

Ring Expansion: From C4 rings to C5 rings

Penghao Chen

Dong Group Seminar

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Namyslo, J. C.; Kaufmann, D. E. *Chem. Rev.* **2003**, *103*, 1485

Seiser, T.; Cramer, N. *Org. Biomol. Chem.*, **2009**, *7*, 2835

Seiser, T.; Saget, T.; Tran, D. N.; Cramer, N. *Angew. Chem. Int. Ed.* **2011**, *50*, 7740.

Murakami, M.; Matsuda, T. *Chem. Commun.*, **2011**, *47*, 1100

Cramer, N.; Seiser, T. *Synlett*, **2011**, 449

Outline

Carbene Insertion

Carbocation Rearrangement

Radical

Acid or Lewis Acid

Carboanion

Transition Metal

Outline

Carbene Insertion

Carbocation Rearrangement

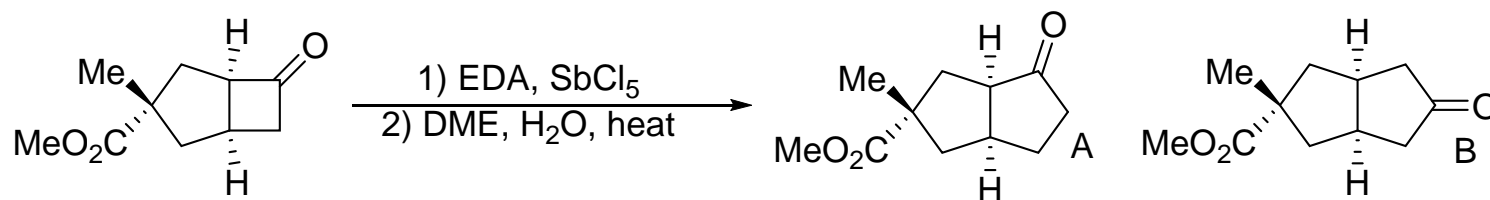
Radical

Acid or Lewis Acid

Carboanion

Transition Metal

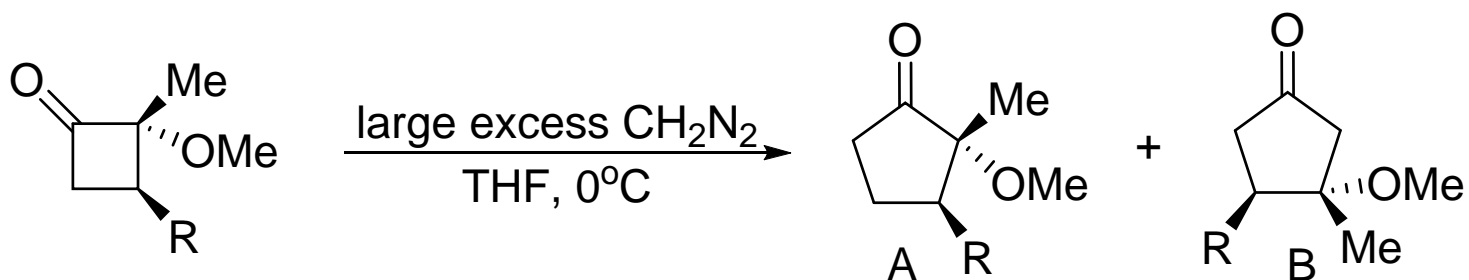
Carbene insertion

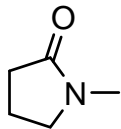
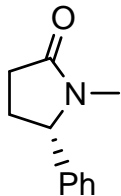


reagent	ring-expansion conditons	ratio A/B	Ca. 50% SM remained
CH ₂ N ₂ (large excess)	Et ₂ O-MeOH (4:1), 0°C, 5 h	50/50	
EDA (1.7 equiv)	Et ₂ O, BF ₃ OEt ₂ , (1.7 equiv), 0°C, 1h	68/32	
EDA (1.7 equiv)	DCM, Et ₃ O ⁺ BF ₄ ⁻ (1.7 equiv), -30°C, 48h	67/33	
EDA (2.1 equiv)	DCM, SbCl ₅ (0.44 equiv). -78°C, 2h	98/2	

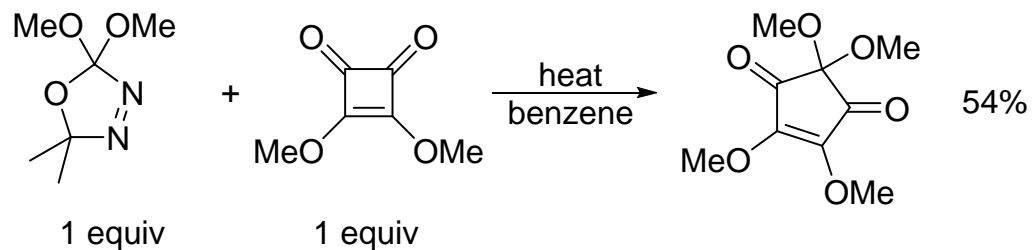
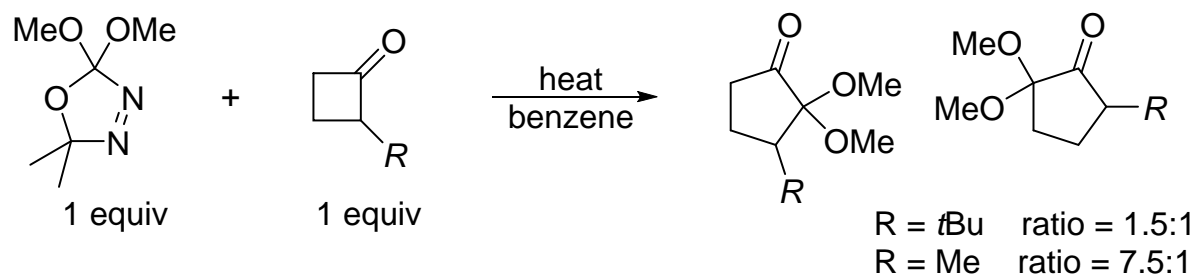
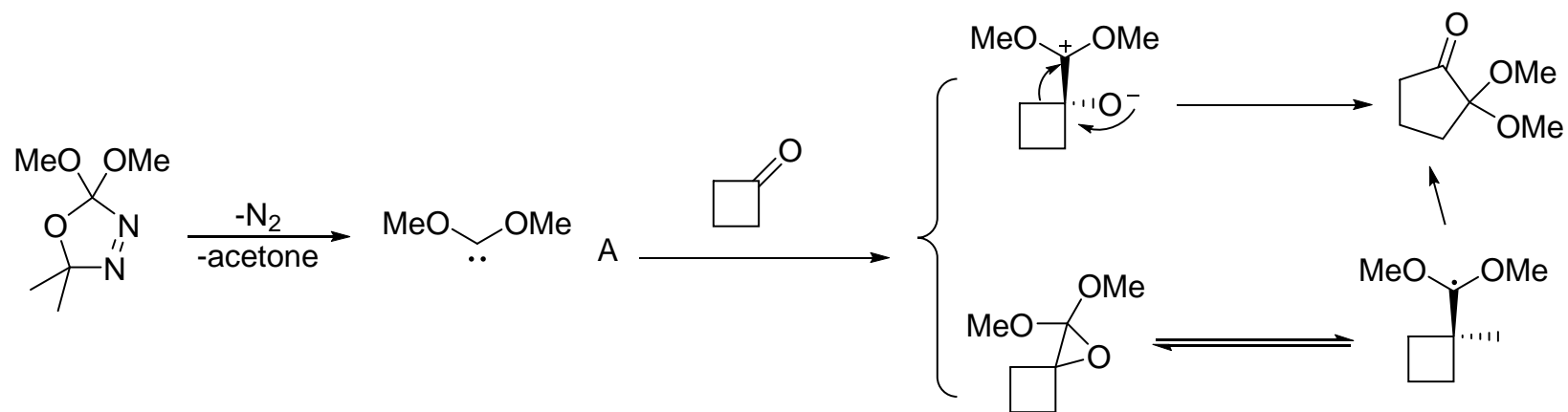
Greene, A. E.; Luche, M. J.; Serra, A. A. *J. Org. Chem.* **1985**, *50*, 3957.

Carbene insertion



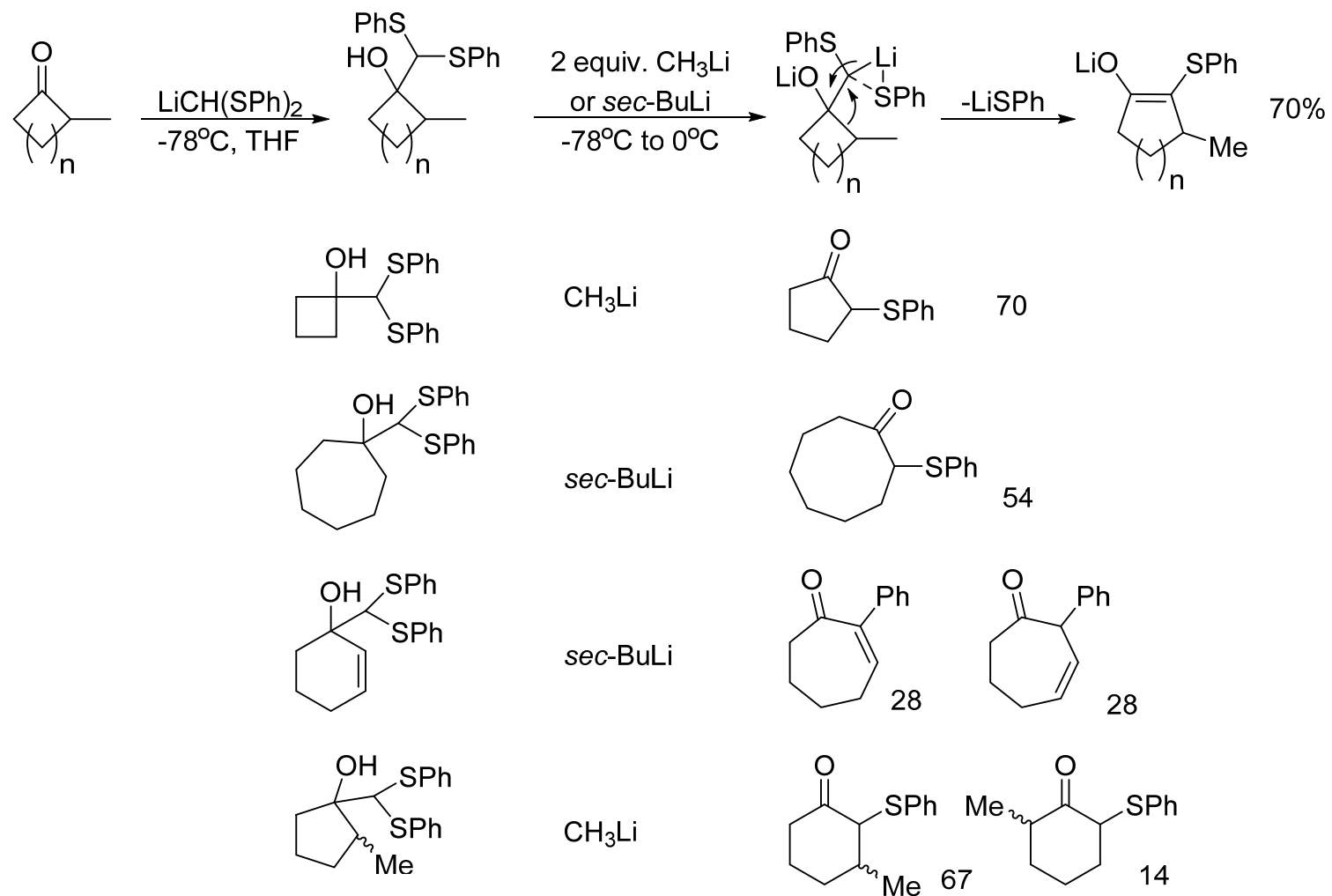
	yield	ratio A/B
$\text{R} = n\text{-C}_4\text{H}_9$	61	59/41
p-HOPh	76	71/29
	89	92/8
	84	100/0

Carbene insertion



Venneri, P. C.; Warkentin, J. *Can. J. Chem.* **2000**, 1194.

Carbene insertion



Abraham, W. D.; Bhupathy, M.; **Cohen, T.** *Tetrahedron Lett.* **1987**, 28, 2203.

