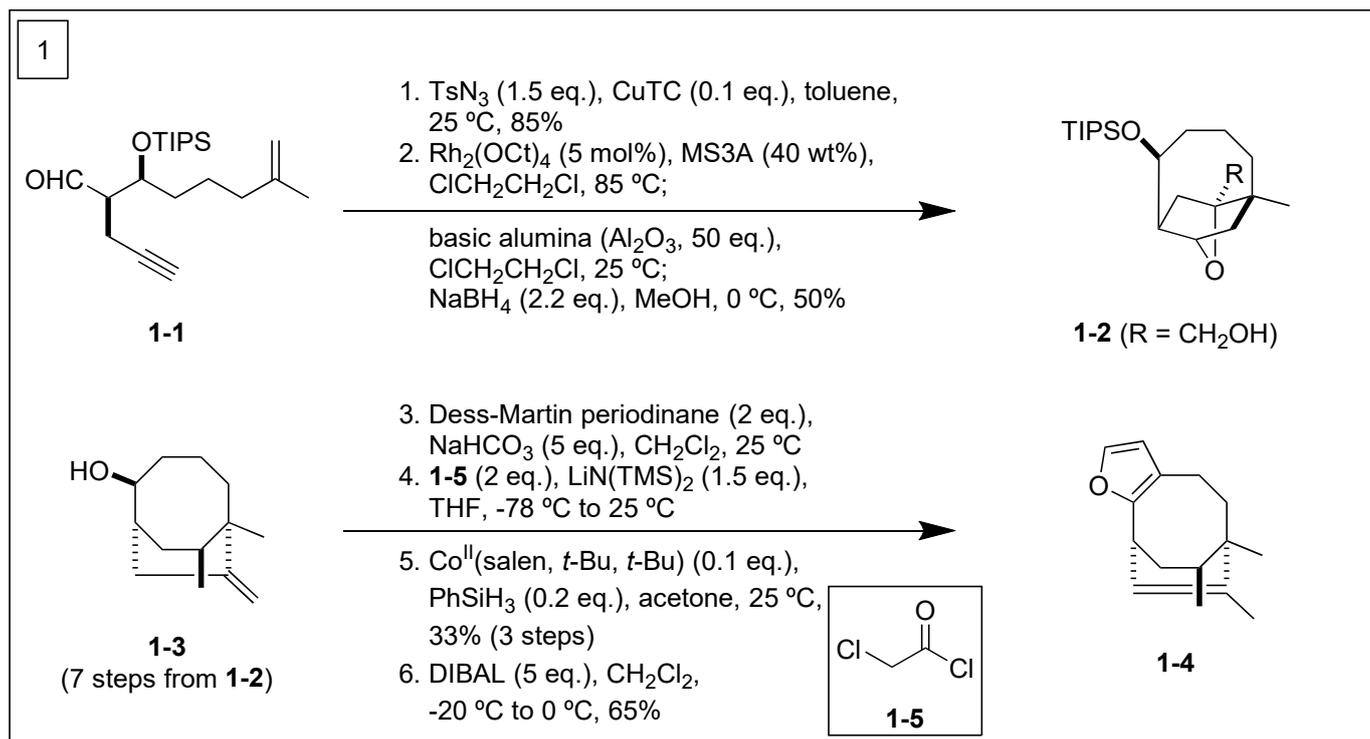
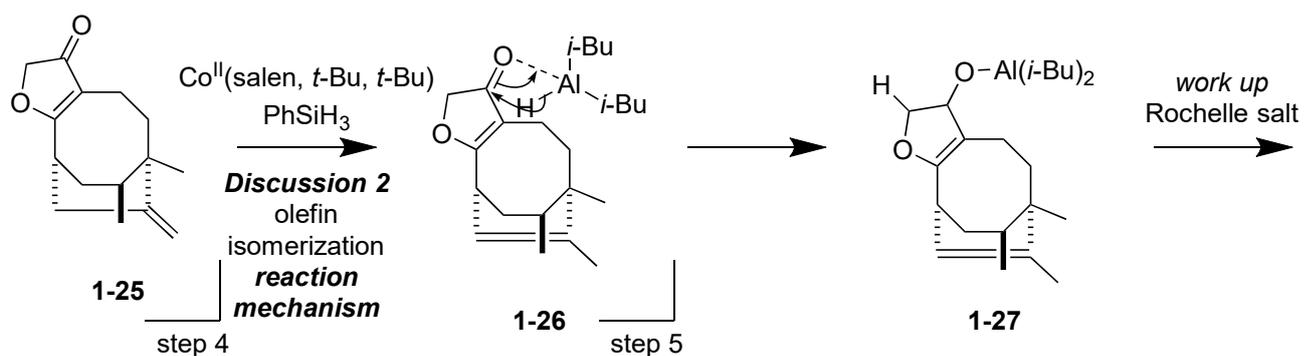
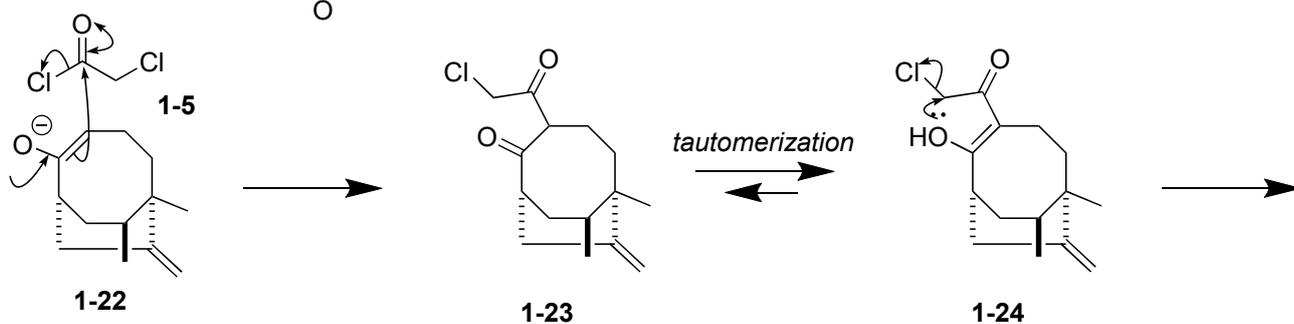
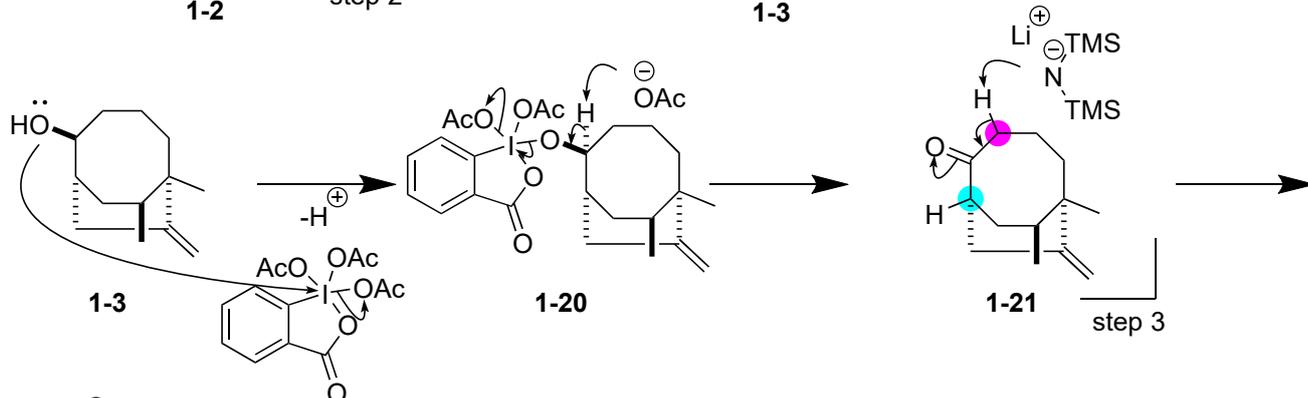
