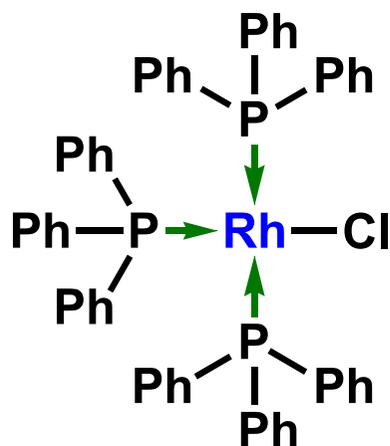


Hydrogenation

(catalytic)
hydrogenation

heterogeneous
homogeneous

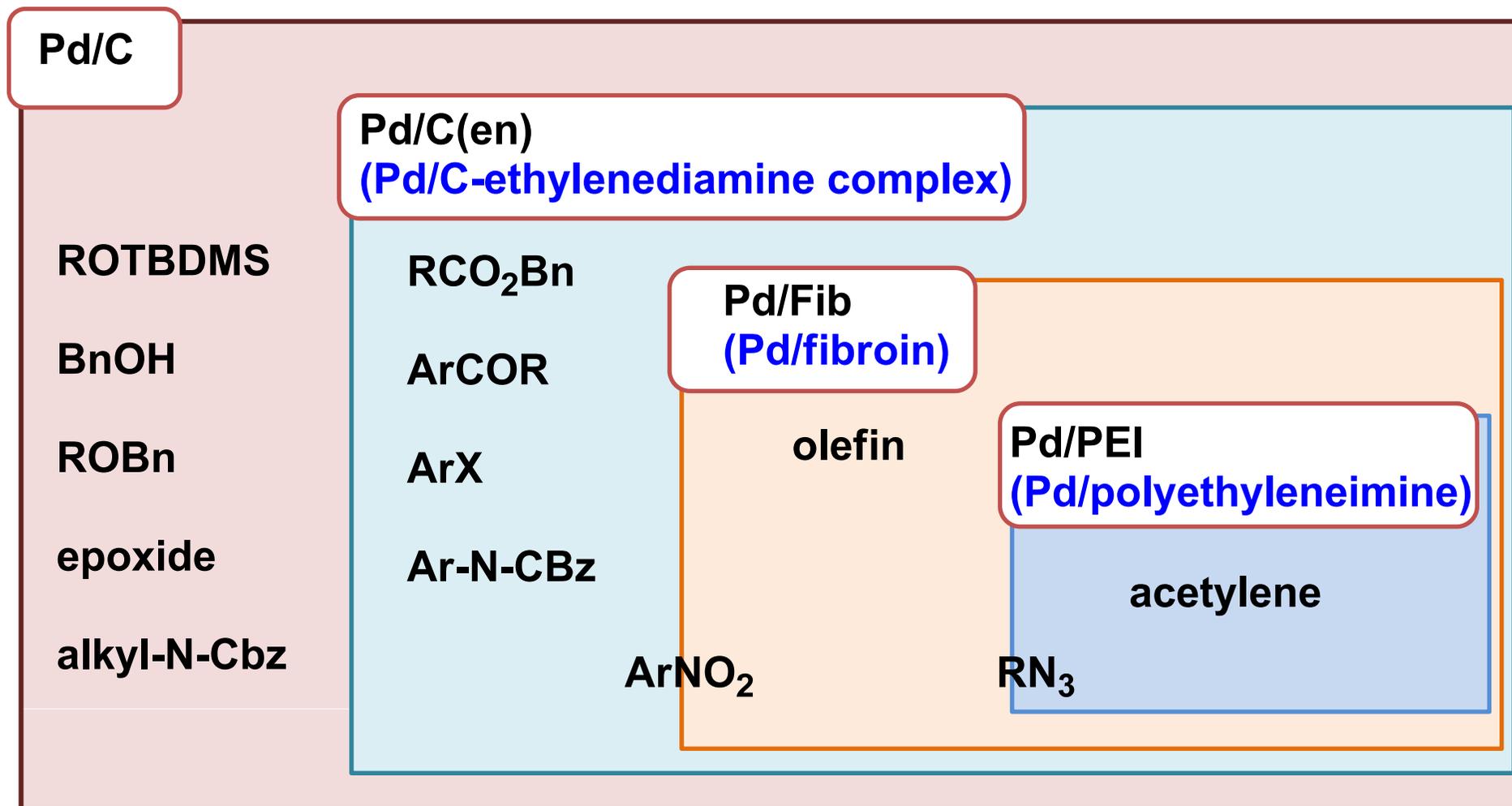


oxidation state: Rh(I)
valence electrons: 16e

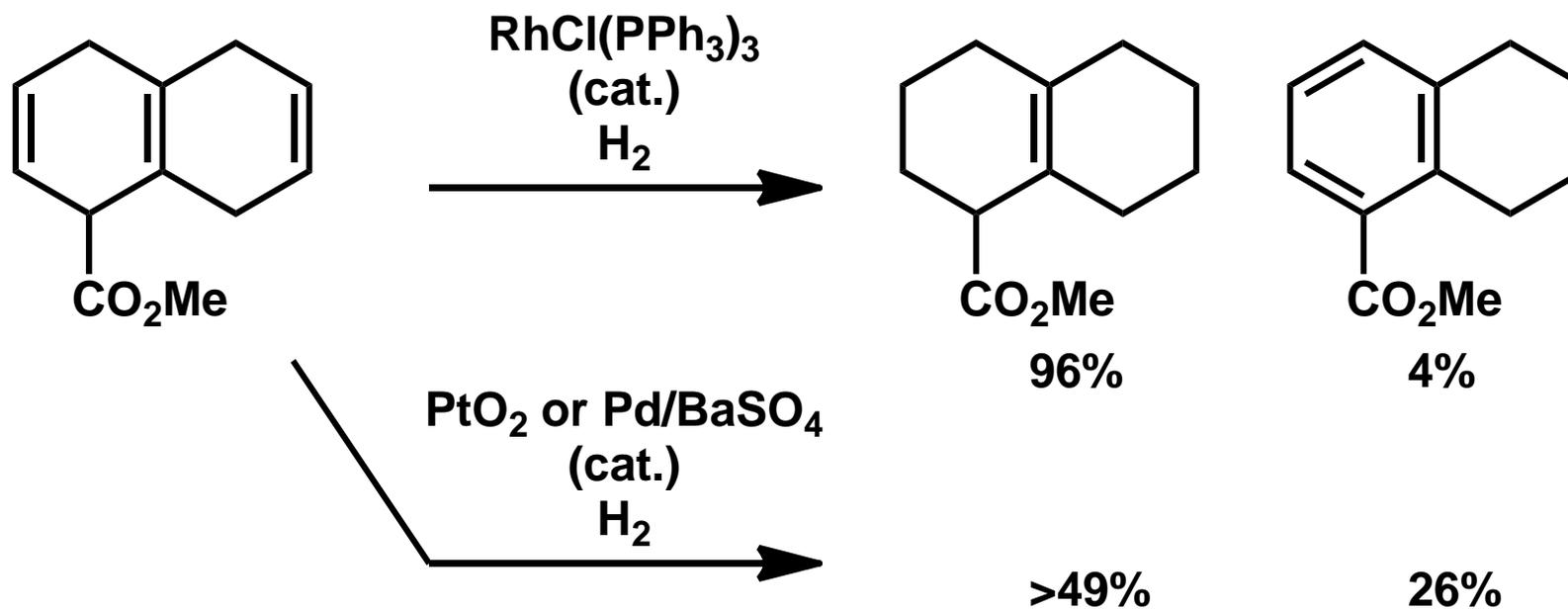
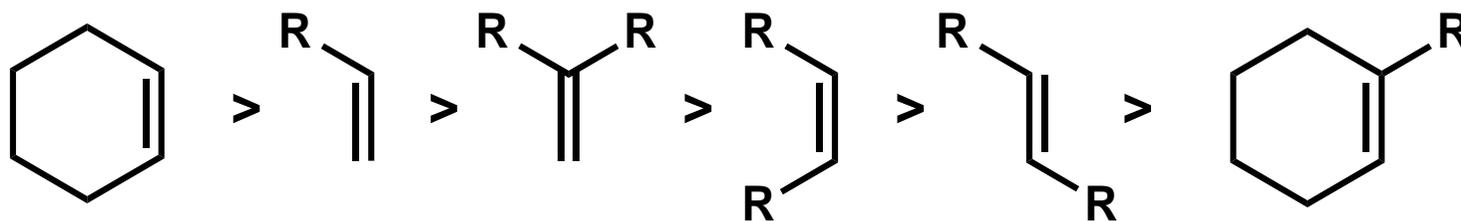
Wilkinson's catalyst

catalyst for
hydrogenation (1966)