Outline

Carbene Insertion

Carbocation Rearrangement

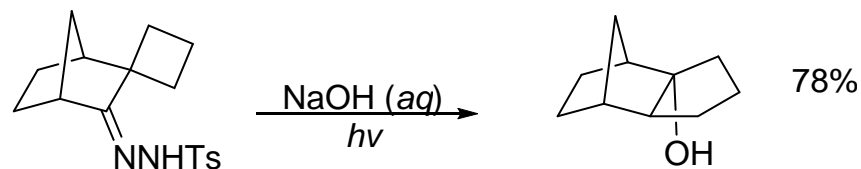
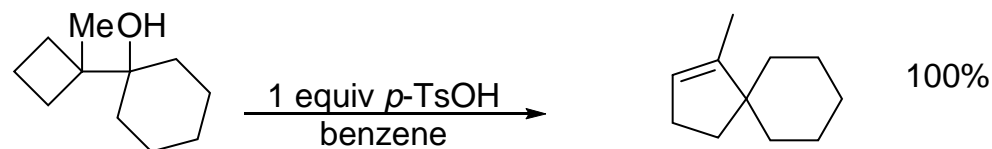
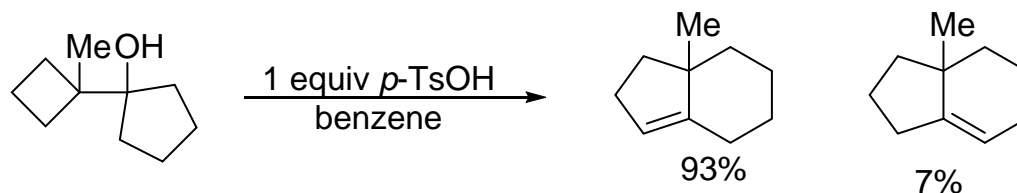
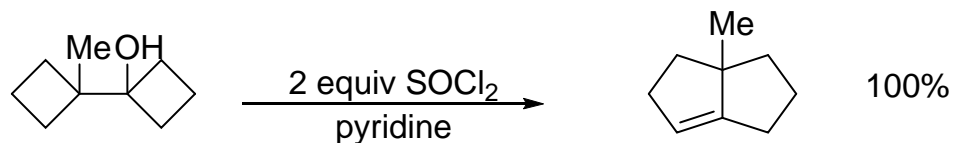
Radical

Acid or Lewis Acid

Carboanion

Transition Metal

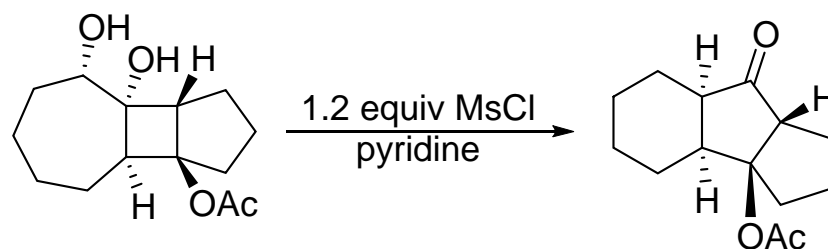
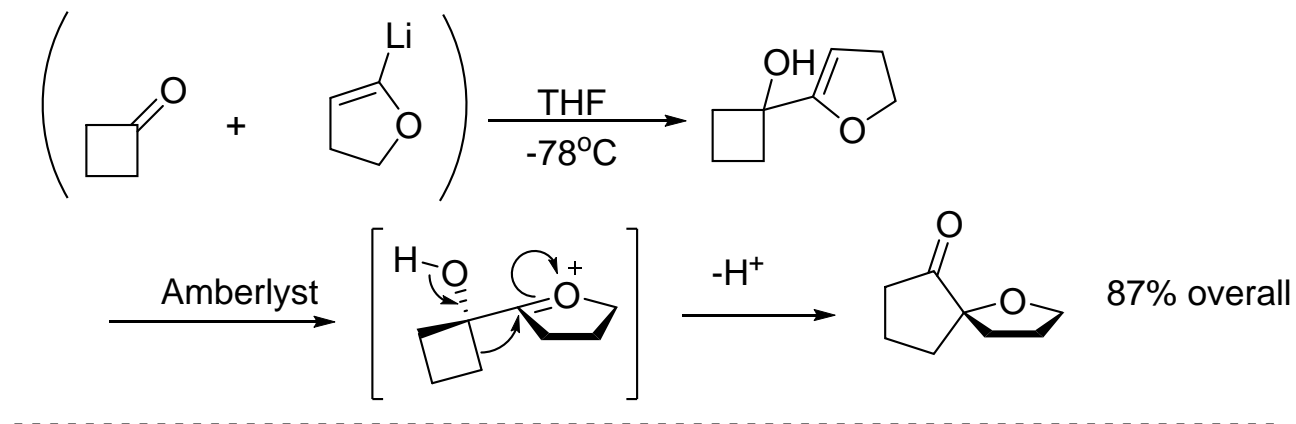
Carbocation Rearrangement



Mandelt, K.; **Fitjer, L.** *Synthesis*, **1998**, 1523

Kirmse, W.; Landscheidt, H.; Siegfried, R. *Eur. J. Org. Chem.* **1998**, 213.

Carbocation Rearrangement

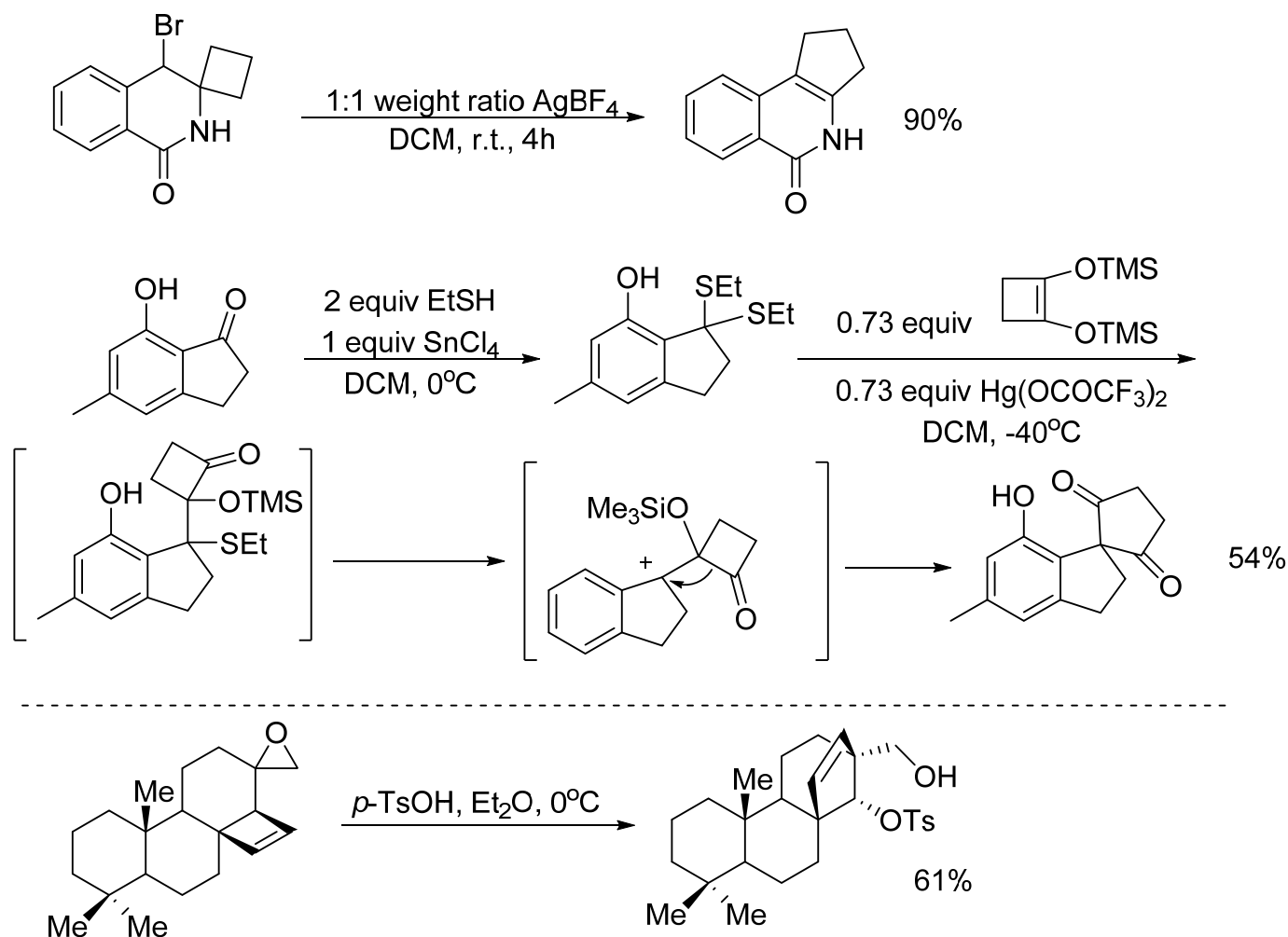


Paquette, L. A.; Kinney, M. J.; Dullweber, U. *J. Org. Chem.* **1997**, *62*, 1713.

Paquette, L. A.; Owen, D. R.; Bibart, R. T.; Seekamp, C. K.; Kahane, A. L.; Lanter, . C.; Corral, M. A. *J. Org. Chem.* **2001**, *66*, 2828.

Jamart-Gregoire, B.; Brosse, N.; Ianelli, S.; Nardelli, M.; **Caubere, P.** *J. Org. Chem.* **1993**, *58*, 4572.

Carbocation Rearrangement



Jahangir; Fisher, L. E.; Clark, R. D.; Muchowski, J. M. *J. Org. Chem.* **1989**, *54*, 2992.

Wendt, J. A.; Gauvreau, P. J.; Bach, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 9921.

Abad, A.; Agullo, C.; Arno, M.; Marin, M. L.; Zaragoza, R. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2987.

Outline

Carbene Insertion

Carbocation Rearrangement

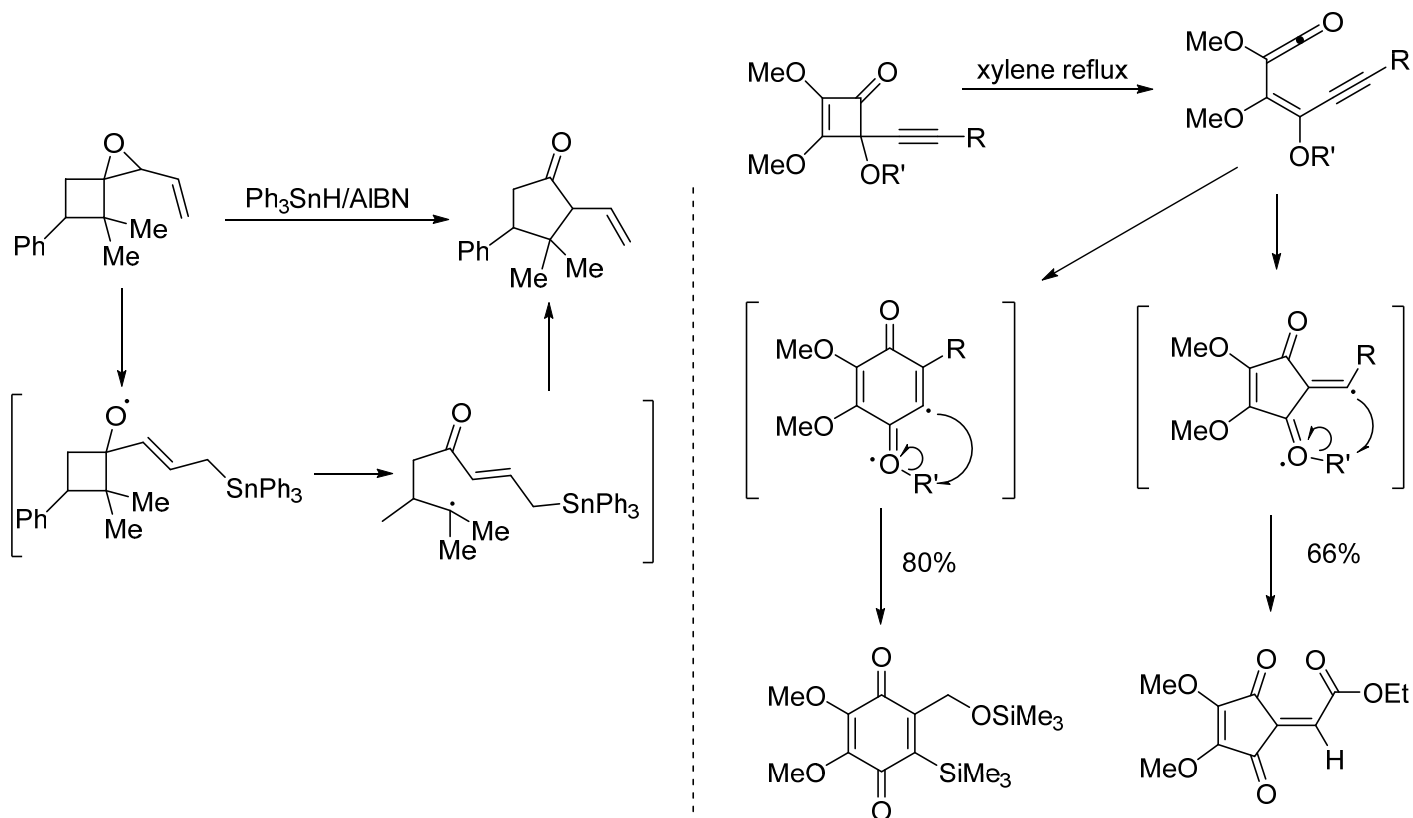
Radical

Acid or Lewis Acid

Carboanion

Transition Metal

Radical



Kim, S.; Lee, S. *Tetrahedron Lett.* **1991**, 32, 6575.

Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.;

Moore, H. W. *J. Am. Chem. Soc.* **1989**, 111, 975.

Outline

Carbene Insertion

Carbocation Rearrangement

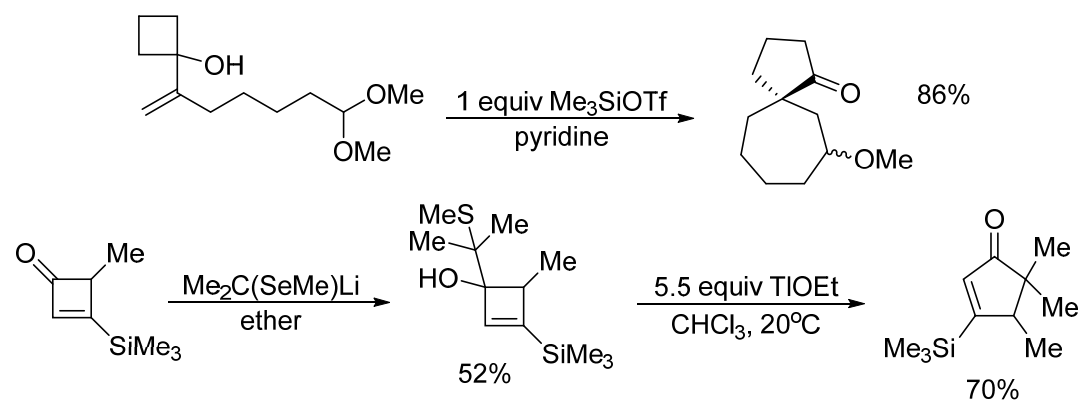
Radical

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Transition Metal

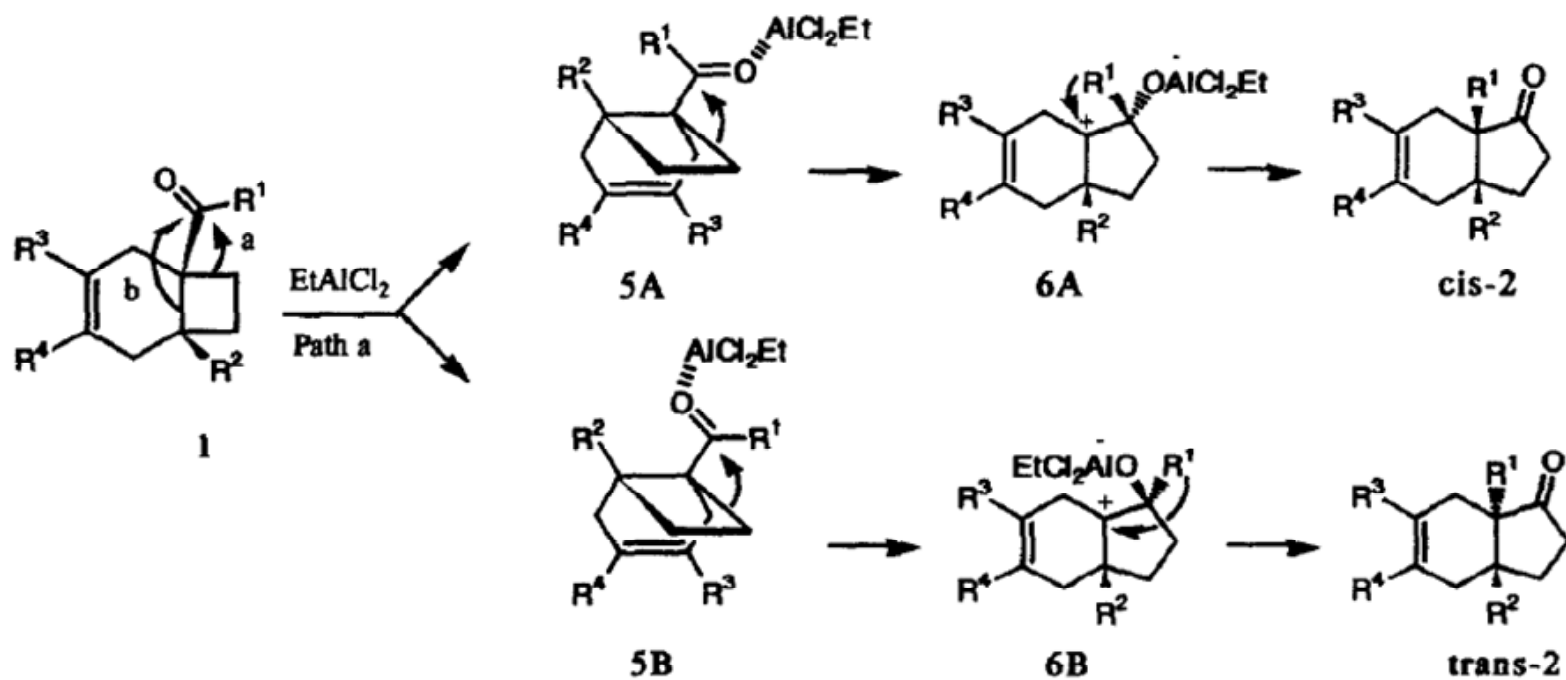
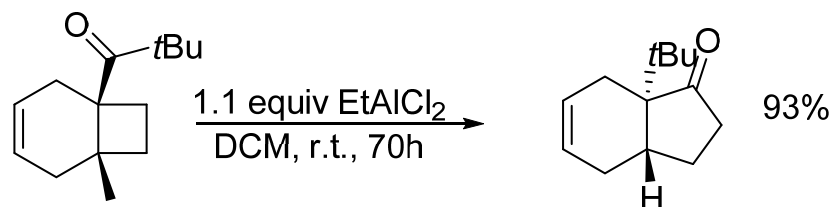
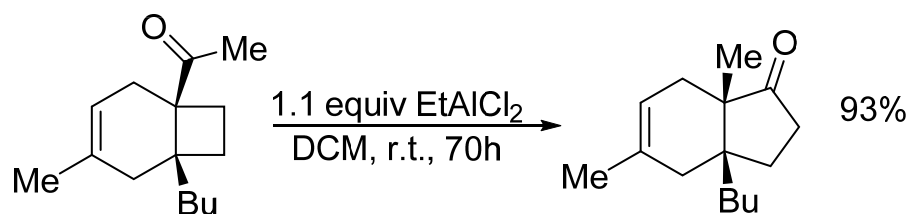
Acid or Lewis Acid



Trost, B. M.; Chen, D. W. C. *J. Am. Chem. Soc.* **1996**, *118*, 12541.

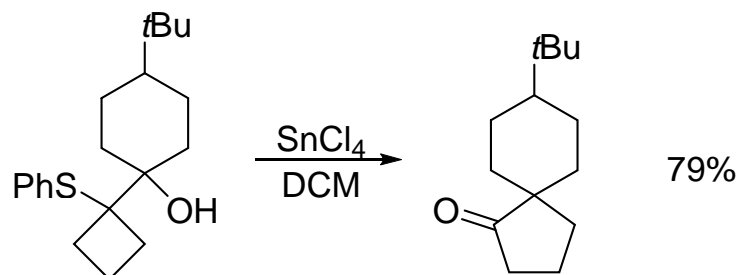
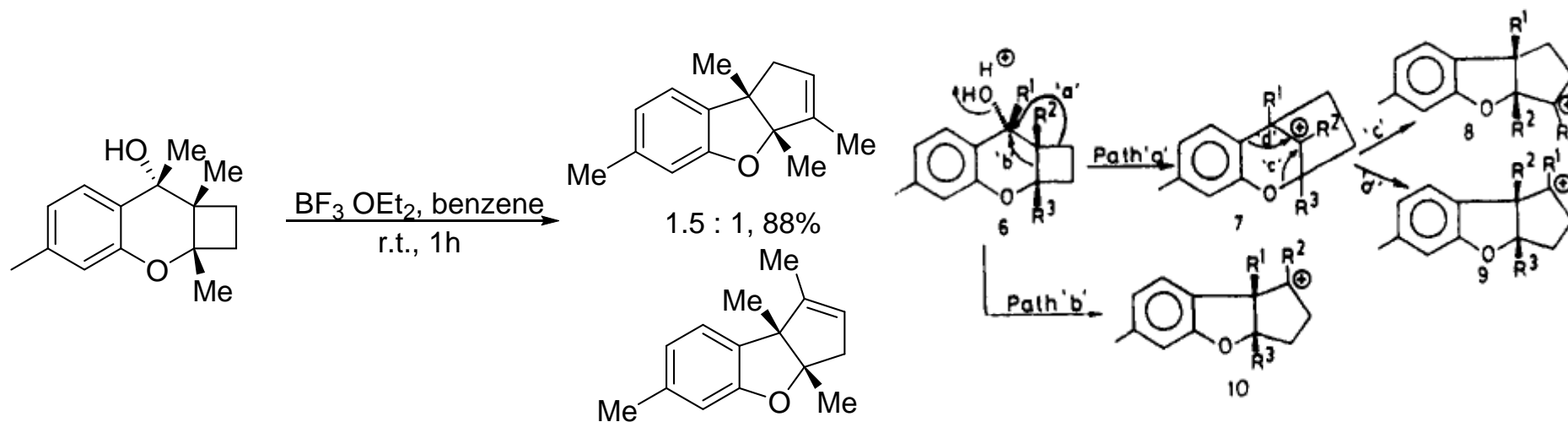
Krief, A.; Laboureur, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 702.

Acid or Lewis Acid



Fujiwara, T.; Tomaru, J.; Suda, A.; Takeda, T. *Tetrahedron Lett.* **1992**, *33*, 2583.
Takeda, T.; Fujiwara, T. *Synlett* **1996**, 481.

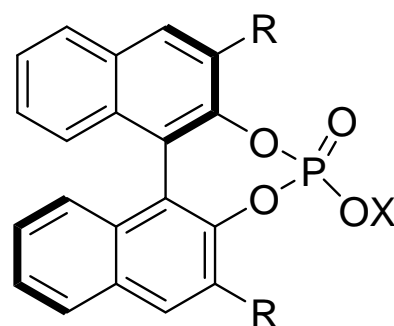
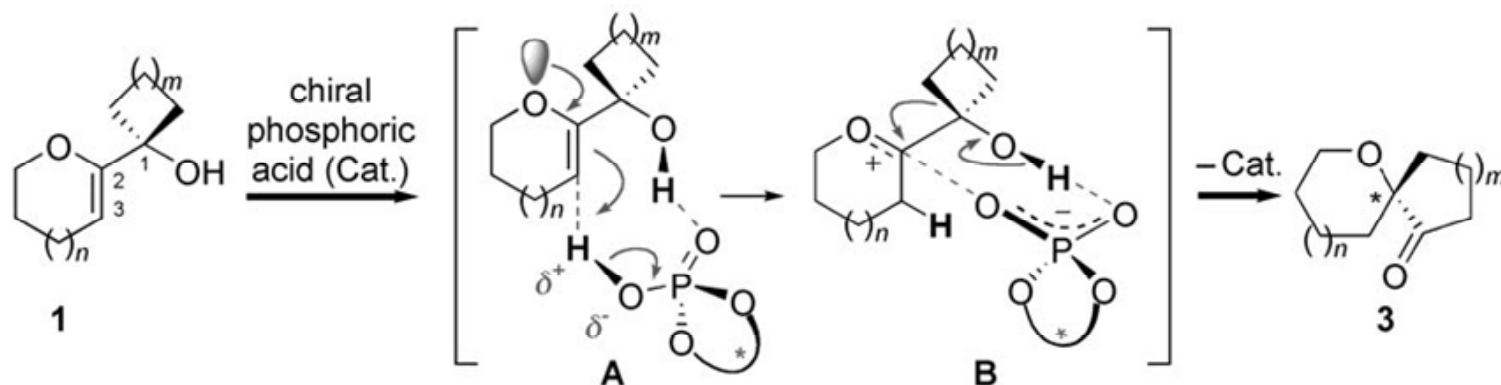
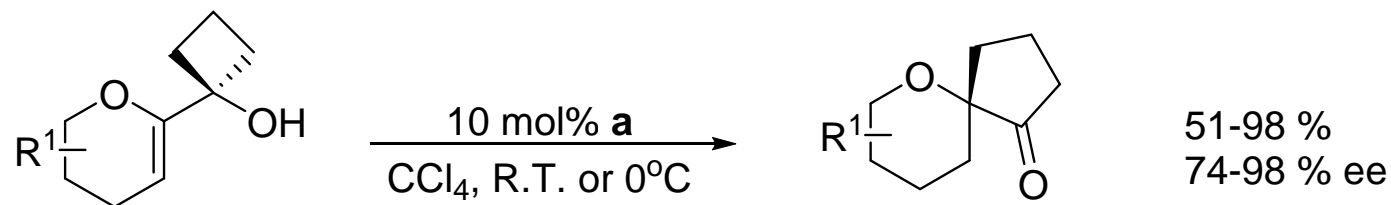
Acid or Lewis Acid



Nath, A.; Ghosh, A.; Venkateswaran, R. V. *J. Org. Chem.* **1992**, *57*, 1467.