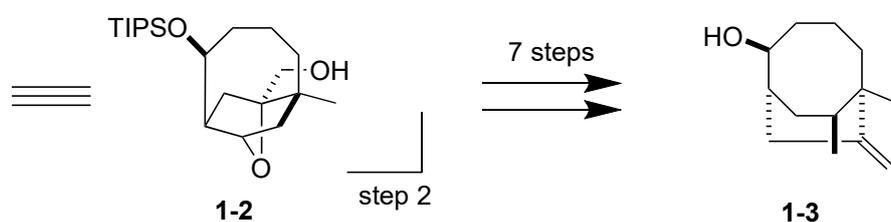
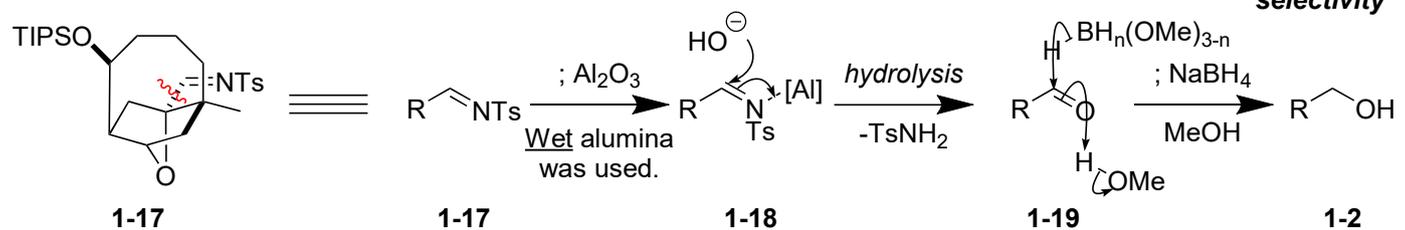
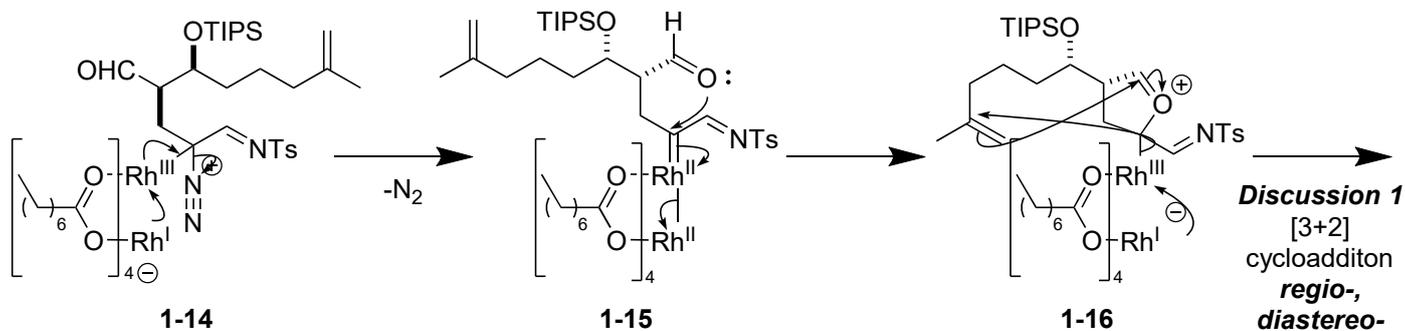