Heterogeneous Pd Catalysts for Hydrogenation



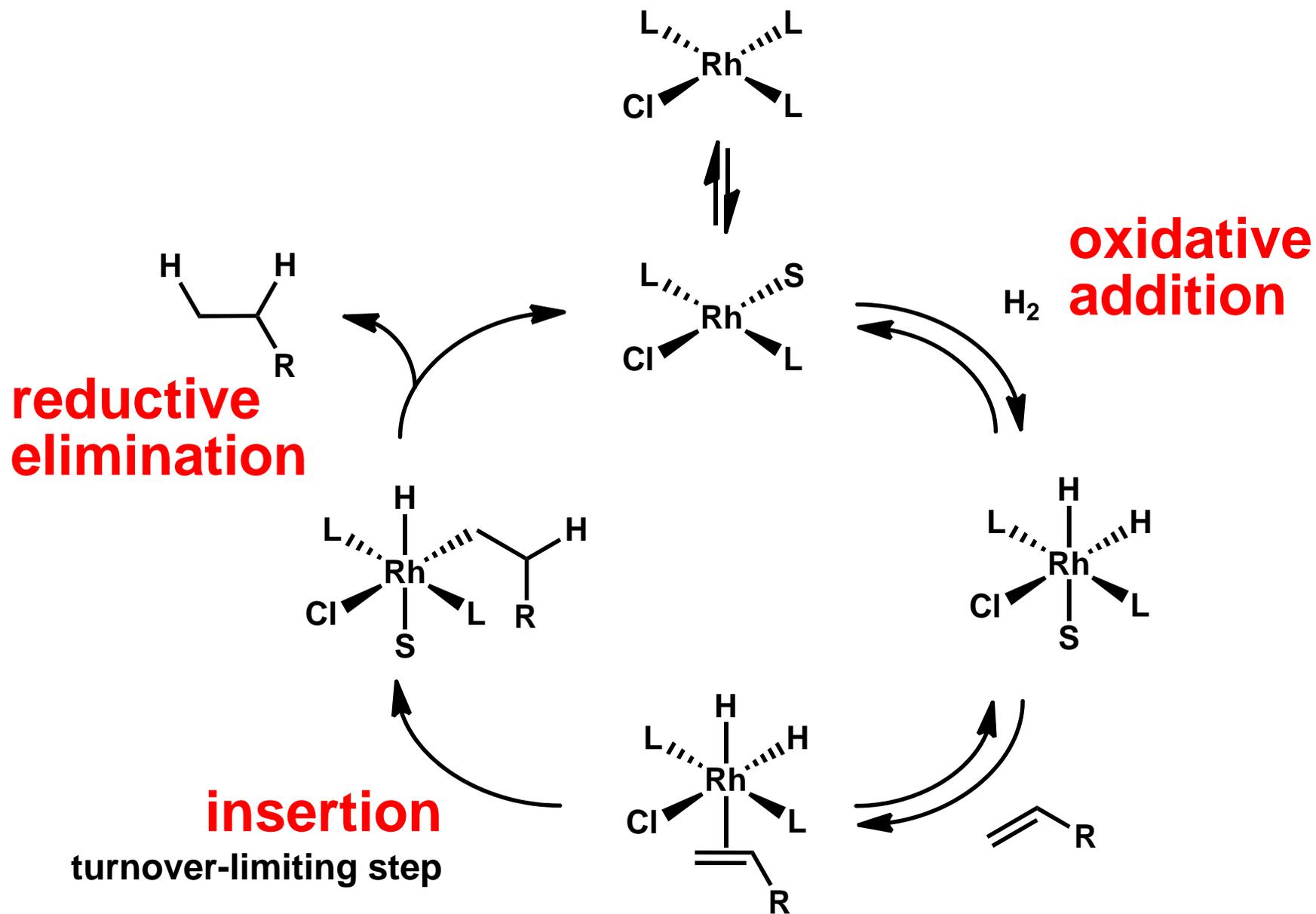
Wilkinson's catalyst $\text{RhCl}(\text{PPh}_3)_3$



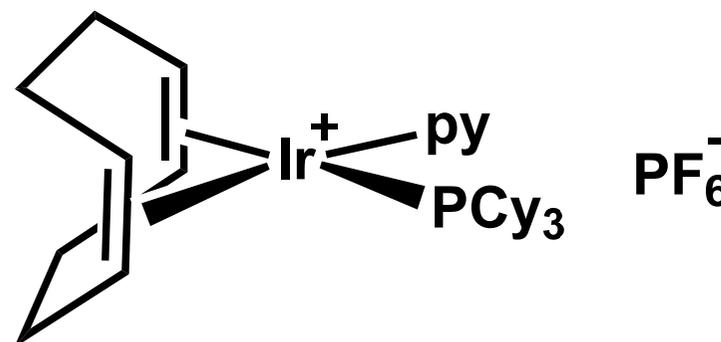
Catalytic Cycle

◆ dihydride

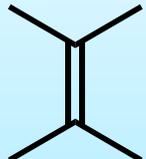
◆ hydrogen-first mechanism



Crabtree's catalyst



TOF (h^{-1}) of hydrogenation

				
$[(\text{cod})\text{Ir}(\text{py})(\text{PCy}_3)]^+\text{PF}_6^-$	6400	4500	4000	0 °C, in CH_2Cl_2
$\text{RhCl}(\text{PPh}_3)_3$	60	70	0	0 °C, in $\text{C}_6\text{H}_6/\text{EtOH}$

Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.

mechanism: Ir(III) and Ir(V) rather than Ir(I) and Ir(III) ?

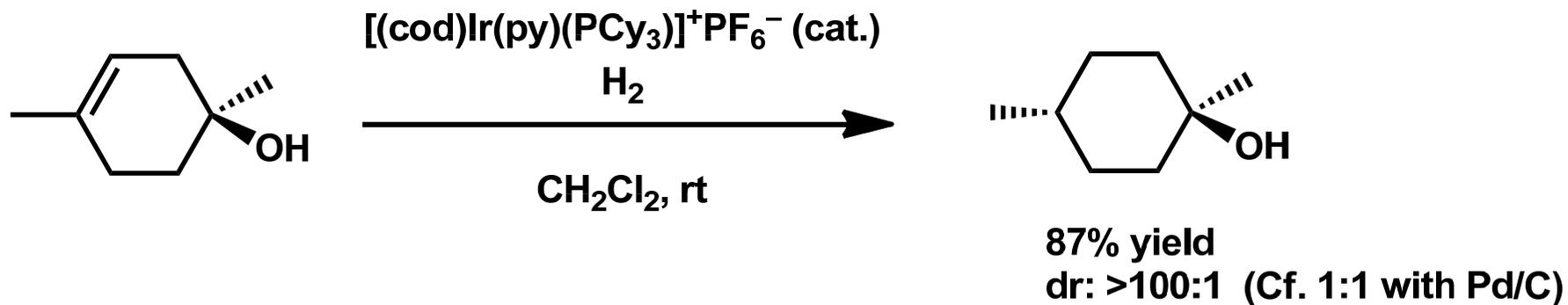
Hall, M. B.; Burgess, K. *Chem. Eur. J.* **2005**, *11*, 6859.