Fitjer, L.; Schlotmann, W.; Noltemeyer, M. *Tetrahedron Lett.* **1995**, *36*, 4985.

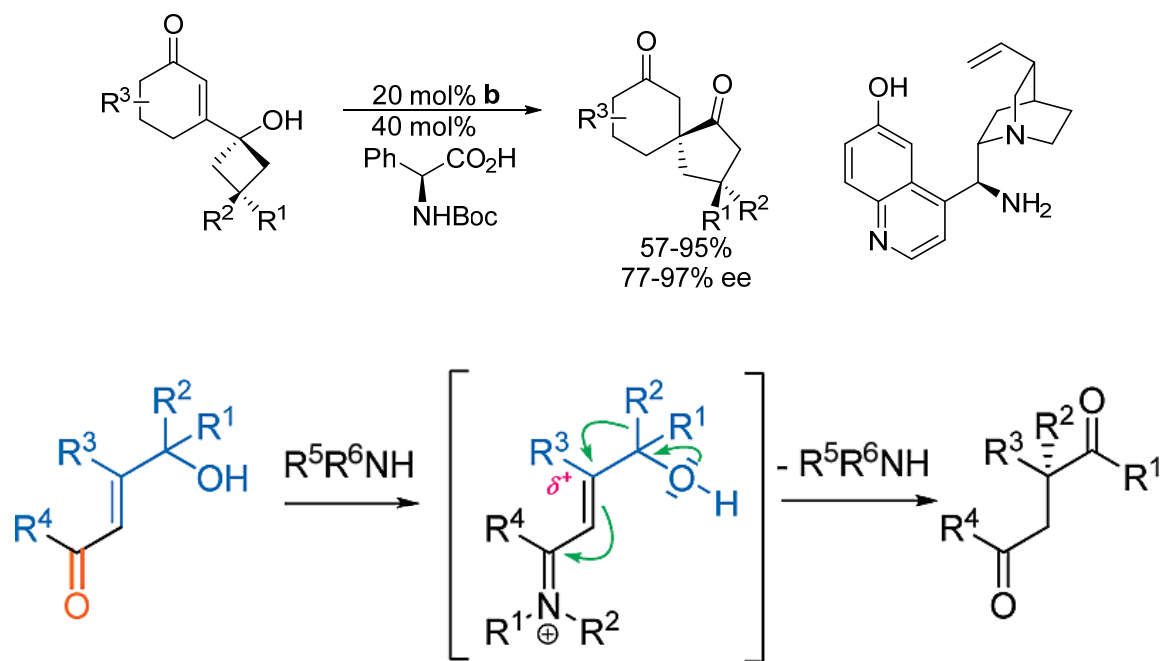
Acid or Lewis Acid



$\text{R} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$
 $\text{X} = \text{H or Ag}$

Zhang Q. W.; Fan C. A.; Zhang H. J.; **Tu Y. Q.**; Zhao Y. M.; Gu P.; Chen Z. M. *Angew. Chem.* **2009**, *121*, 8724; *Angew. Chem. Int. Ed.* **2009**, *48*, 8572.

Acid or Lewis Acid



Zhang E.; Fan C. A.; **Tu Y. Q.**; Zhang F. M.; Song Y. L.; *J. Am. Chem. Soc.* **2009**, *131*, 14626.

Outline

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Carbocation Rearrangement

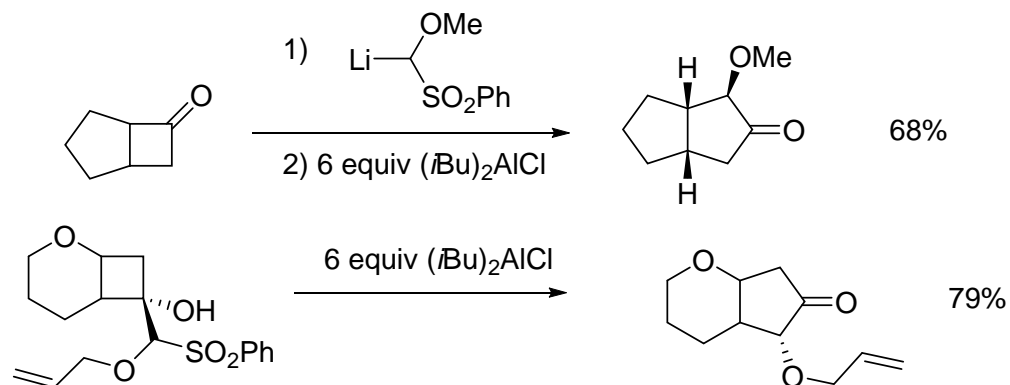
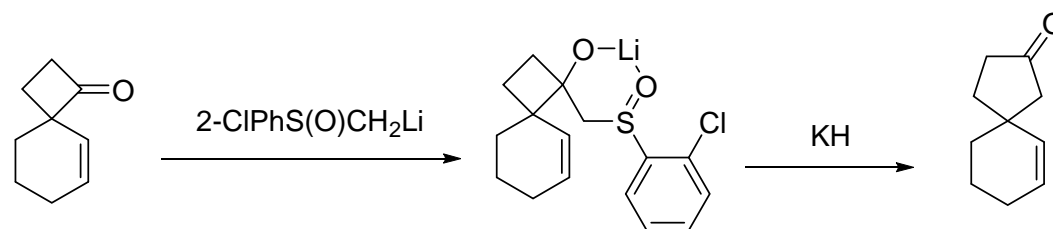
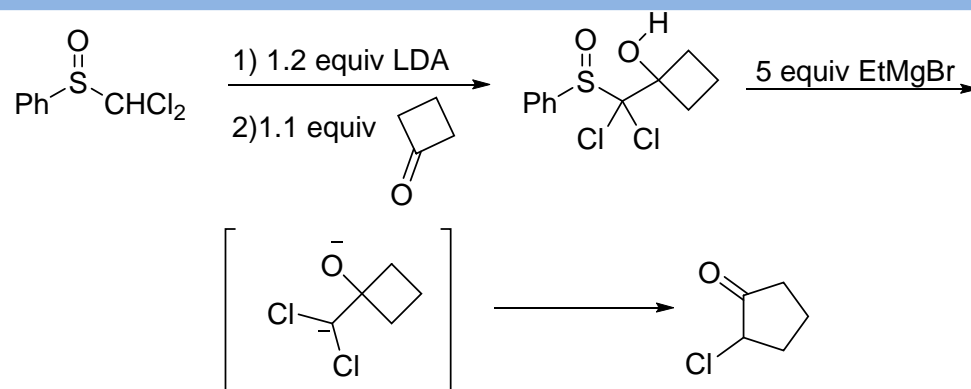
Radical

Acid or Lewis Acid

Carboanion

Transition Metal

Carboanion



Trost, B. M.; Mikhail, G. K. *J. Am. Chem. Soc.* **1987**, *109*, 4124.

Satoh, T.; Mizu, Y.; Kawashima, T.; Yamakawa, K. *Tetrahedron* **1995**, *51*, 703.

Gadwood, R. C.; Mallick, I. M.; DeWinter, A. J. *J. Org. Chem.* **1987**, *52*, 774.

Outline

Carbene Insertion

Carbocation Rearrangement

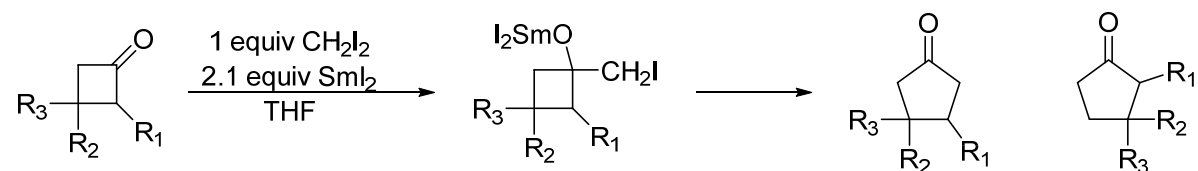
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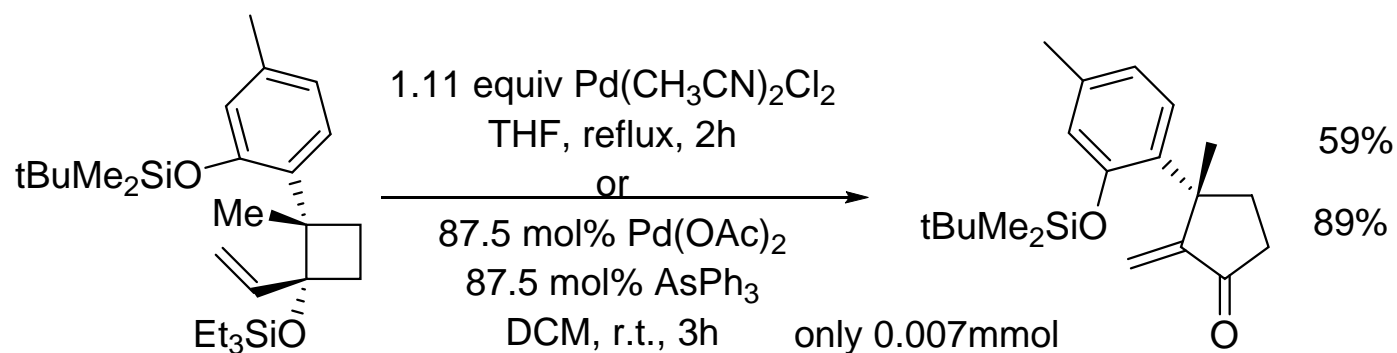
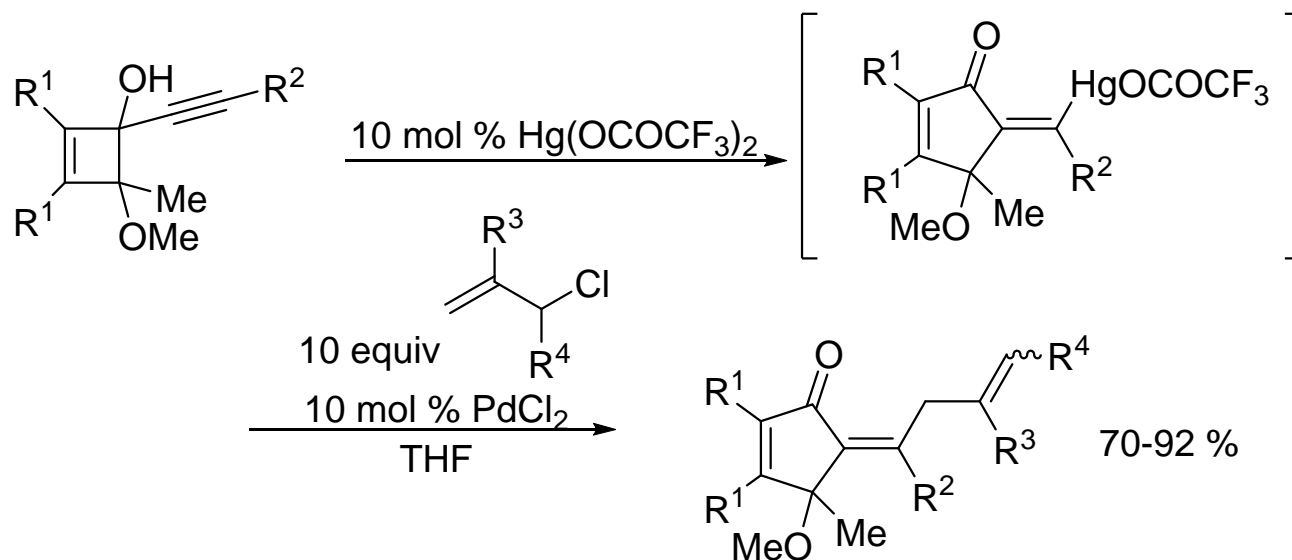
Transition Metal



R1	R2	R3	Time(h)	iodohydrin	cyclopentanone
H	Ph	H	0.5	44	16
H	Ph	H	15	trace	61
H	<i>n</i> Bu	H	0.5	34	41
H	<i>n</i> Bu	H	15	trace	88
	-(CH ₂) ₄ -	H	15	trace	40 (1:1)
	-(CH ₂) ₅ -	H	15	trace	82 (97:3)

Fukuzawa, S.-i.; Tsuchimoto, T. *Tetrahedron Lett* . 1995, 36, 5937.