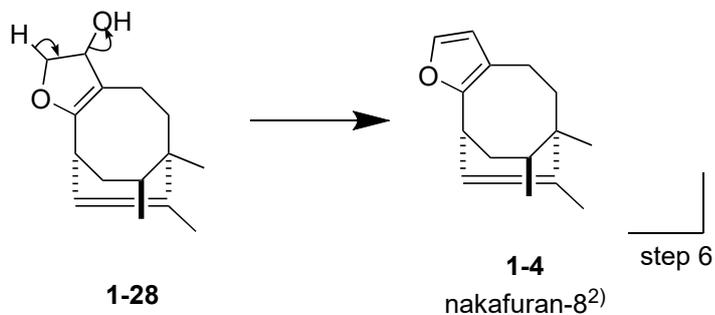
Problem Session (2) -Answer-

2021/11/06 Wataru Shigematsu

Topic: Ring construction by [3+2] dipolar cycloadditions catalyzed by Rhodium (II) catalyst

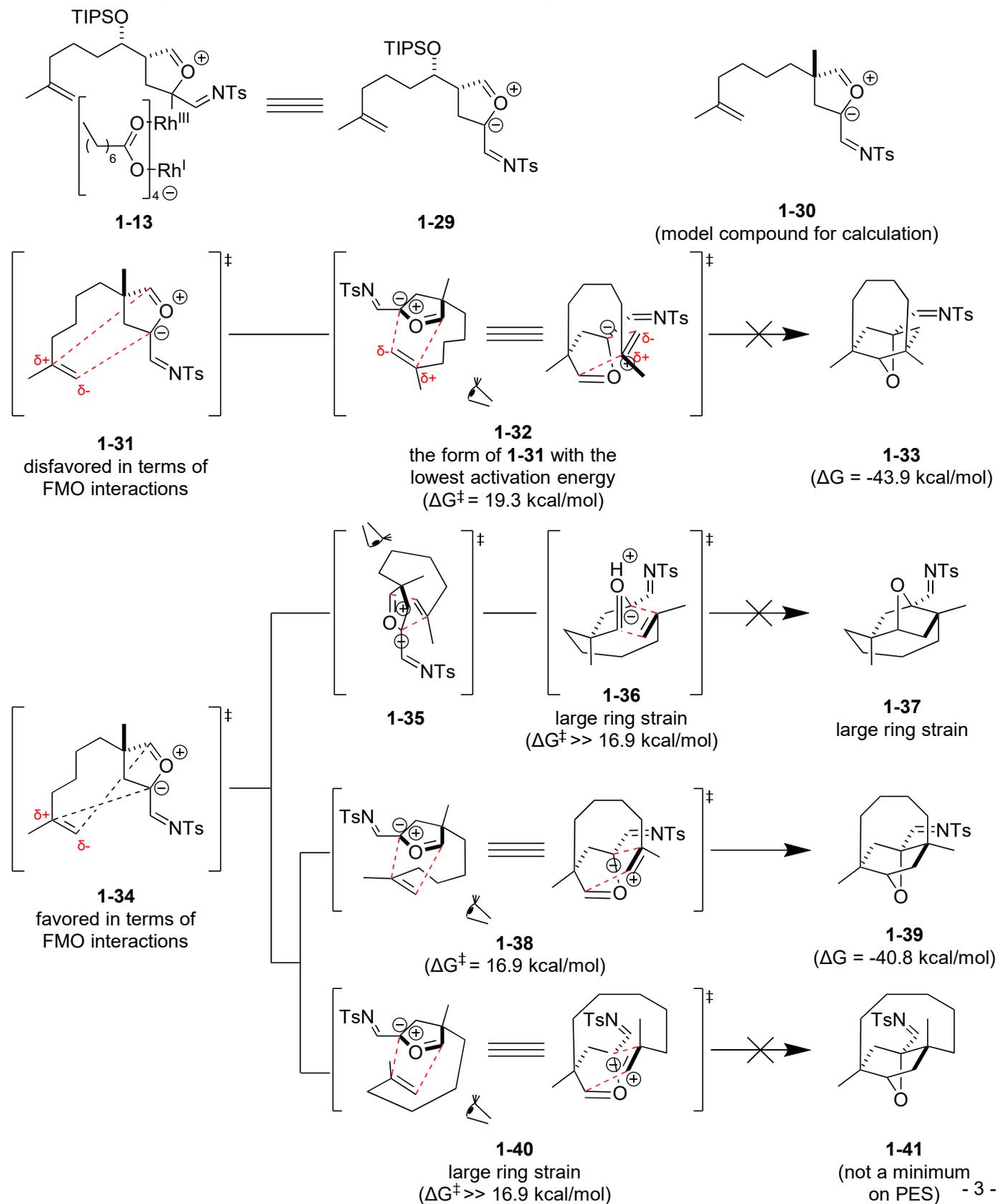


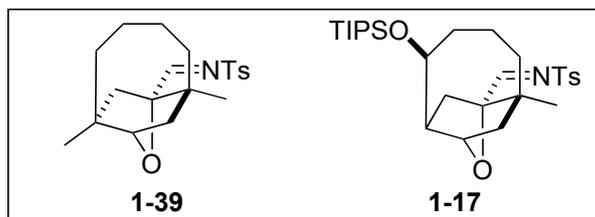




- 1) Worrell, B. T.; Malik, J. A.; Fokin, V. V. *Science*, **2013**, *340*, 457.
- 2) Schulte, G.; Sheuer, P. J.; McConnell, O. J. *Helv. Chim. Acta*, **1980**, *63*, 2159.