TON = turnover number = moles of product / moles of catalyst

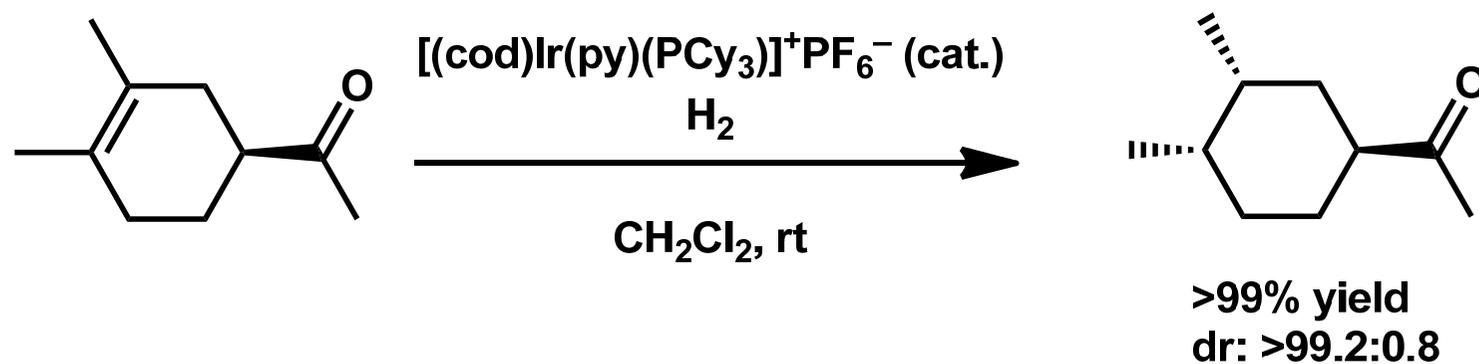
TOF = turnover frequency = TON / time

Directing Effects

OH, CO₂Me, C=O, or OMe

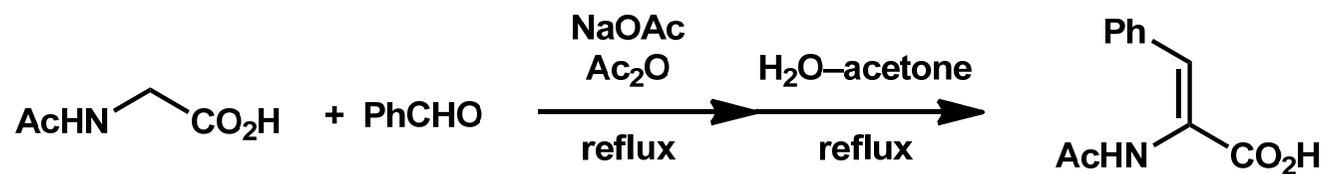
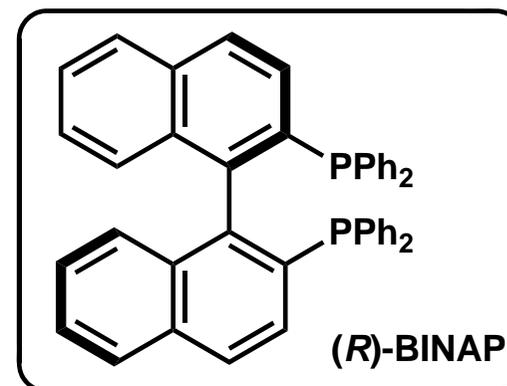
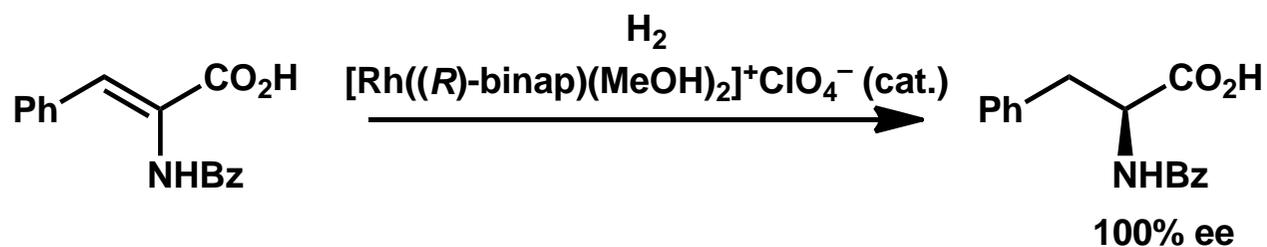
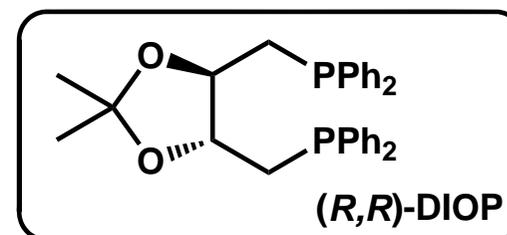
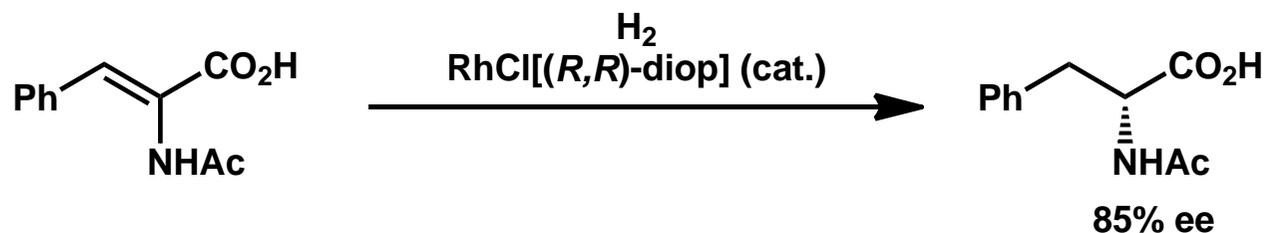
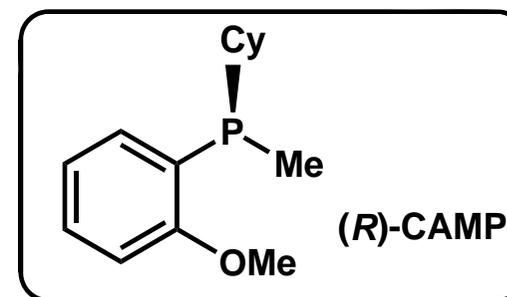
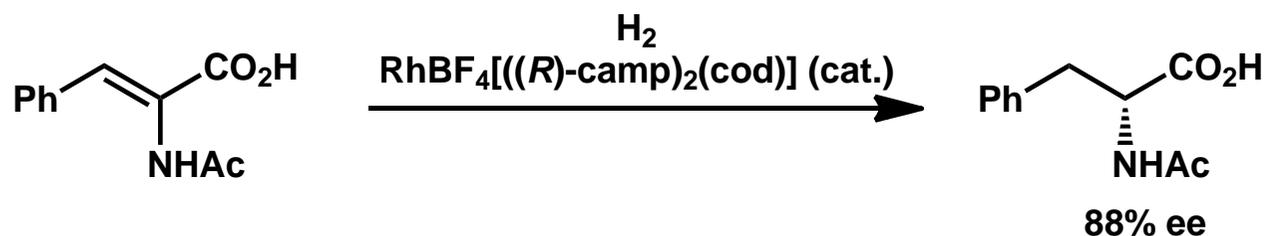


Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072.

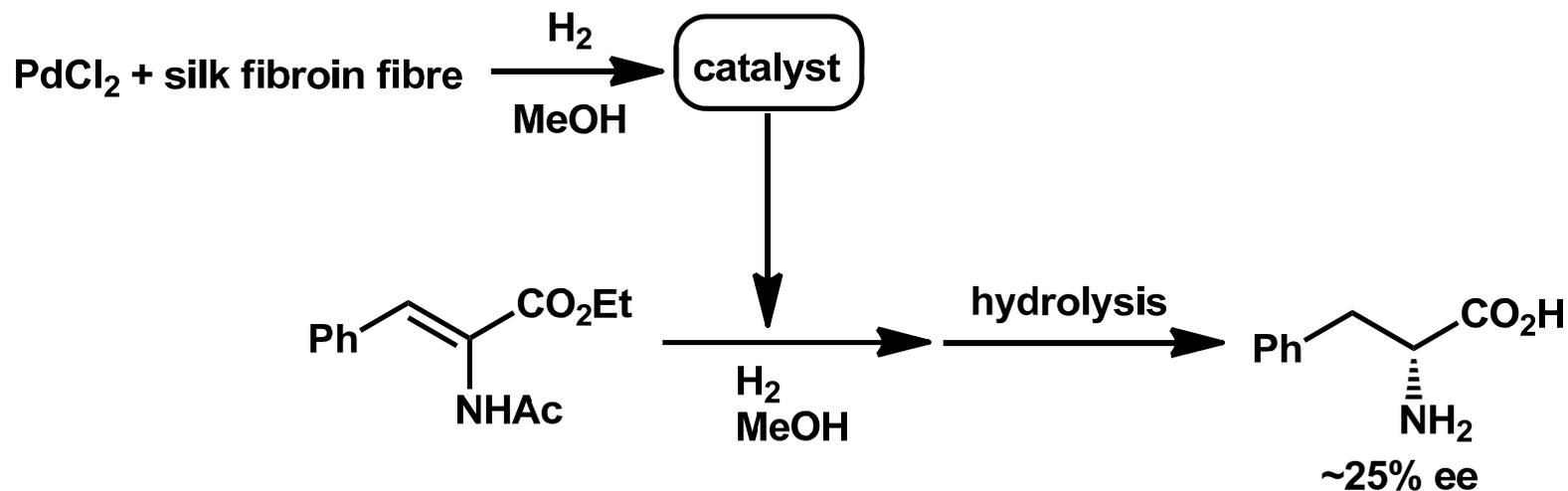


Crabtree, R. H.; Davis, M. W. *J. Am. Chem. Soc.* **1986**, *51*, 2655.

Catalytic Asymmetric Hydrogenation



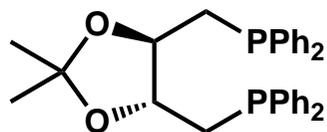
「演習で学ぶ有機反応機構」
化学同人 A019



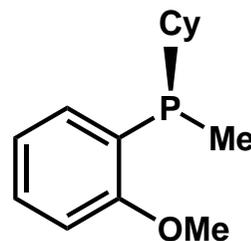
Akabori, S. et al. *Nature* 1956, 178, 323.