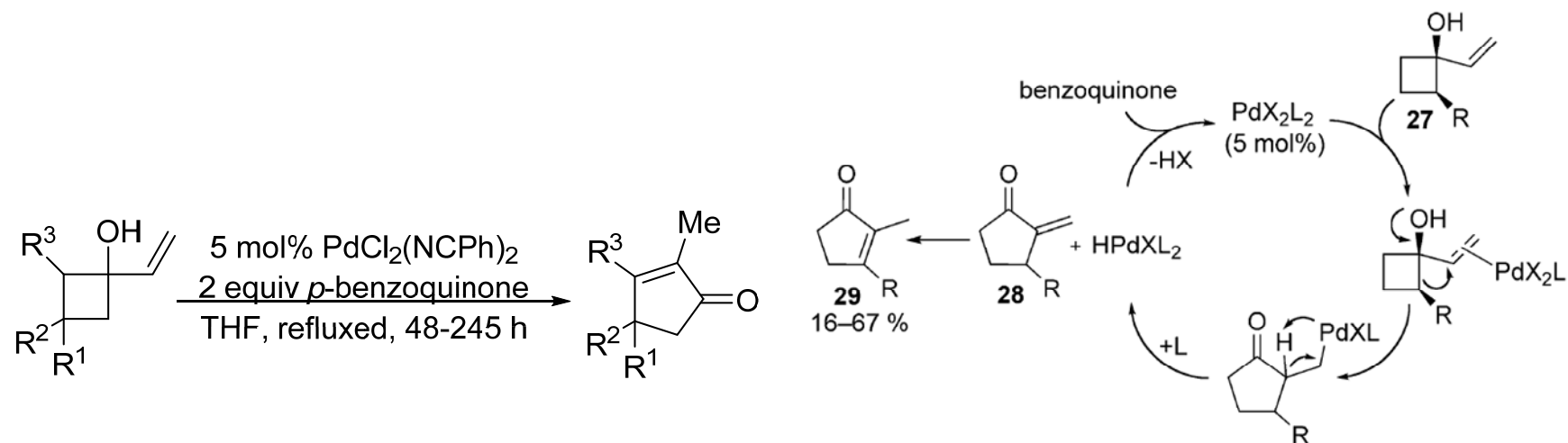
Transition Metal



Liebeskind, L. S.; Bombrun, A. *J. Org. Chem.* **1994**, *59*, 1149.

Nemoto, H.; Nagamochi, M.; Ishibashi, H.; Fukumoto, K. *J. Org. Chem.* **1994**, *59*, 74.

Transition Metal

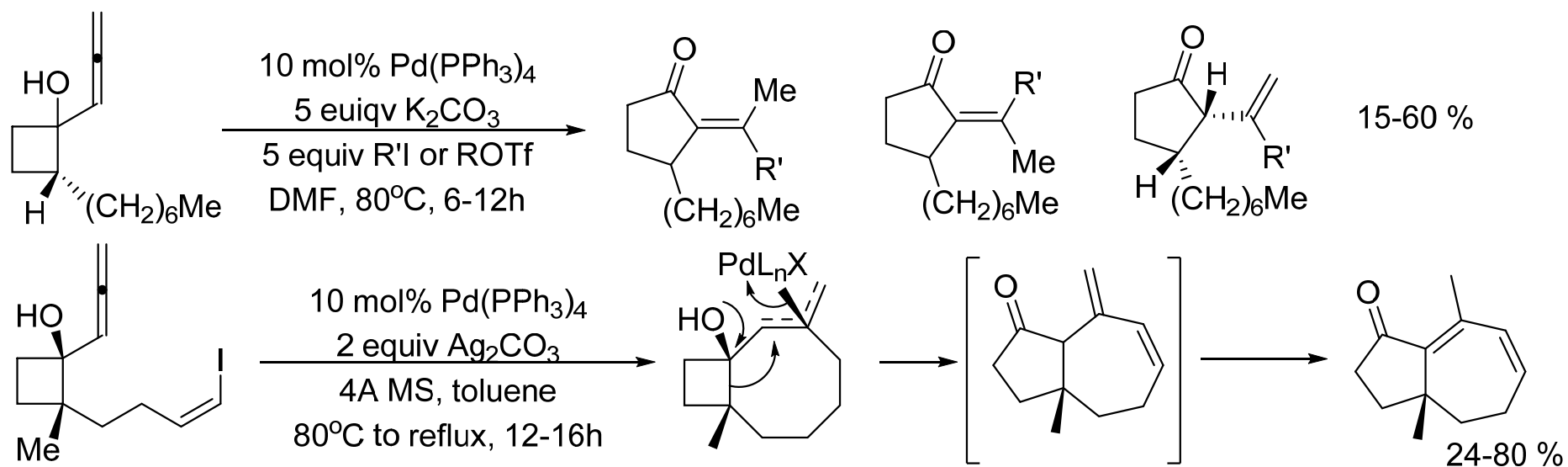


Clark G. R.; Thiensathit S. *Tetrahedron Lett.* **1985**, *26*, 2503.

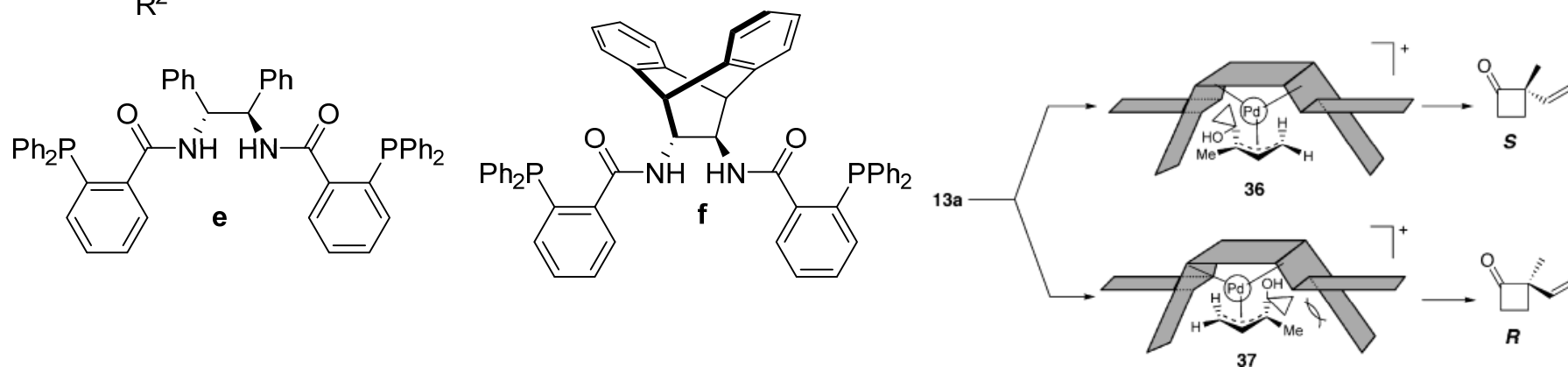
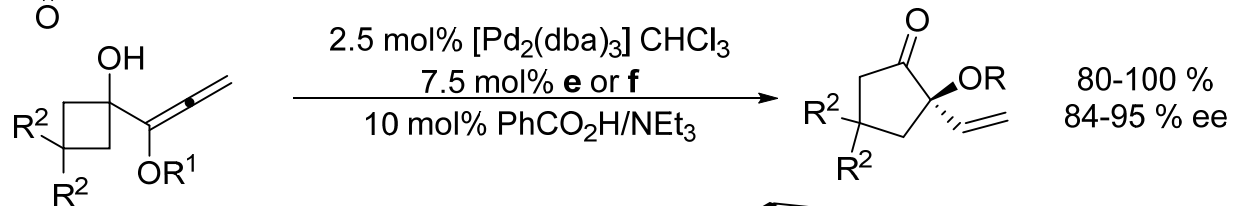
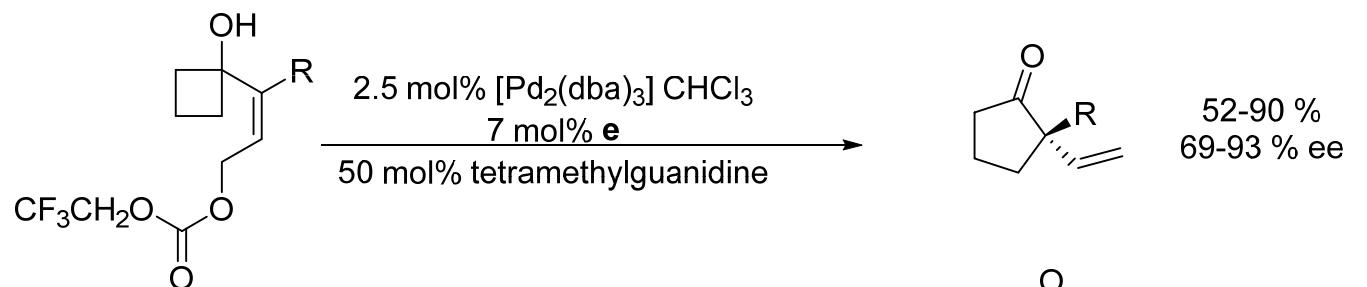
Sethofer S. G.; Staben S. T.; Hung O. Y.; Toste F. D. *Org. Lett.* **2008**, *10*, 4315.

Schweinitz A.; Chtchemelina A.; Orellana A. *Org. Lett.* **2011**, *13*, 232.

Transition Metal



Transition Metal

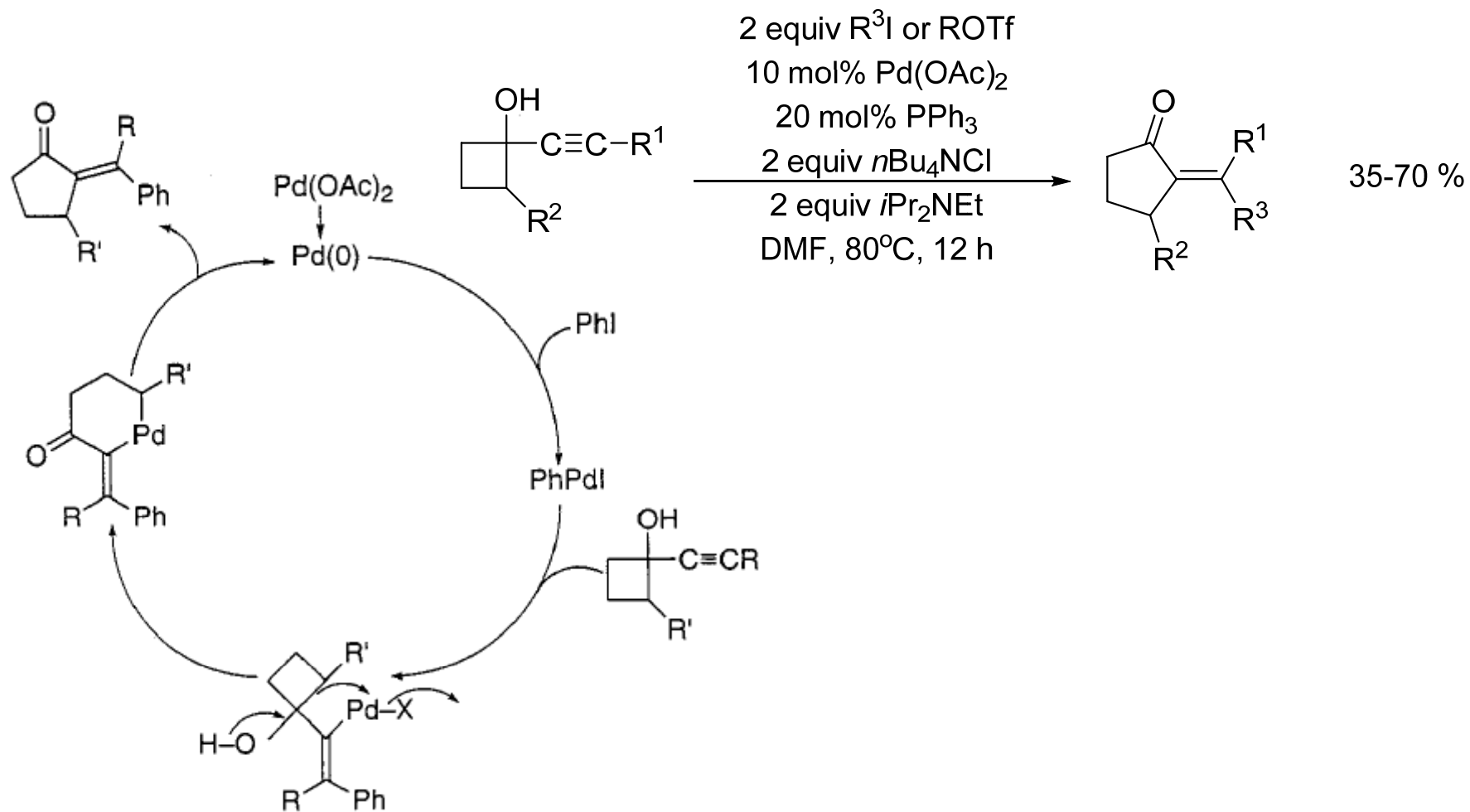


Trost B. M.; Yasukata T. *J. Am. Chem. Soc.* **2001**, *123*, 7162.