Discussion 1: Regio- and diastereoselectivity of [3+2] dipolar cycloaddition

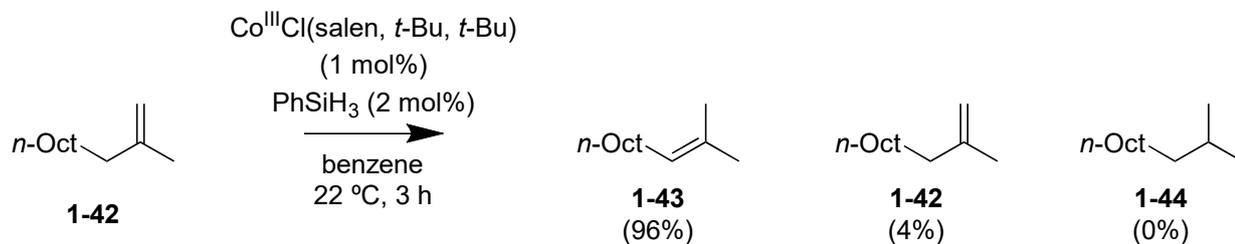




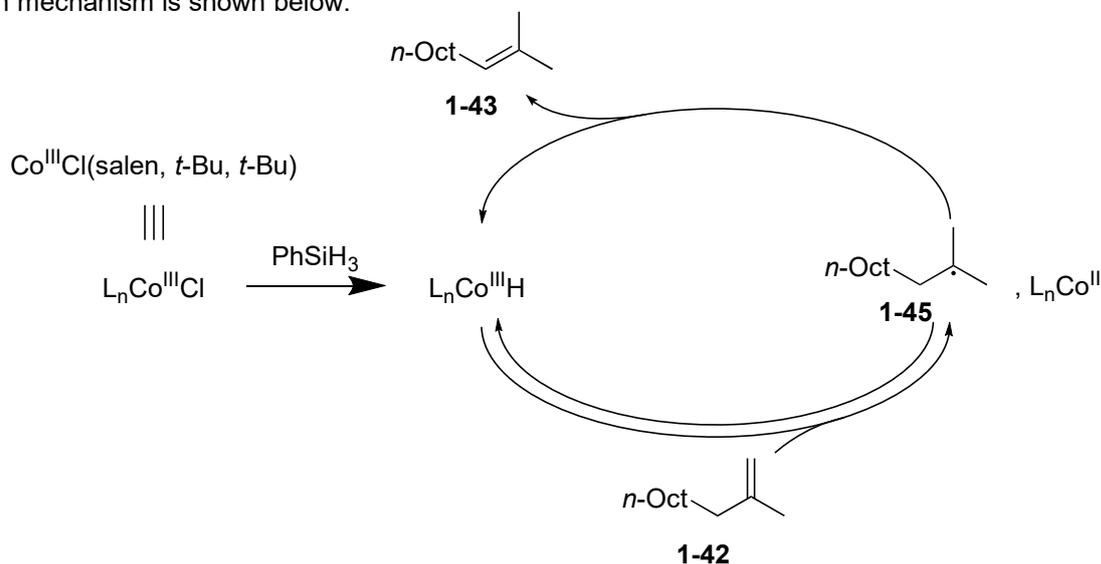
Discussion 2: Olefin isomerization

1-2. Studies of Shenvi's group

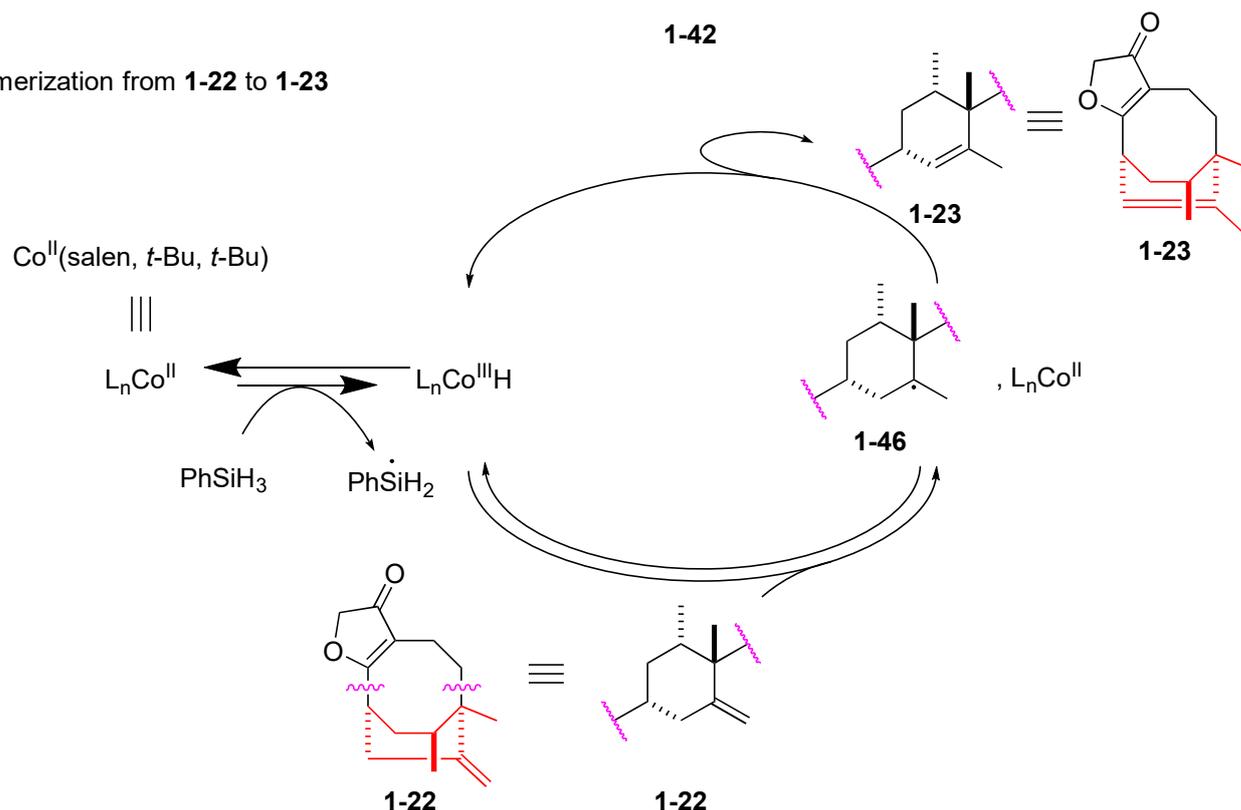
1-2-1. Isomerization of 2-methyl-1-decene **1-42**



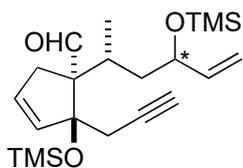
Shenvi's group reported the isomerization of 2-methyl-1-decene with Co^{III} catalyst with PhSiH_3 . Proposed reaction mechanism is shown below.