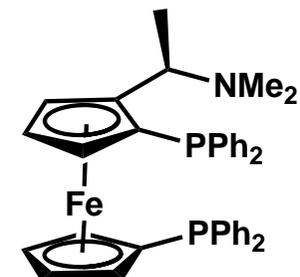
Horner, et al. (1968)
Knowles, et al. (1968)



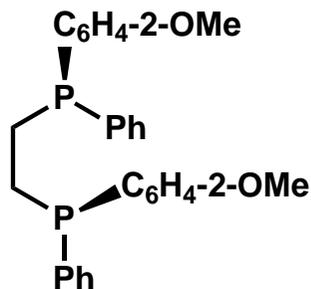
DIOP
Kagan, et al. (1971)



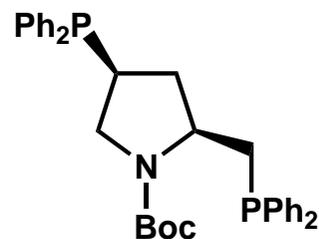
CAMP
Knowles, et al. (1972)



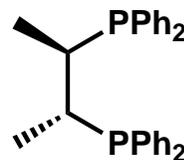
BPPFA
Hayashi, Kumada, et al. (1974)



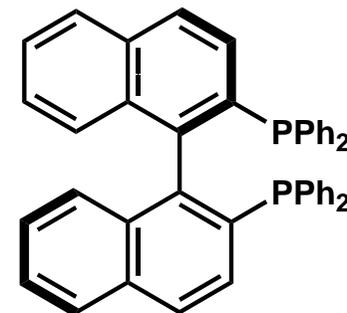
DIPAMP
Knowles, et al. (1975)



BPPM
Achiwa (1976)



chiraphos
Bosnich, et al. (1977)

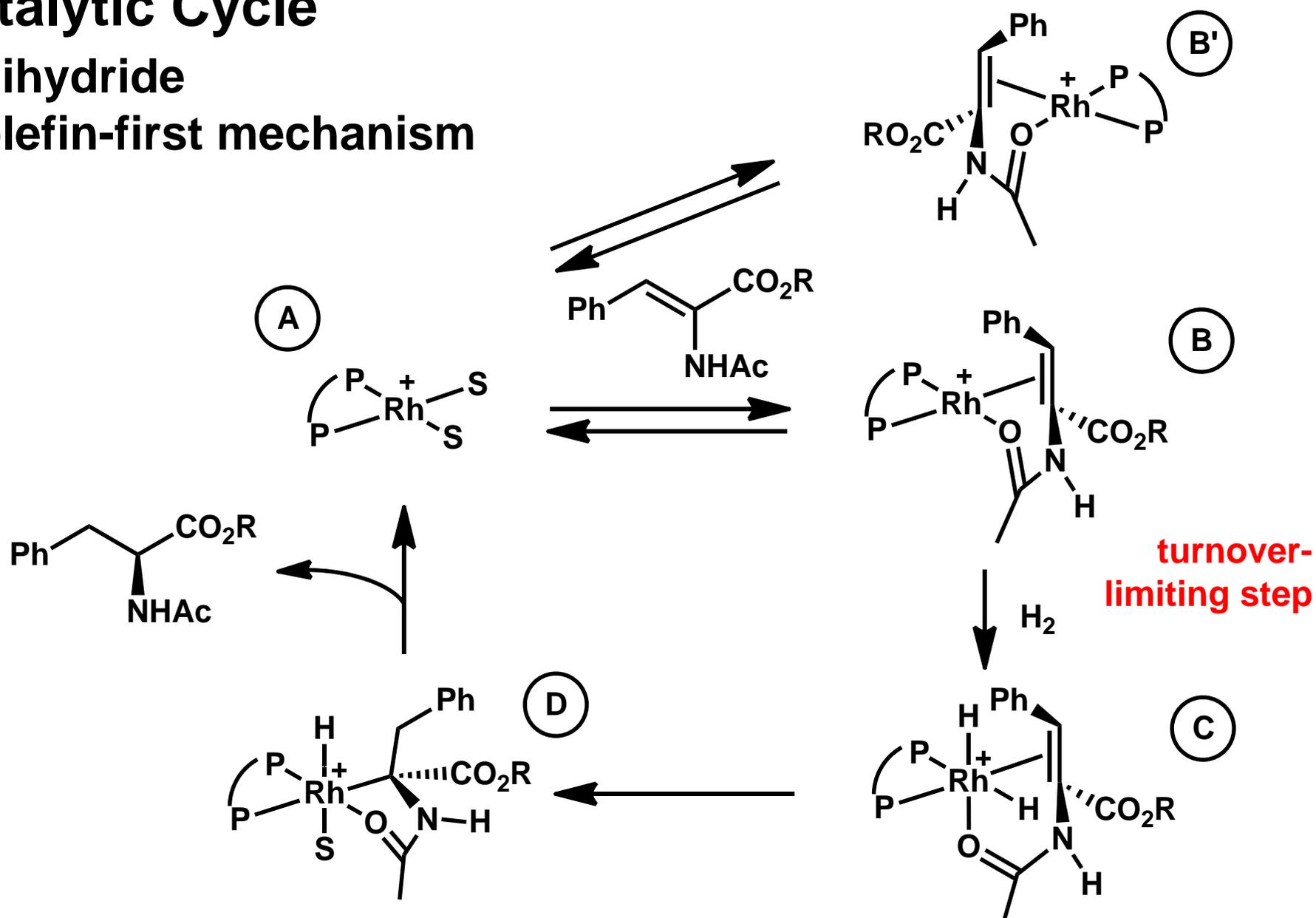


BINAP
Noyori, et al. (1980)

Catalytic Cycle

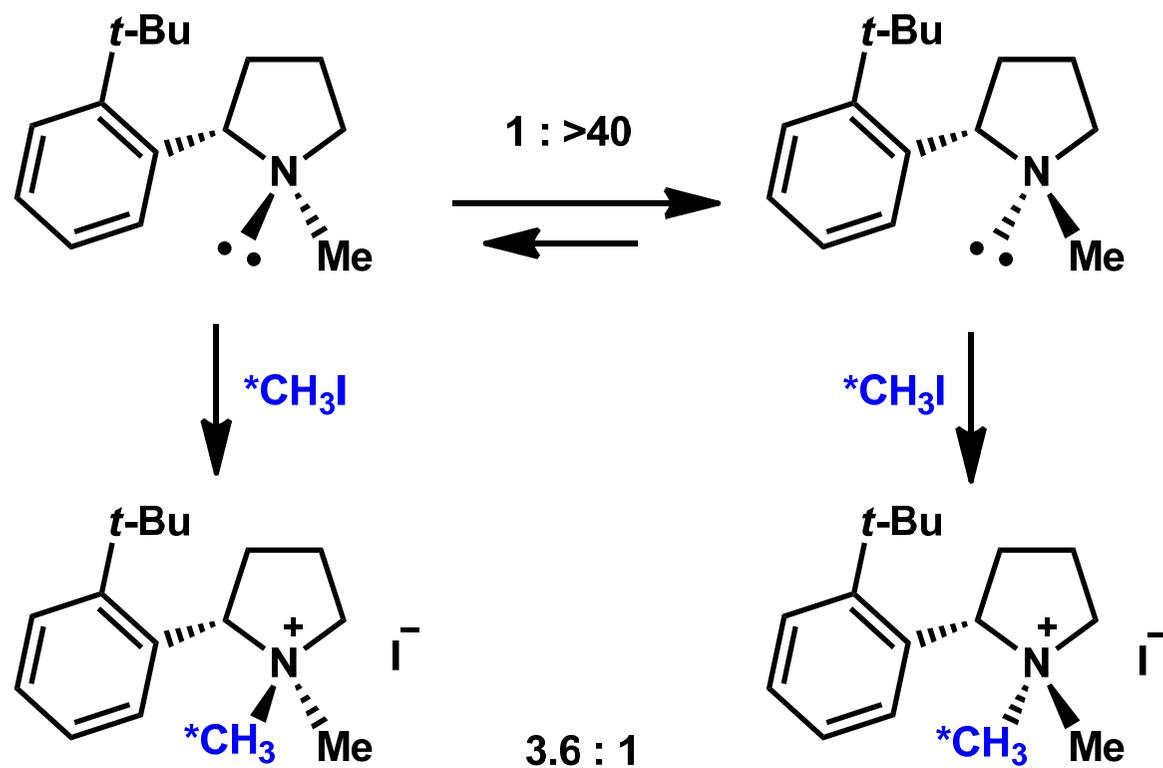
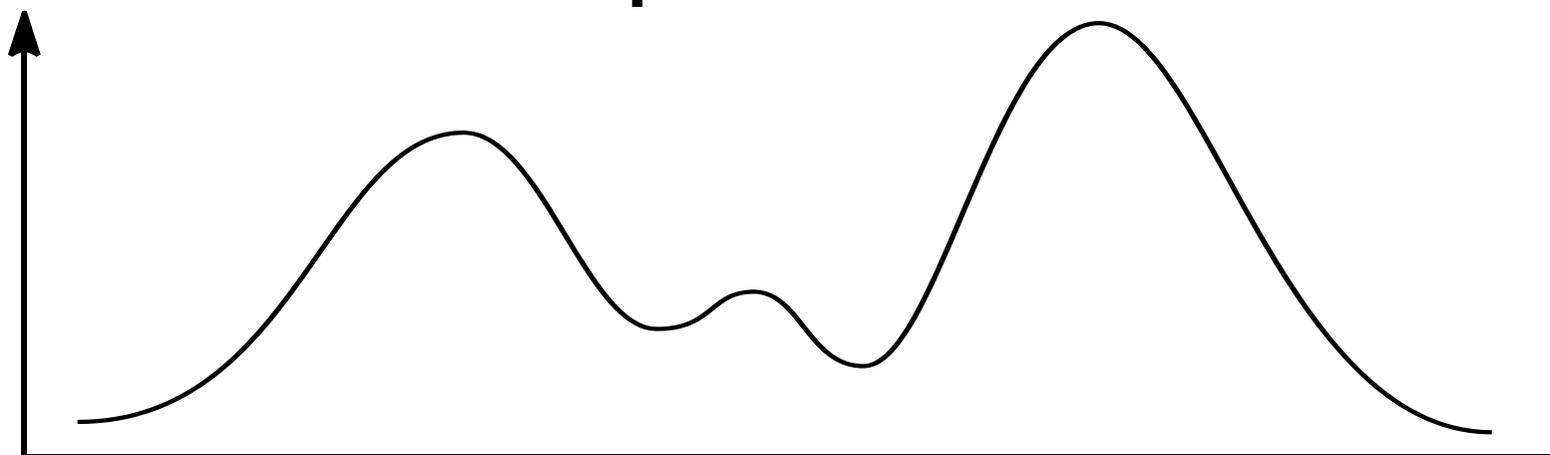
◆ dihydride