Trost B. M.; Xie J. *J. Am. Chem. Soc.* **2006**, *128*, 6044.

Trost B. M.; Xie J. *J. Am. Chem. Soc.* **2008**, *130*, 6231,

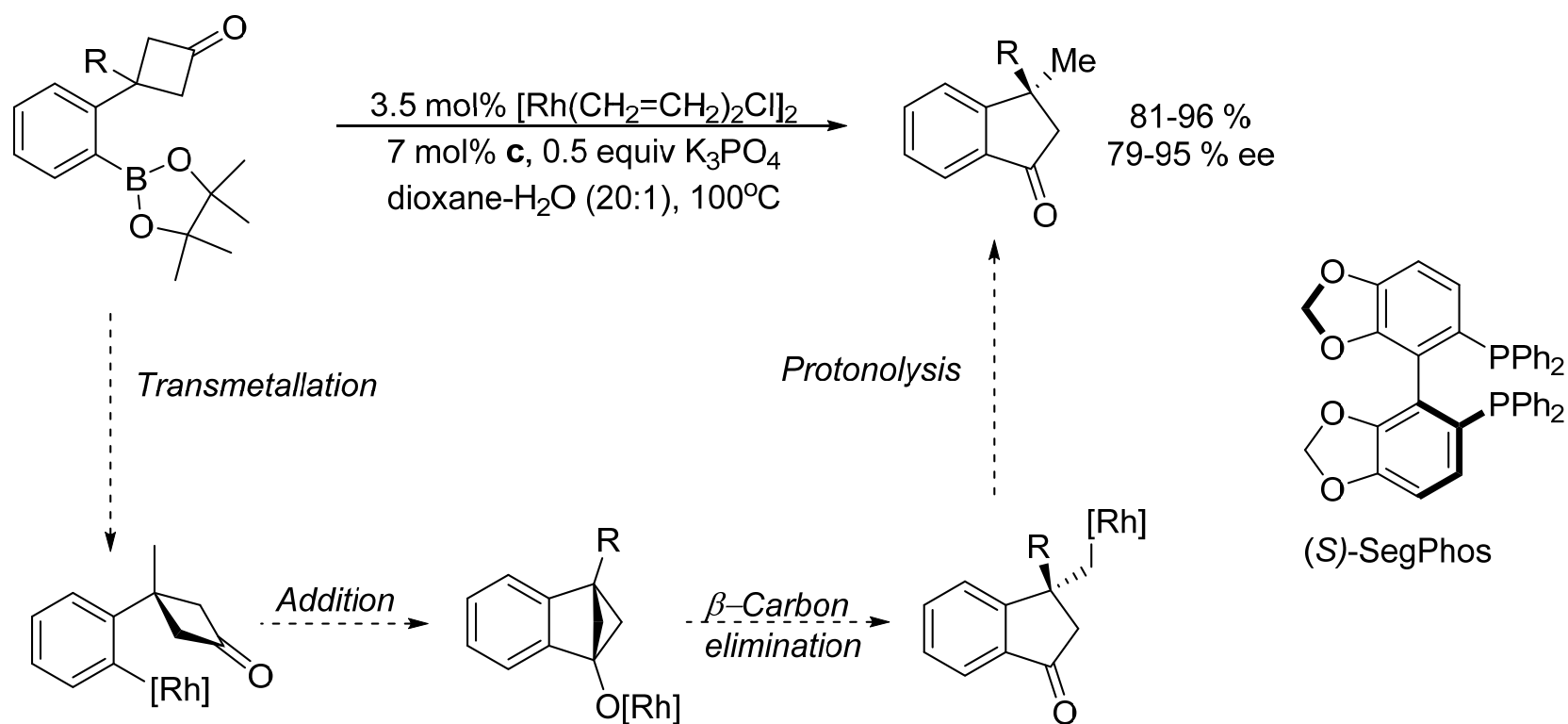
Transition Metal



Larock R. C.; Reddy C. K. *Org. Lett.* **2000**, *2*, 3325.

Larock R. C.; Reddy C. K. *J. Org. Chem.* **2002**, *67*, 2027.

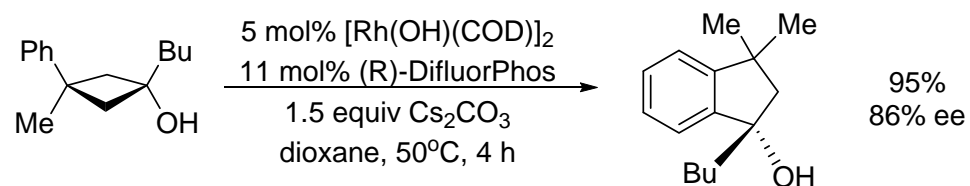
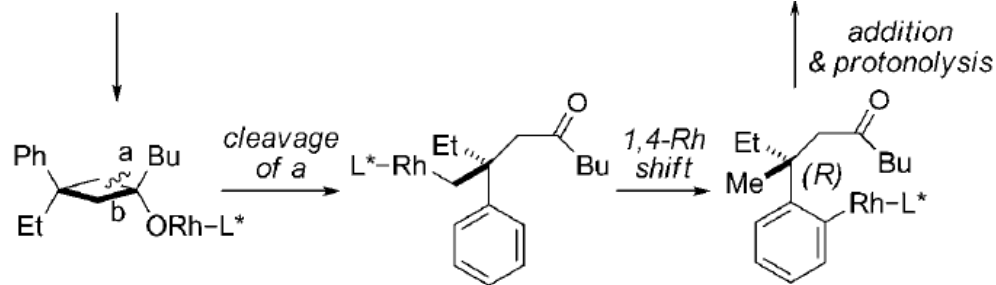
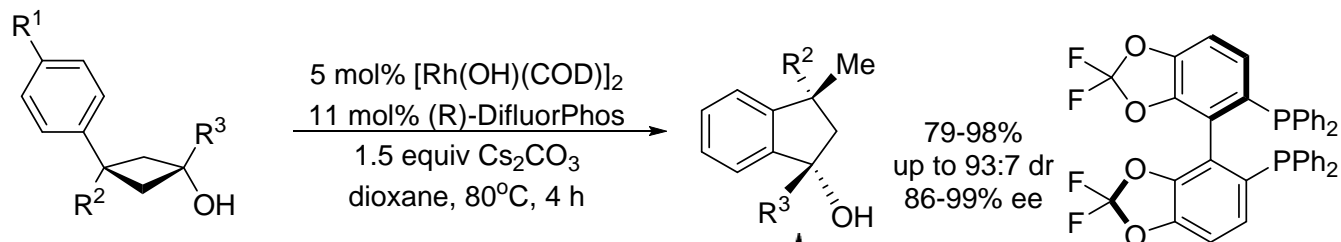
Transition Metal



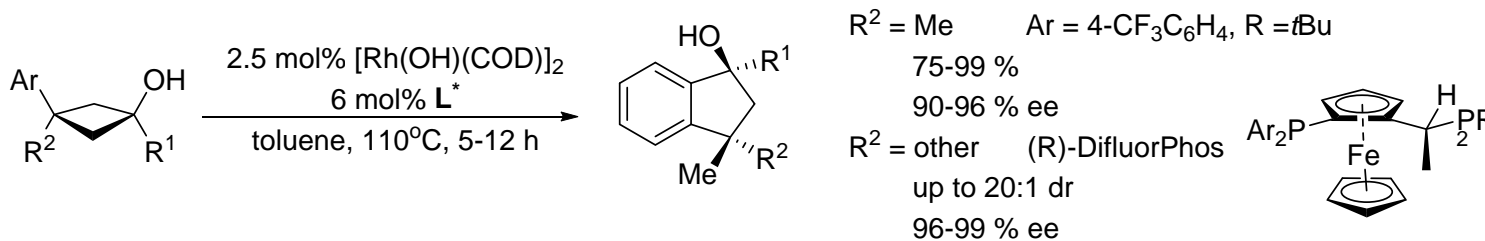
Matsuda T.; Shigeno M.; Makino M.; **Murakami M.** *Org. Lett.* **2006**, *8*, 3379.

Transition Metal

Murakami



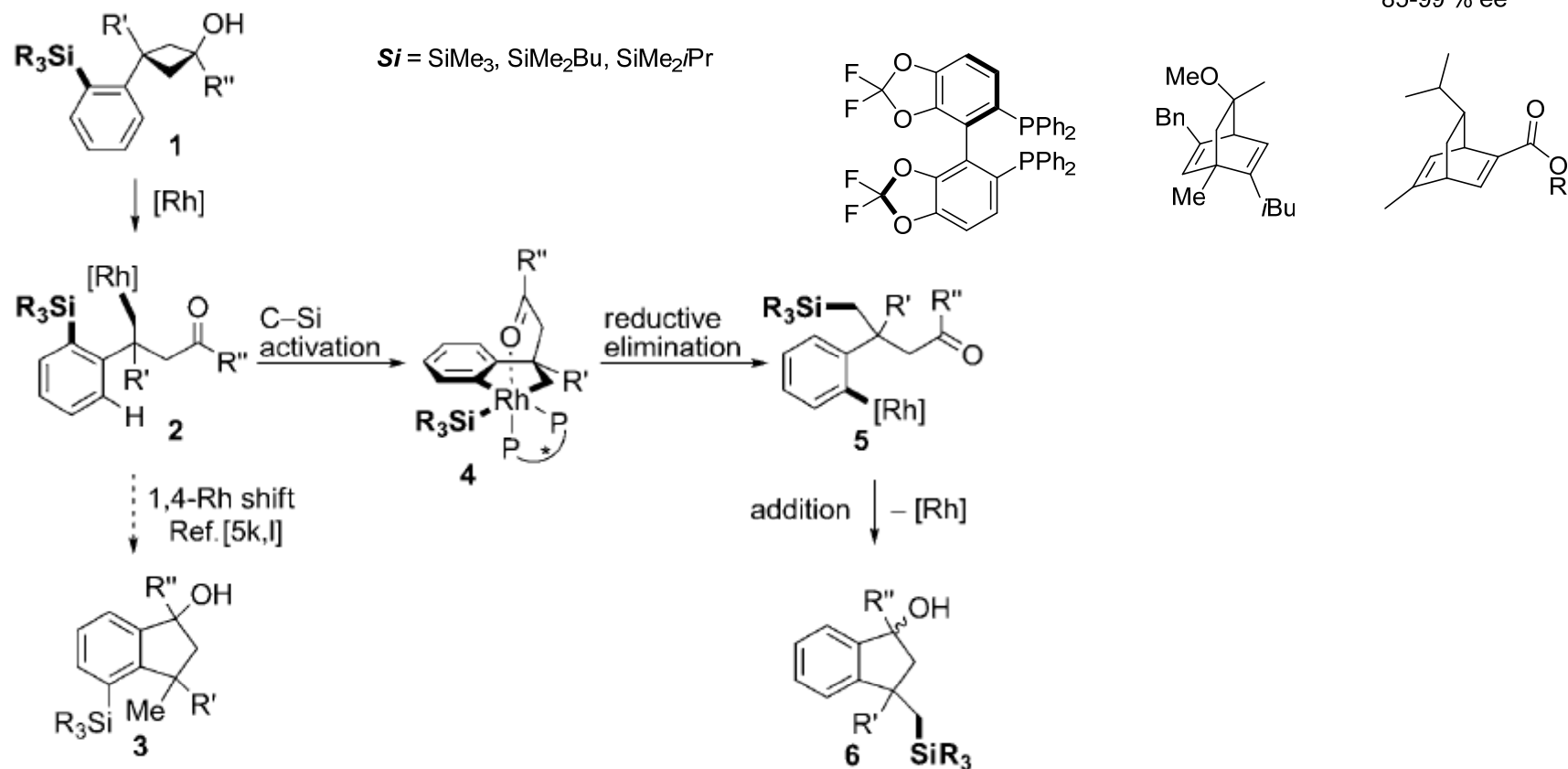
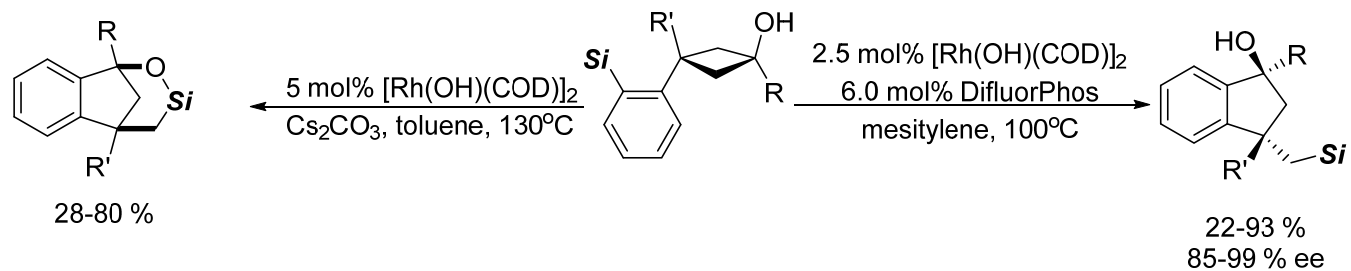
Cramer



Seiser T.; Roth O. A.; Cramer N. *Angew. Chem. Int. Ed.*, **2009**, *48*, 6320.