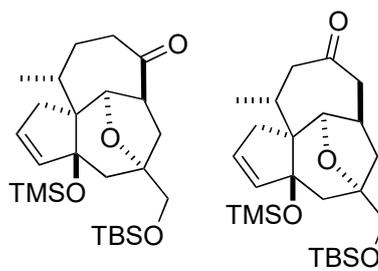
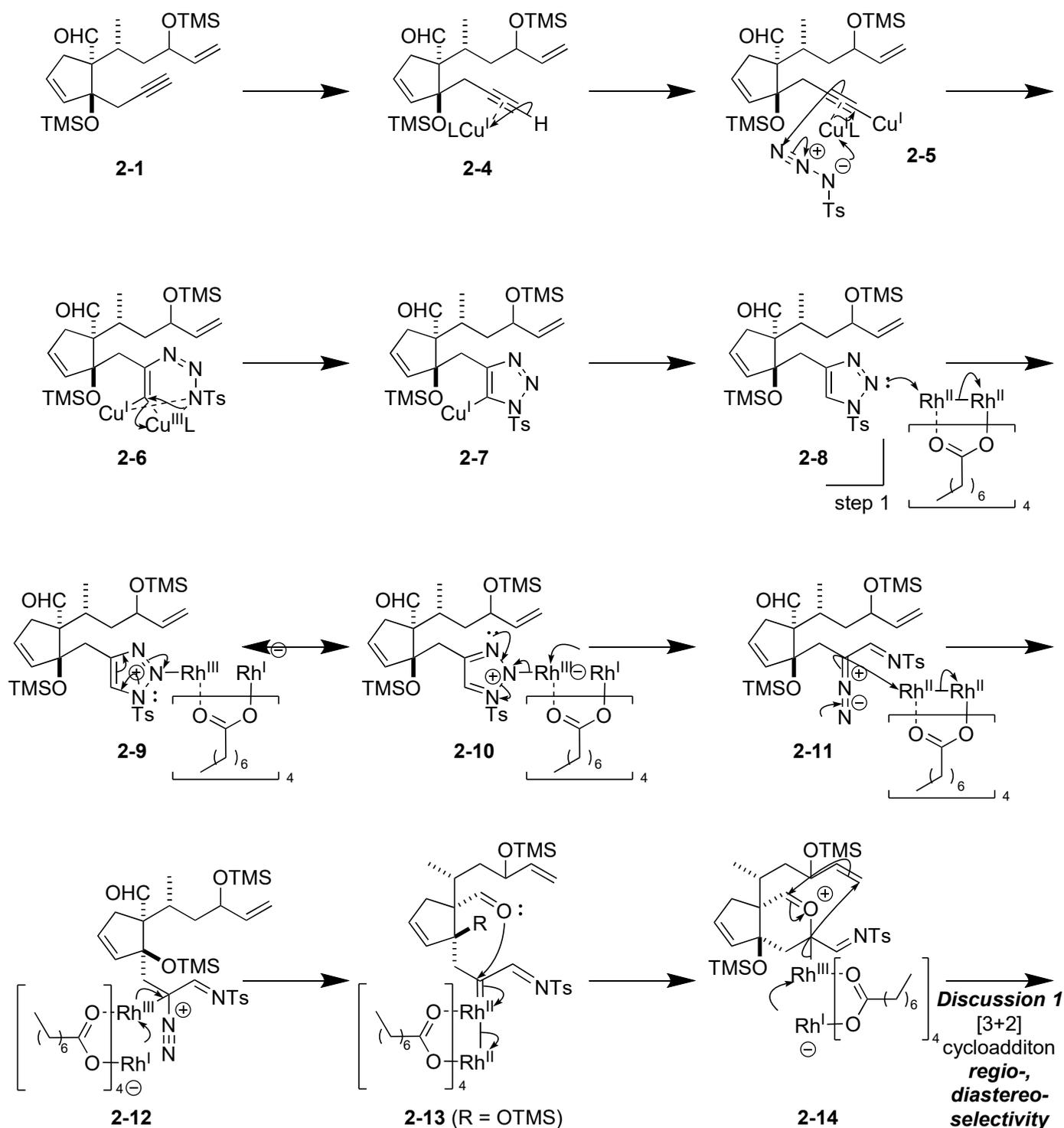
1-2-2. Isomerization from **1-22** to **1-23**

