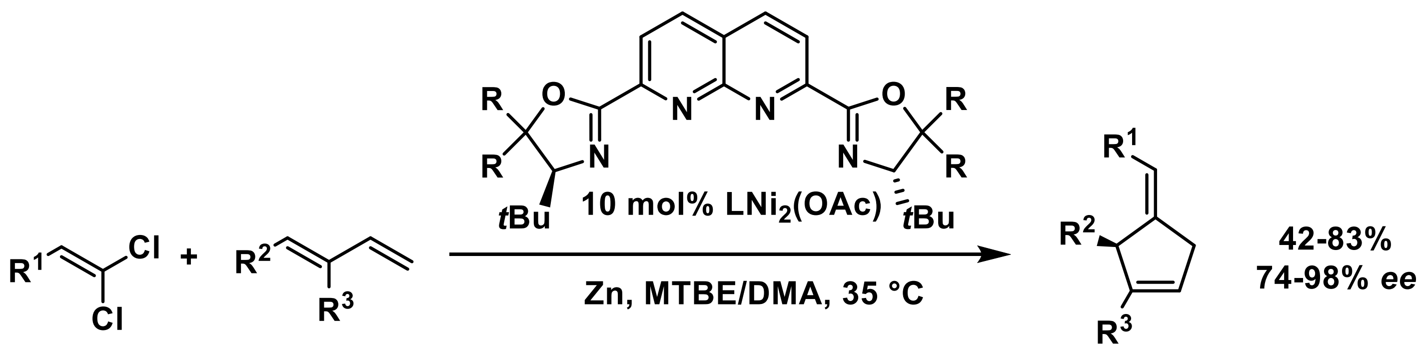
4.4.5 Other Reactions: Bis-Ni catalysis

Cramer: Cyclopropanation[1]



Uyeda: [4+1] cycloaddition[2]



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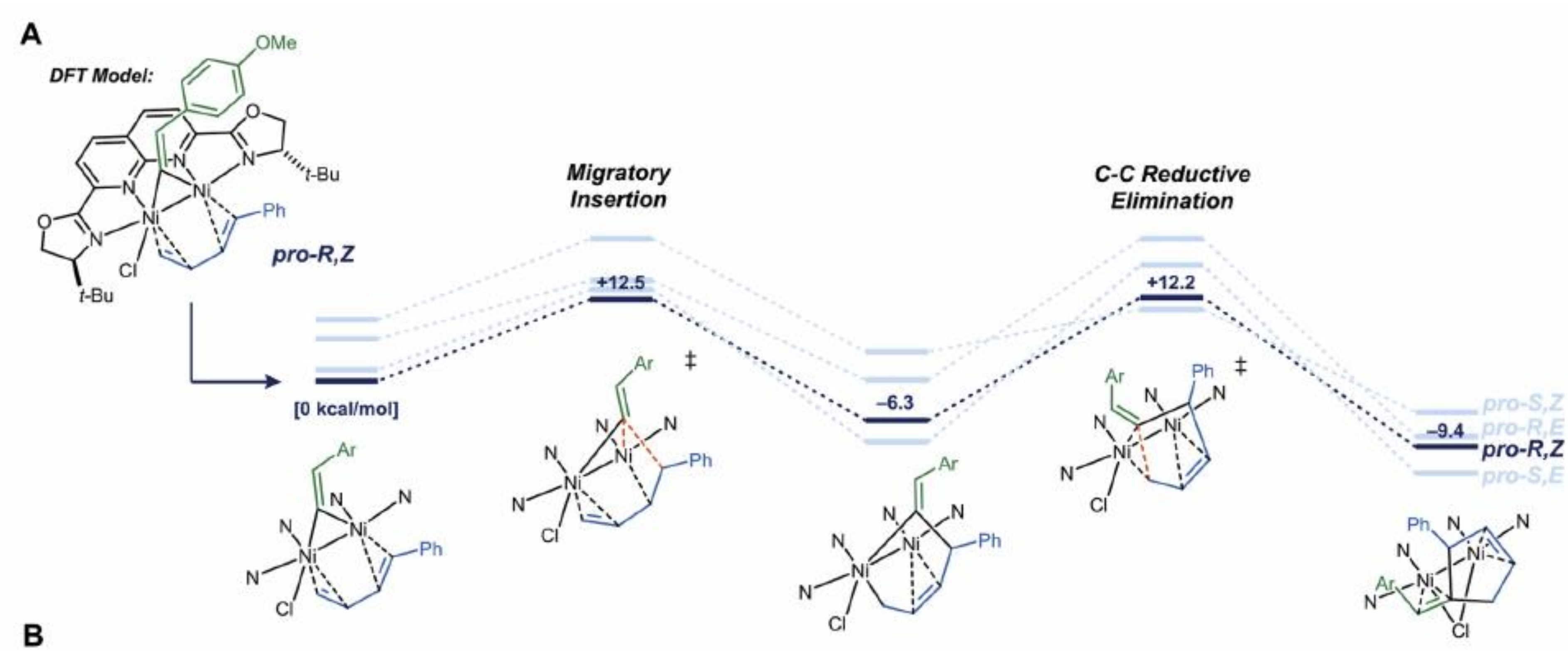
4.4.5 Other Reactions: Bis-Ni catalysis



Behlen, M. J.; Uyeda, C. *J. Am. Chem. Soc.* **2020,** *142*, 17294-17300.