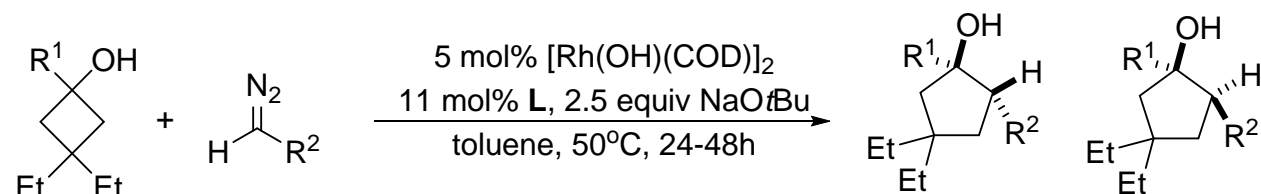
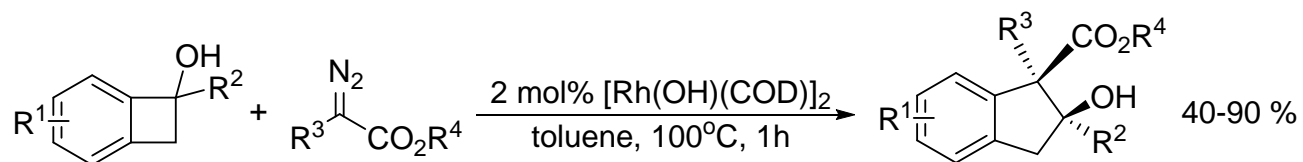
Shigeno M.; Yamamoto T.; Murakami M. *Chem.–Eur. J.*, **2009**, *15*, 12929.

Transition Metal

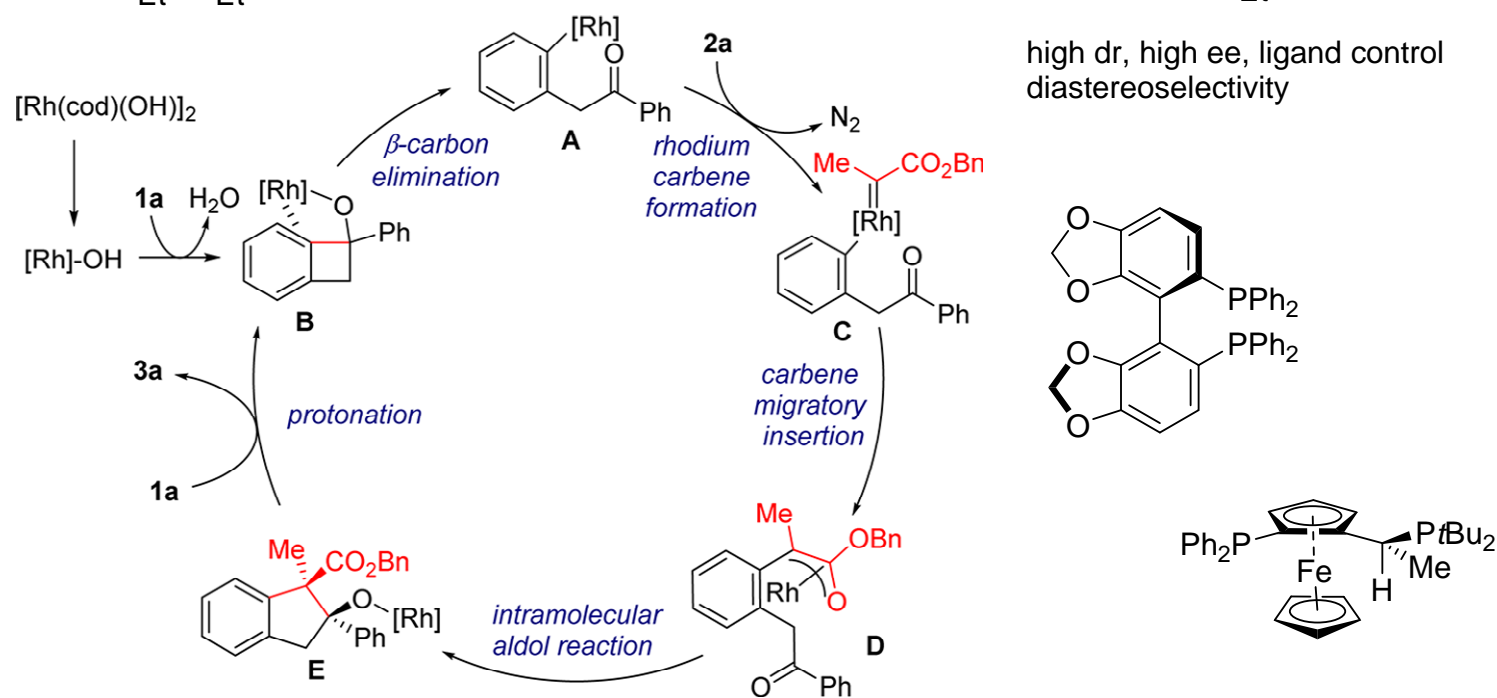


Seiser, T.; Cramer, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 10163.

Transition Metal



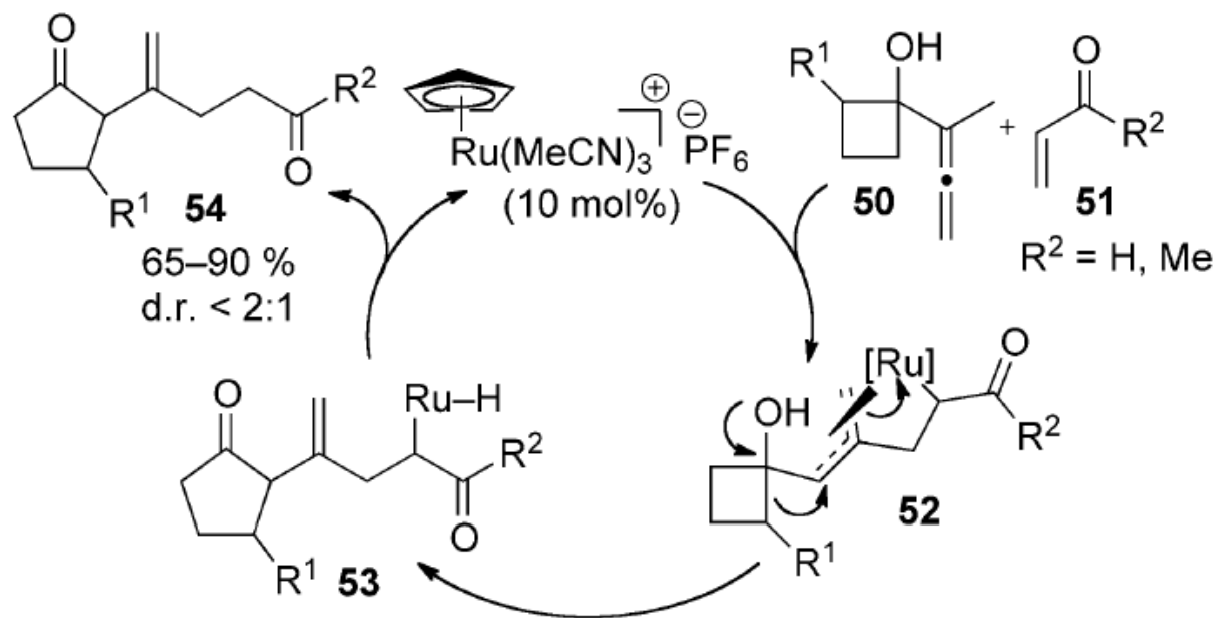
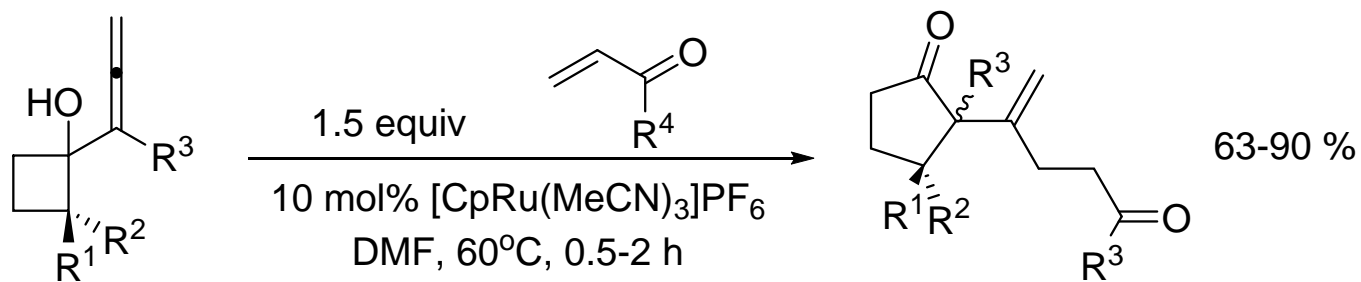
high dr, high ee, ligand control diastereoselectivity



Xia, Y.; Liu, Z.; Liu, Z.; Ge, R.; Ye, F.; Hossain, M.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2014**, *136*, 3013.

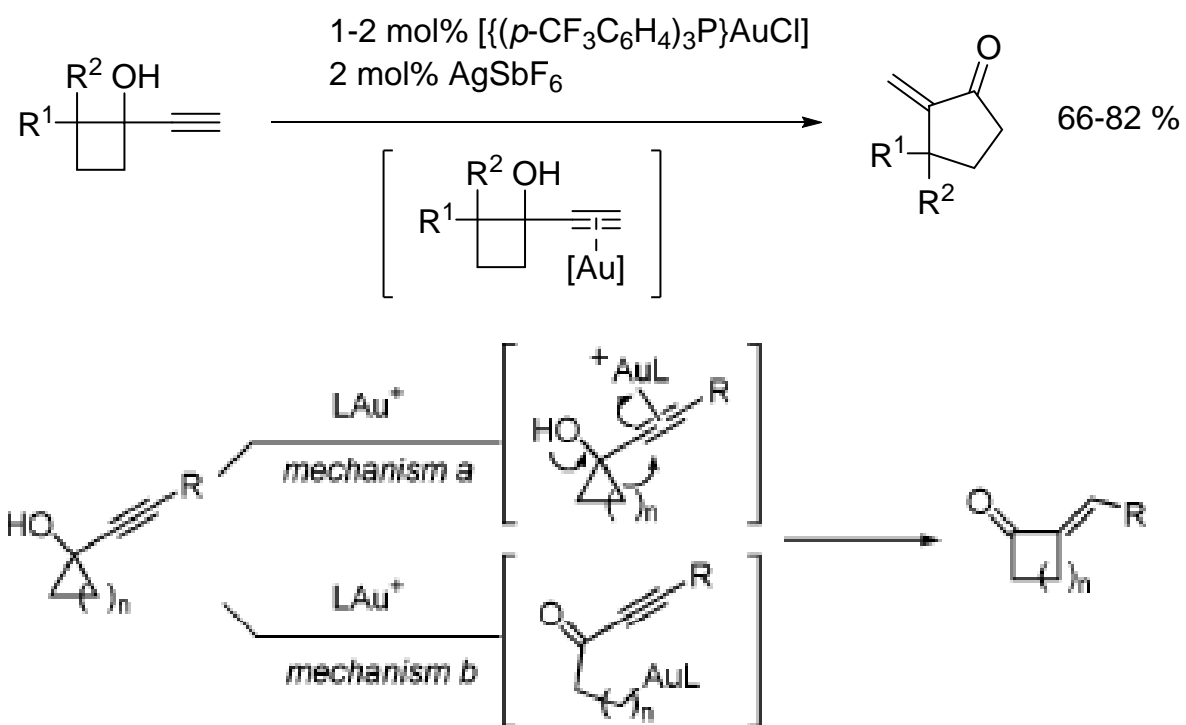
Yada, A.; Fujita, S.; Murakami, M. *J. Am. Chem. Soc.* Just accepted

Transition Metal



Yoshida M.; Sugimoto K.; Ihara M. *Tetrahedron Lett.* **2001**, *42*, 3877.