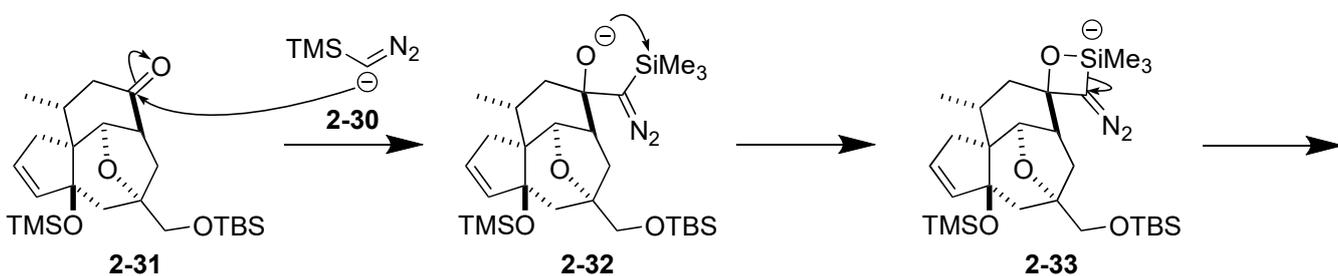
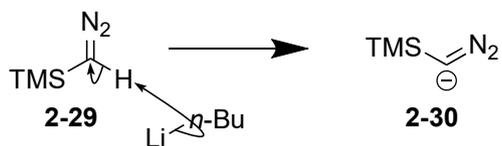
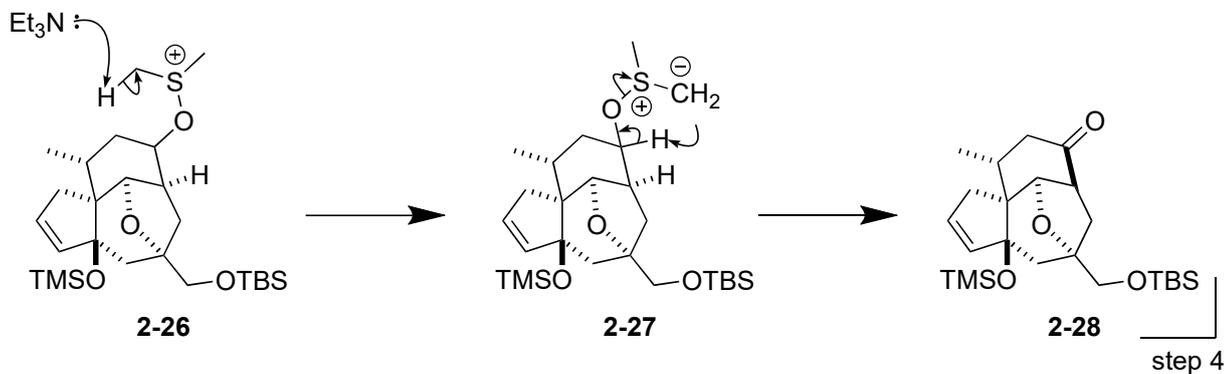
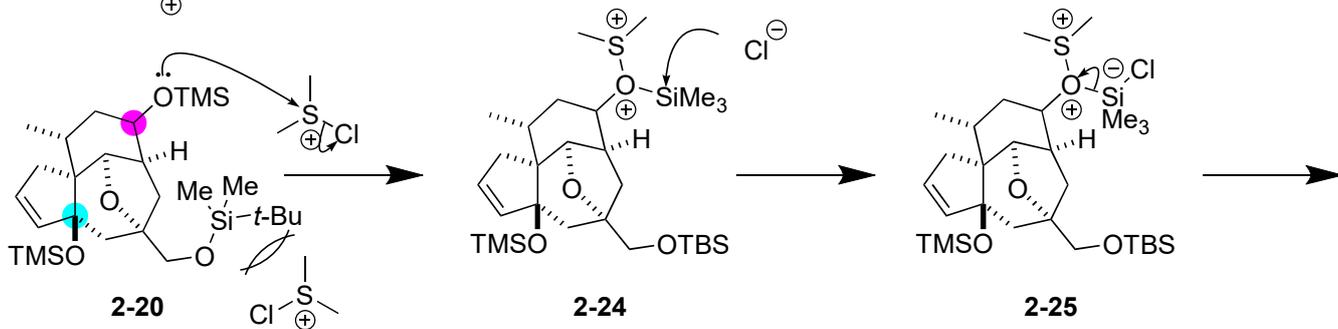