◆ olefin-first mechanism

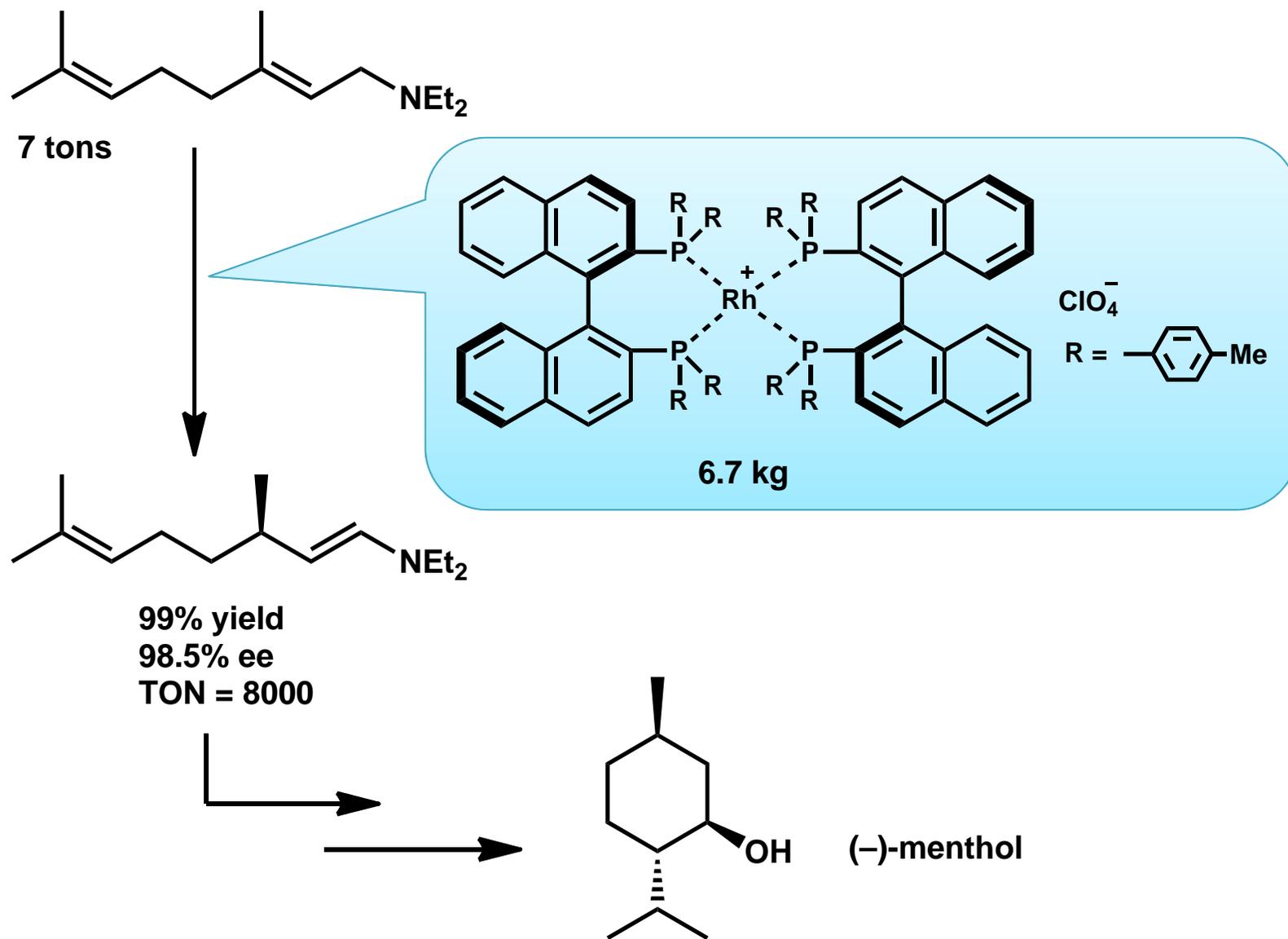


Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994.
Cf.) For hydrogen-first mechanism in cationic Rh catalysis: Gridnev, I. D.; Imamoto, T. *Acc. Chem. Res.* **2004**, *37*, 633.

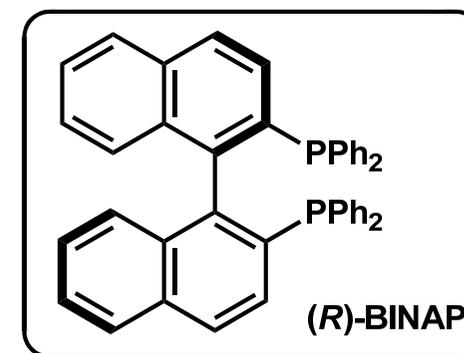
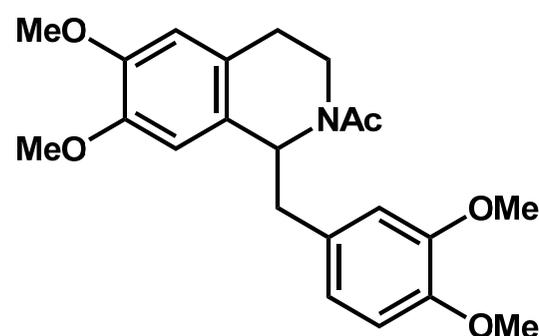
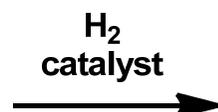
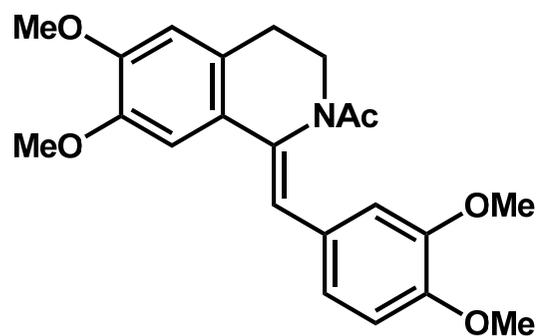
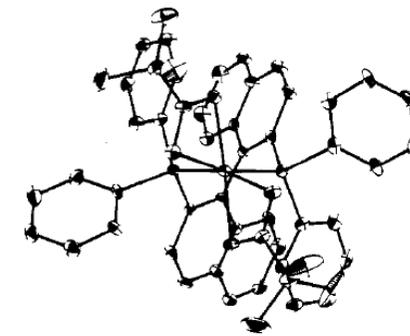
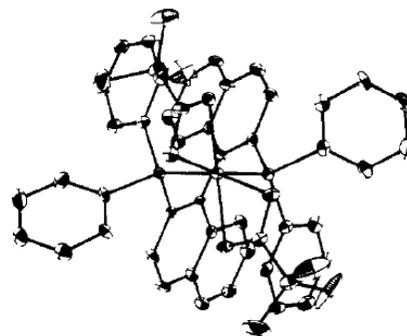
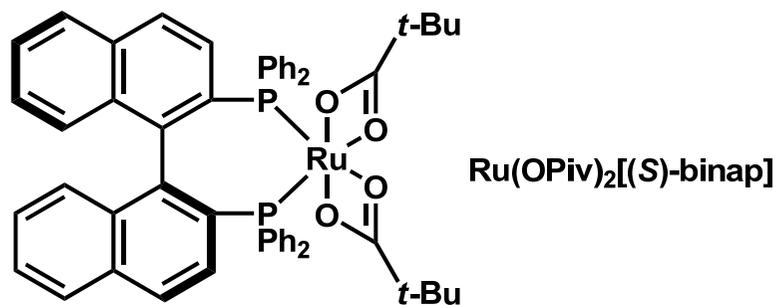
Curtin–Hammett Principle



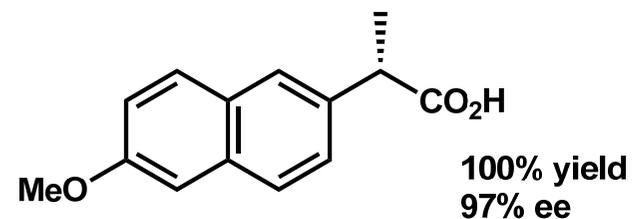
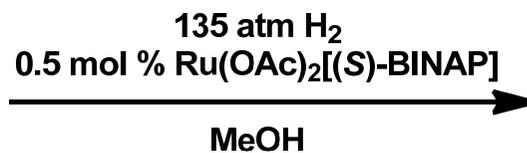
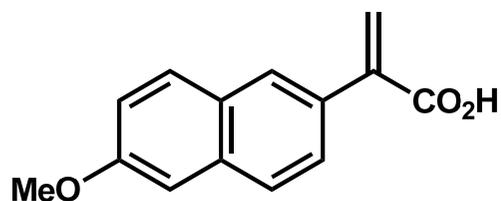
Enantioselective Isomerization



Tani, K.; Yamagata, S.; Akutagawa, S.; Kumobayashi, S.; Takemoto, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208. 芥川進 有合化 **1986**, *44*, 513.