Transition Metal



Markham J. P.; Staben S. T.; Toste F. D. *J. Am. Chem. Soc.* **2005**, *127*, 9708.

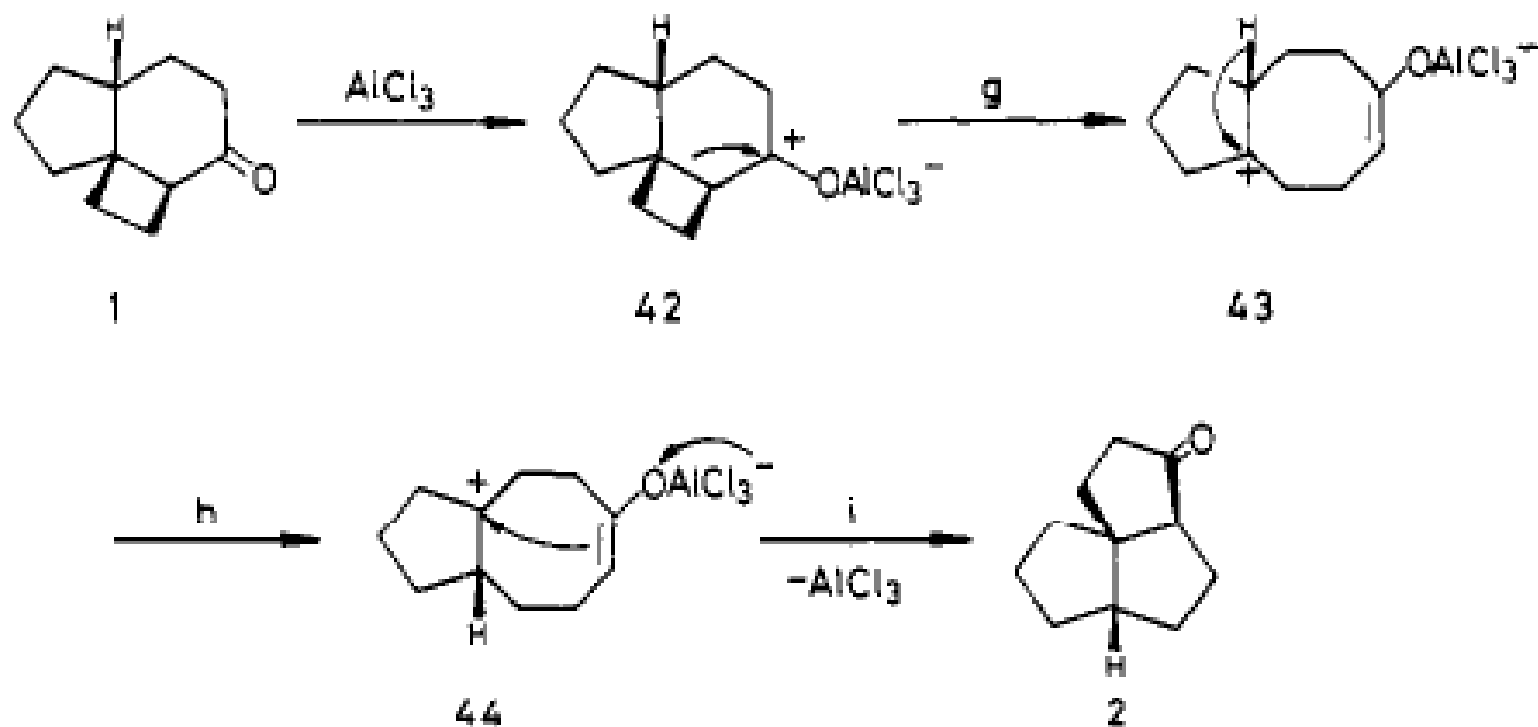
Summary

- 1. Carbene precursor**
- 2. Relatively strained structure**
- 3. Good leaving group**
- 4. Strong Lewis acid**
- 5. Incorporating reacting moieties**

Acknowledge

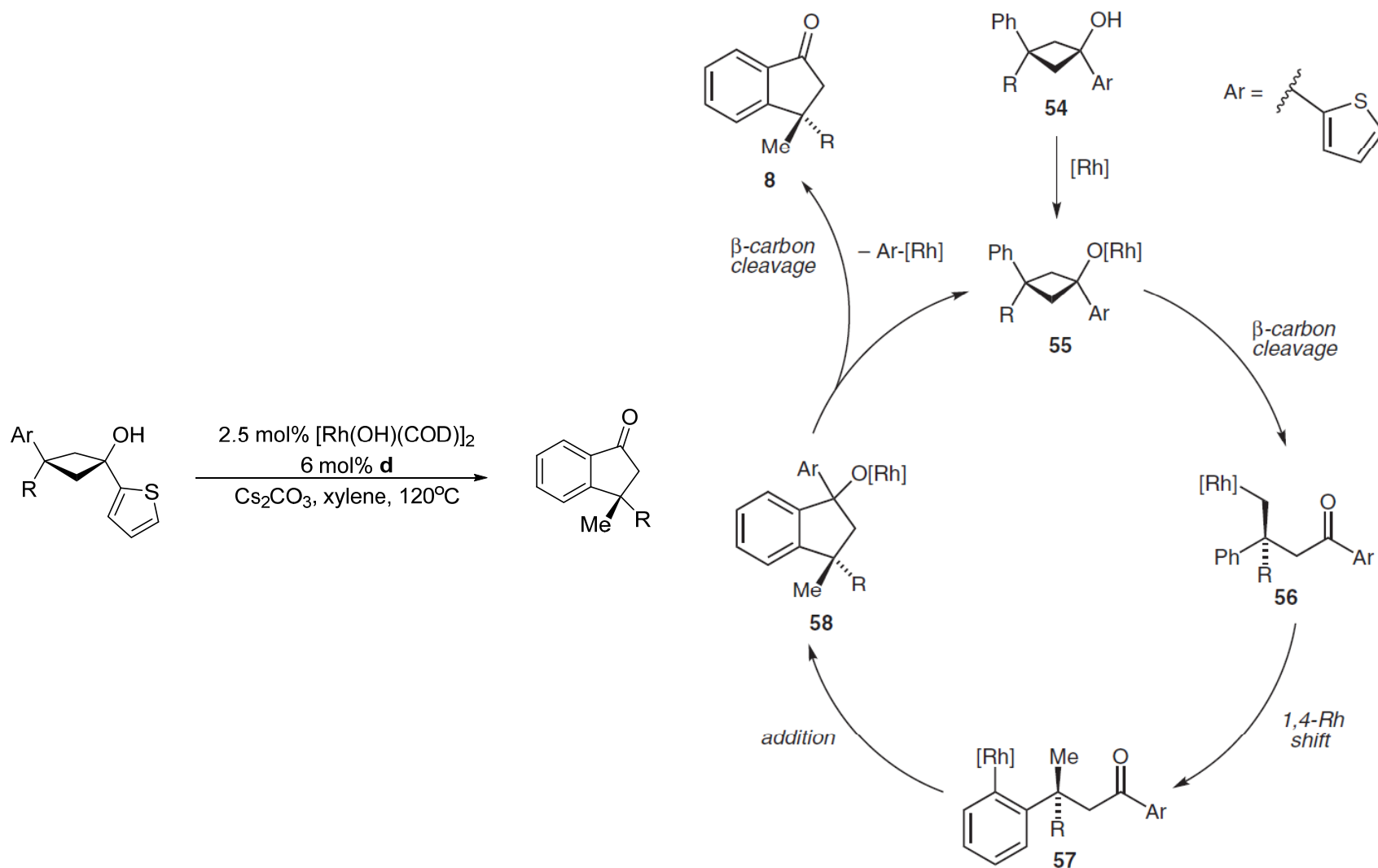


Answer Key



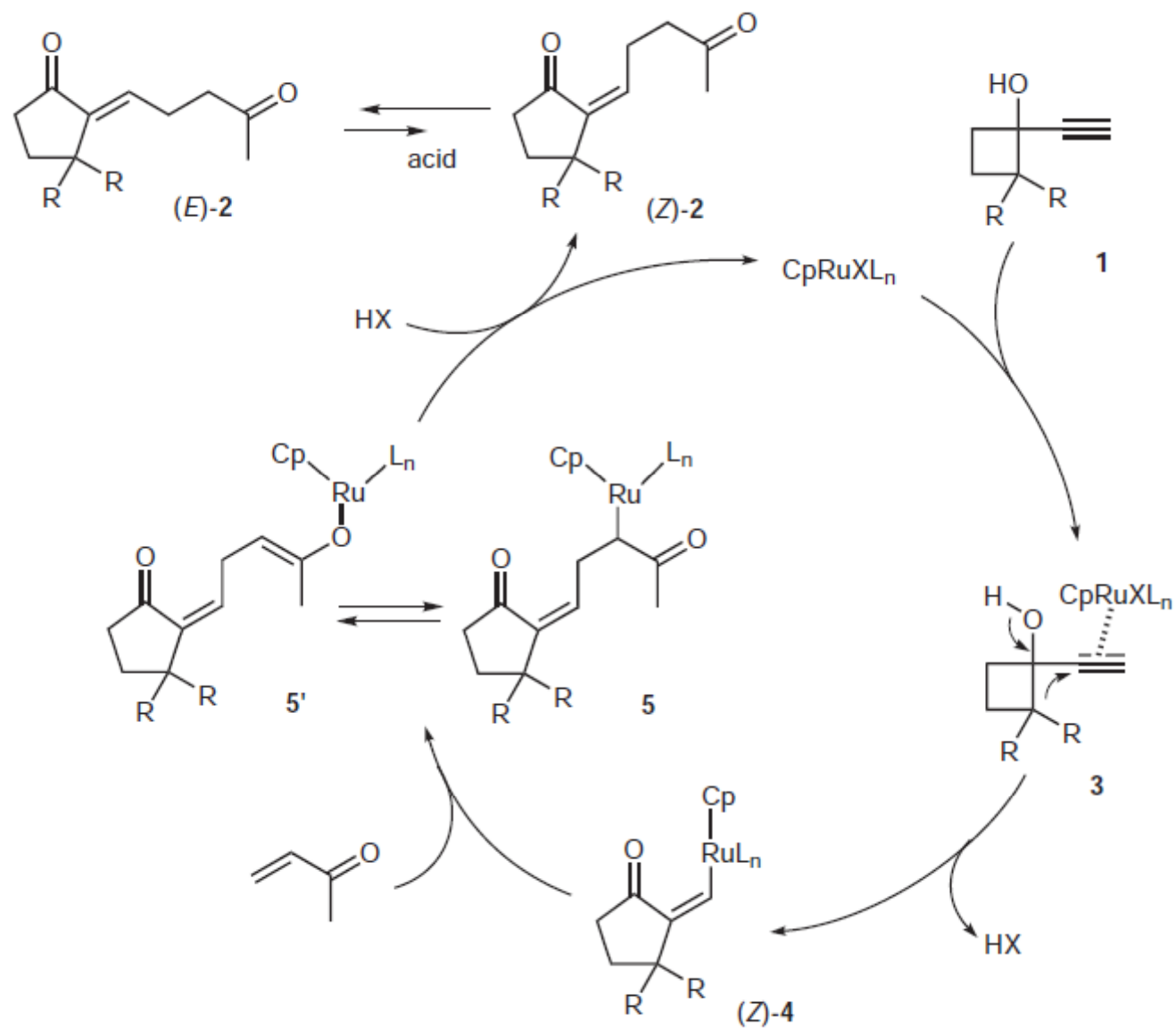
Kakiuchi, K.; Ue, M.; Tsukahara, H.; Shimizu, T.; Miyao, T.; Tobe, Y.; Odaira, Y.; Yasuda, M.; Shima, K. *J. Am. Chem. Soc.* **1989**, *111*, 3707.

Answer Key



Seiser, T.; Cathomen, G.; Cramer, N. *Synlett* **2010**, 1699.

Answer Key



Sugimoto K.; Yoshida M.; Ihara M. *Synlett* **2006**, 1923.