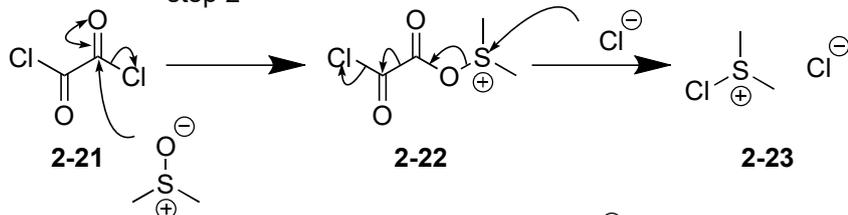
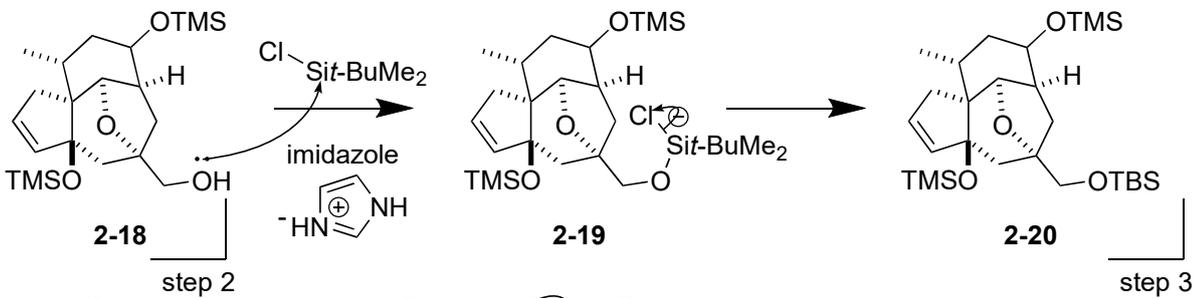
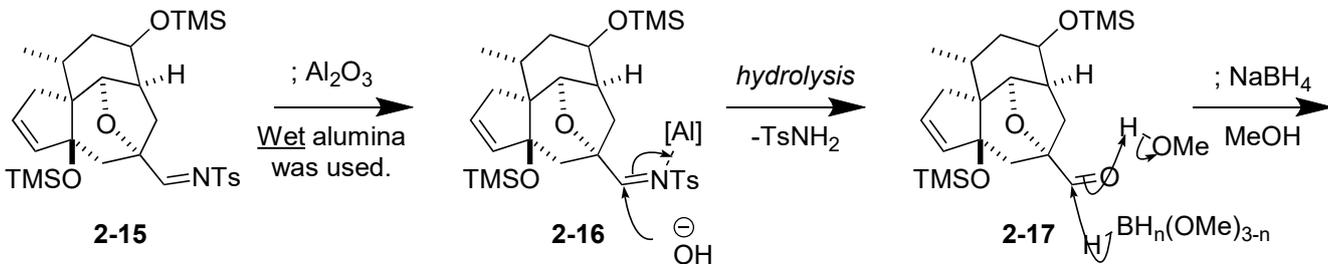