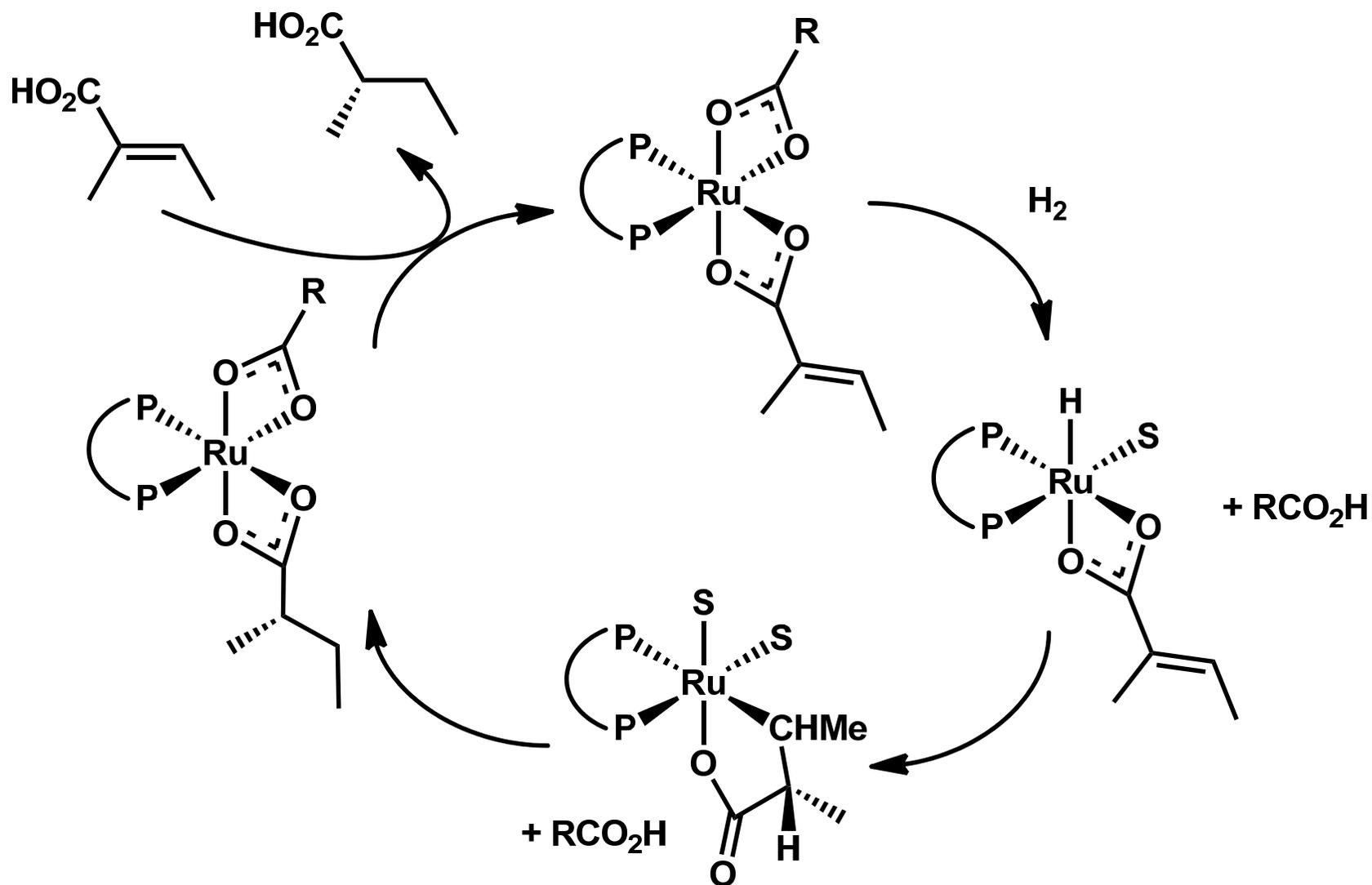


catalyst	% ee	confign.
$[\text{Rh}((R)\text{-binap})(\text{cod})]^+\text{ClO}_4^-$	69	S
$\text{Ru}(\text{OAc})_2[(R)\text{-BINAP}]$	>99.5	R



Catalytic Cycle

◆ monohydride



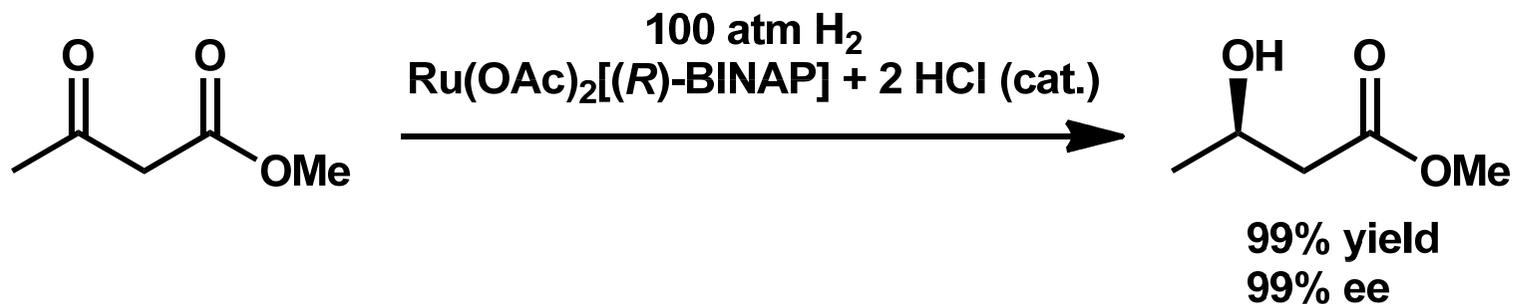
Morris, R. H. In *Handbook of Homogeneous Hydrogenation*; de Vries, J. G.; Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, 2007.