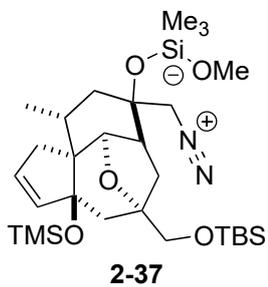
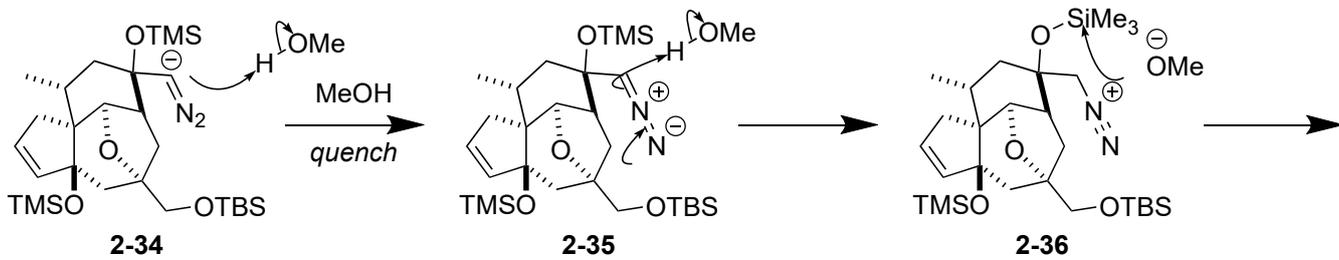
2



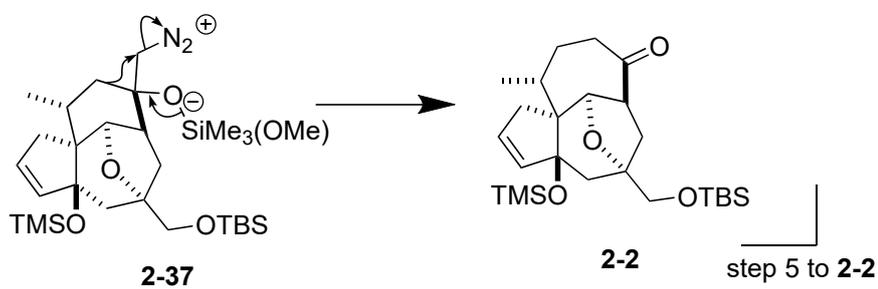
1. TsN_3 (1.1 eq.), CuTC (0.1 eq.), toluene, 25 °C, 90%
2. $\text{Rh}_2(\text{OAc})_4$ (2 mol%), MS3A (30 wt%), toluene, 90 °C; basic alumina (Al_2O_3 , 50 eq.), CH_2Cl_2 , 25 °C; NaBH_4 (2 eq.), MeOH, 0 °C, 55%
3. TBSCl (2 eq.), imidazole (3 eq.), CH_2Cl_2 , 0 °C
4. $(\text{ClCO})_2$ (1.16 eq.), DMSO (2.8 eq.), CH_2Cl_2 , -78 °C; Et_3N (7 eq.), -78 °C to 25 °C, 81% (2 steps)
5. TMSCHN_2 (1.5 eq.), *n*-BuLi (1.5 eq.), THF, -78 °C, 90% (**2-2**:**2-3** = 1:1)

Hou, B.-L.; Li, L.-X.; Li, C.-C. *Org. Lett.* **2021**, *23*, 7771.

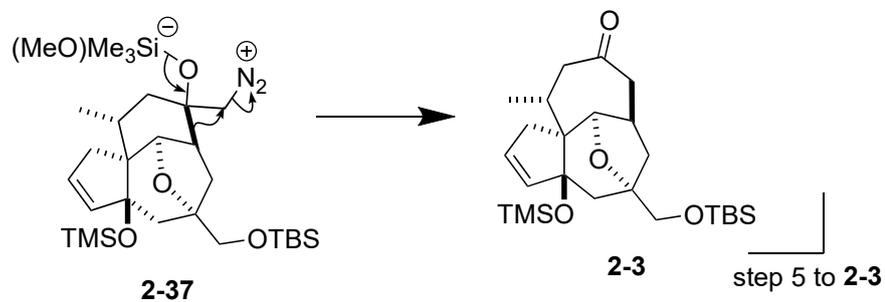




-from **2-37** to **2-2**-



-from **2-30** to **2-3**-



Discussion 1: Regio- and diastereoselectivity of [3+2] dipolar cycloaddition