pK_a H—H 35

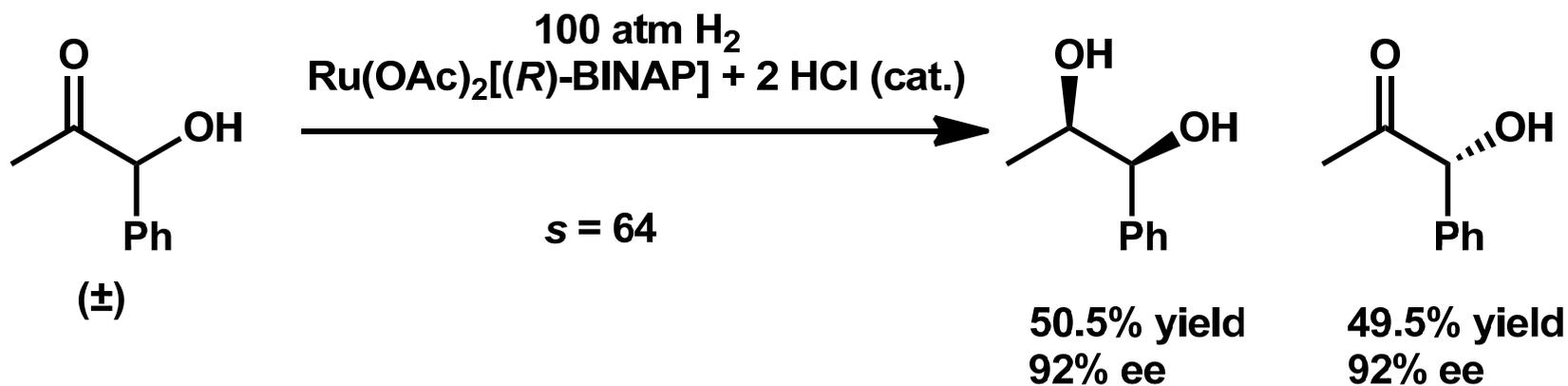
H—H 0–20
|
M

Hydrogenation of Ketones

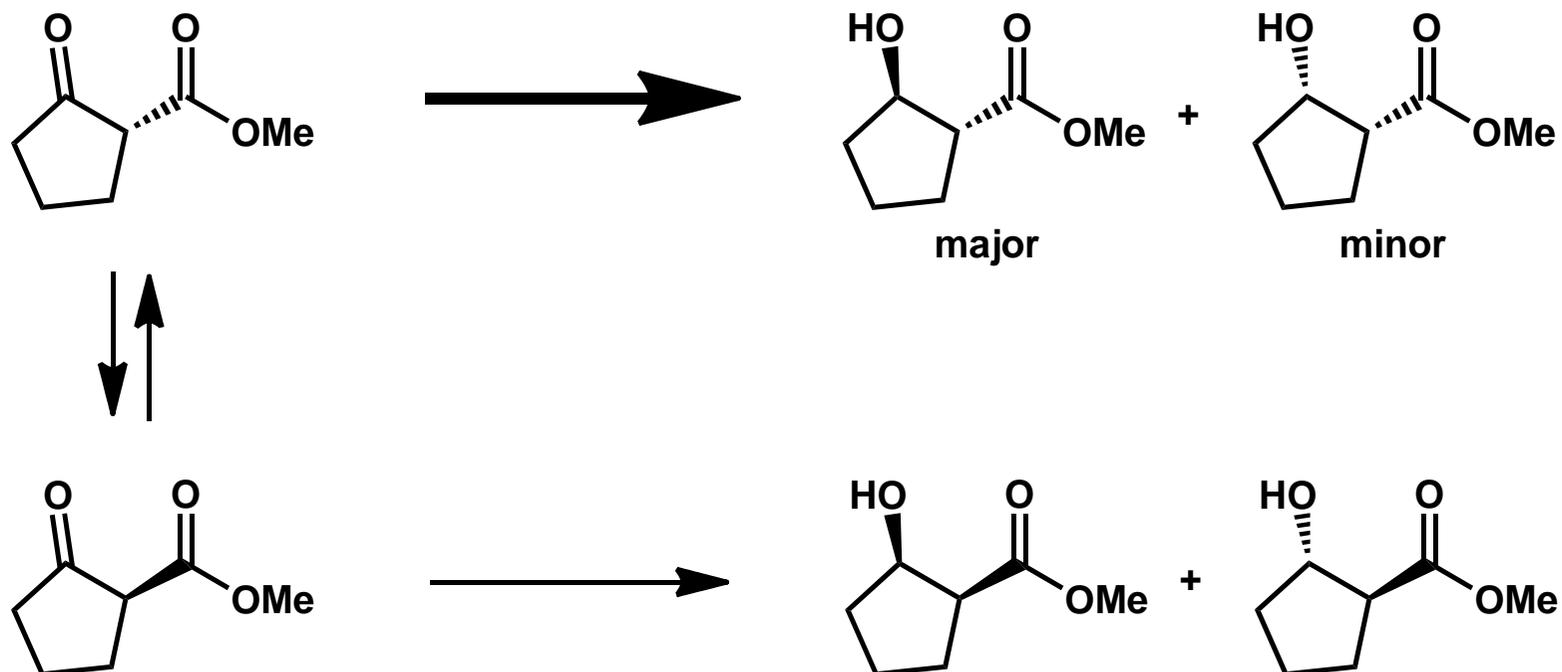
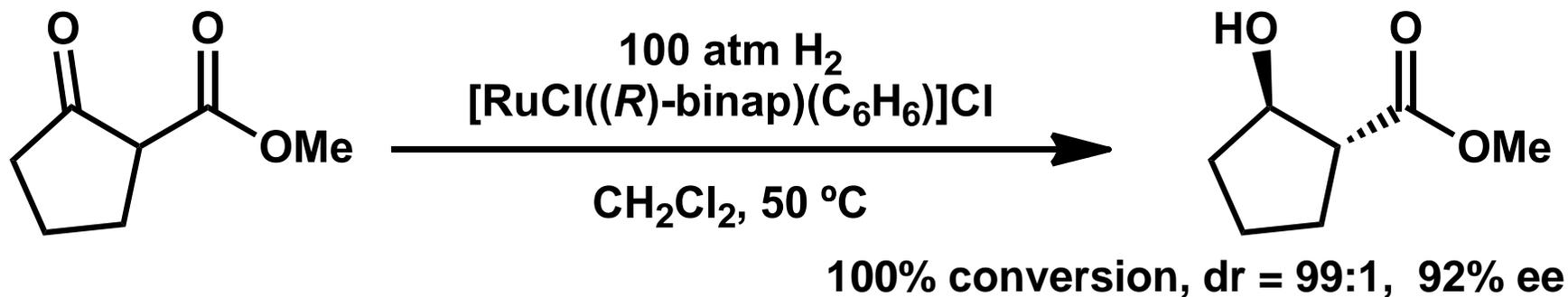
Enantioselective Hydrogenation



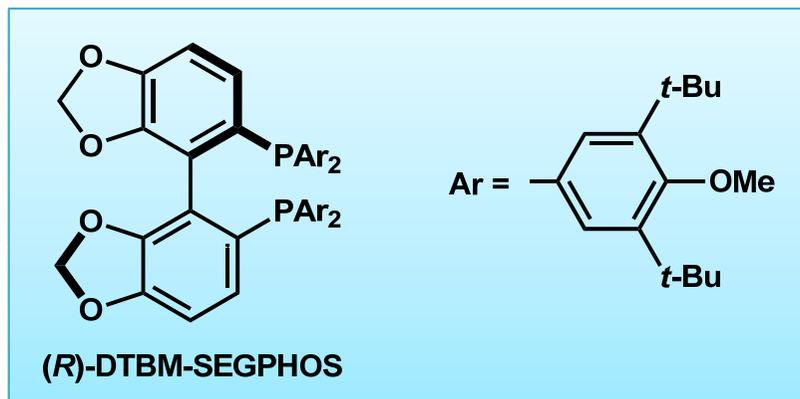
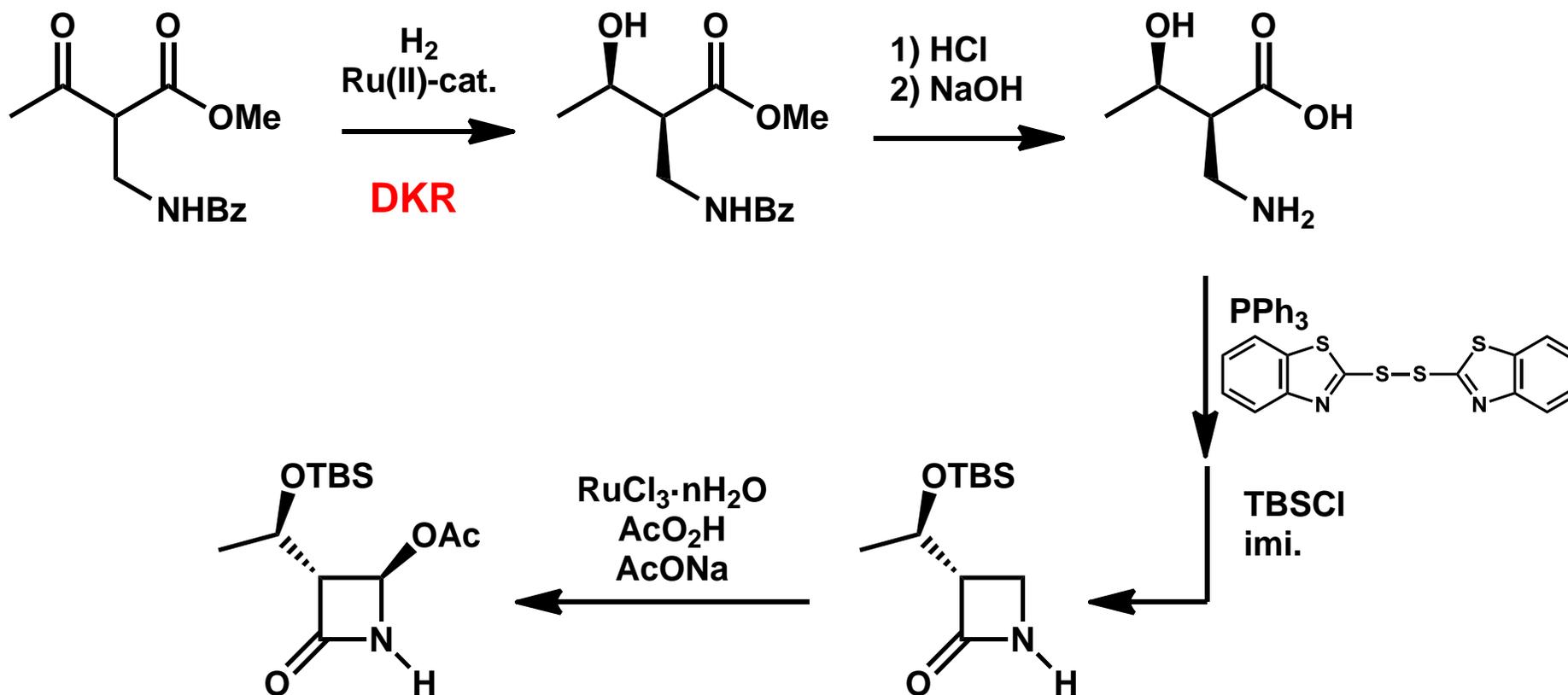
Kinetic Resolution



Dynamic Kinetic Resolution (DKR)

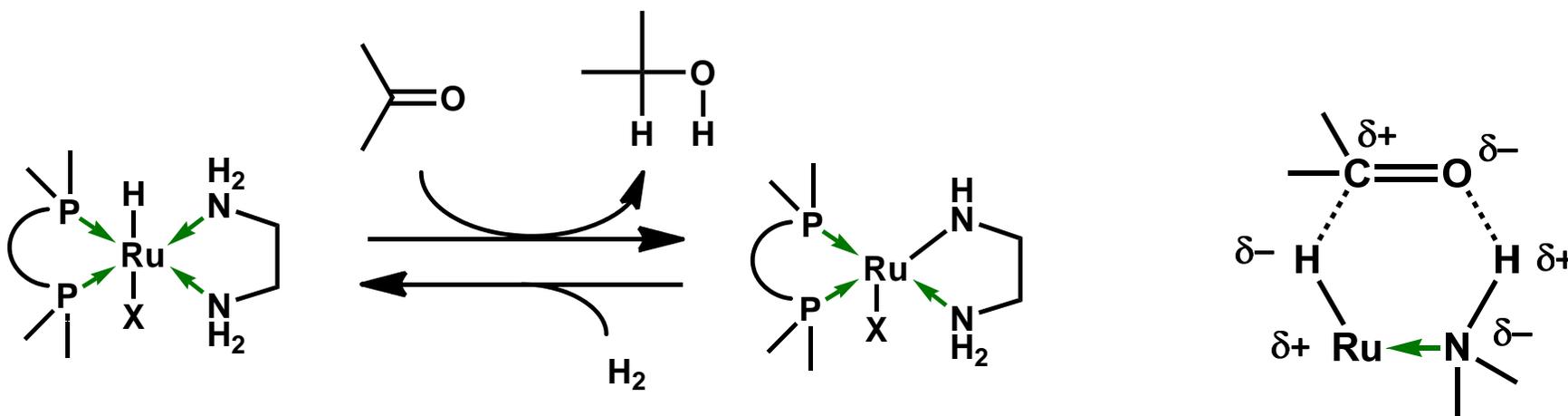
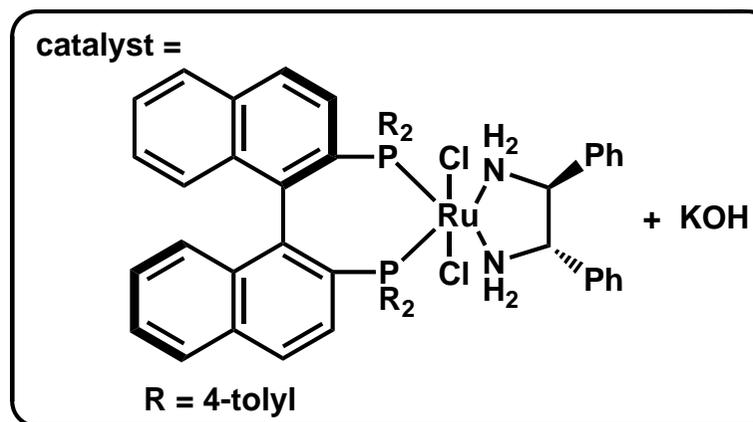
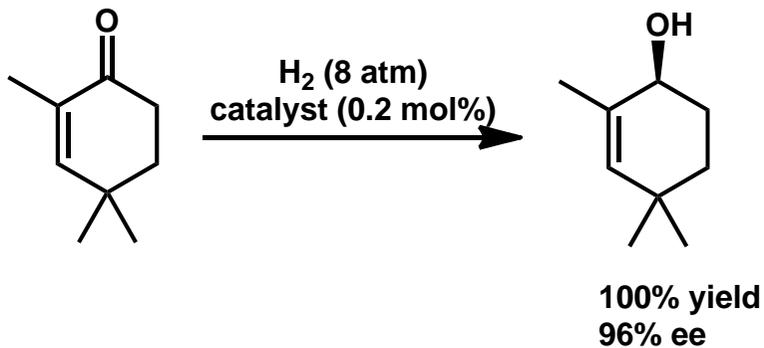


Route to a Key Intermediate of Carbapenem



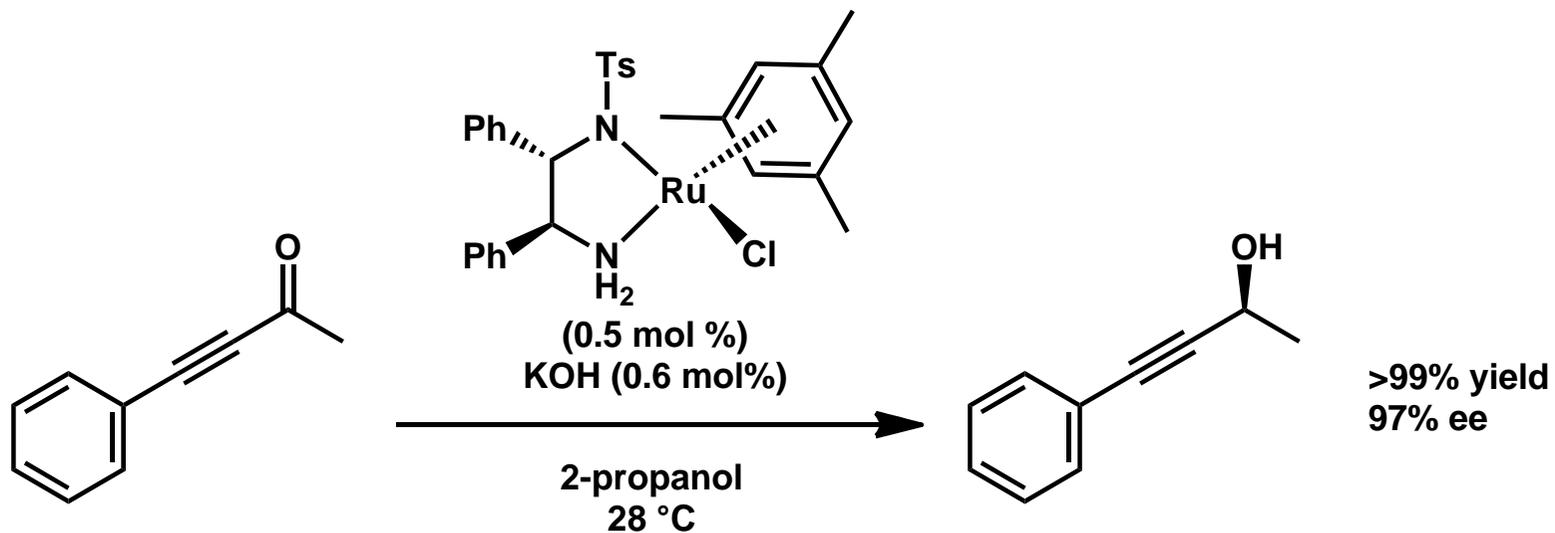
Shimizu, H. et al. *Acc. Chem. Res.*
2007, 40, 1385.

BINAP/1,2-Diamine–Ru(II) Complex

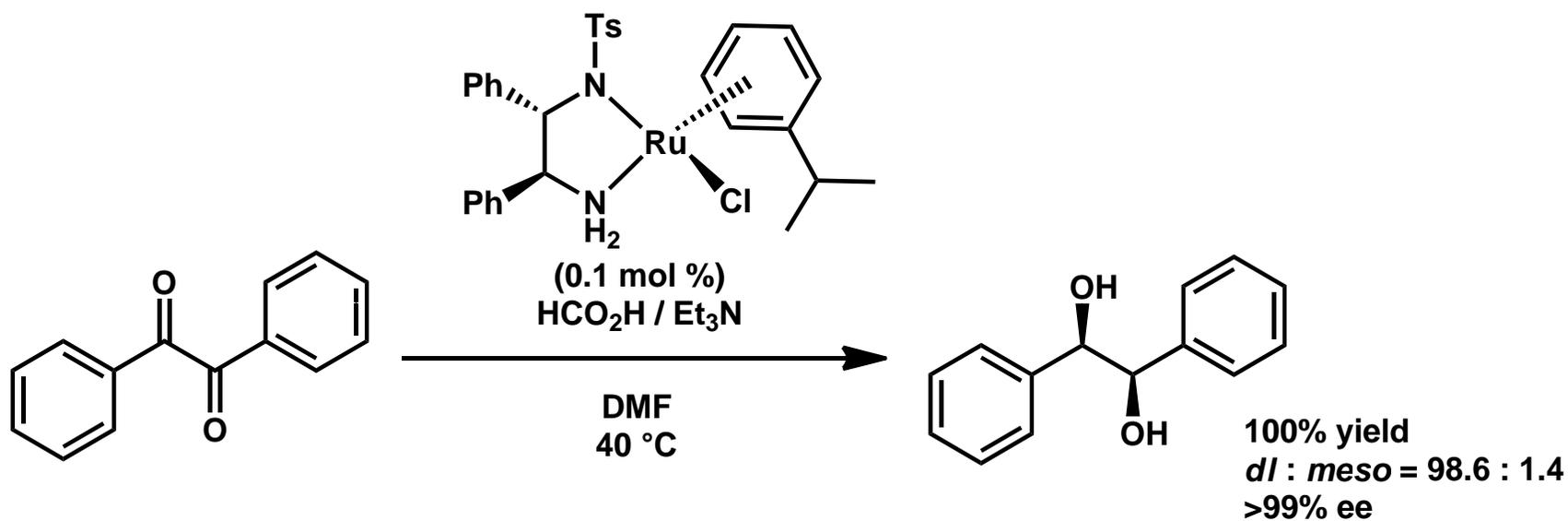


For mechanistic studies, see: Noyori, R. et al. *J. Am. Chem. Soc.* **2003**, 125, 13490.
 Bergens, S. H. et al. *J. Am. Chem. Soc.* **2008**, 130, 11979.

Asymmetric Transfer Hydrogenation



Noyori, R. et al. *J. Am. Chem. Soc.* **1997**, *119*, 8738.



Ikariya, T. et al. *Org. Lett.* **1999**, *1*, 1119.