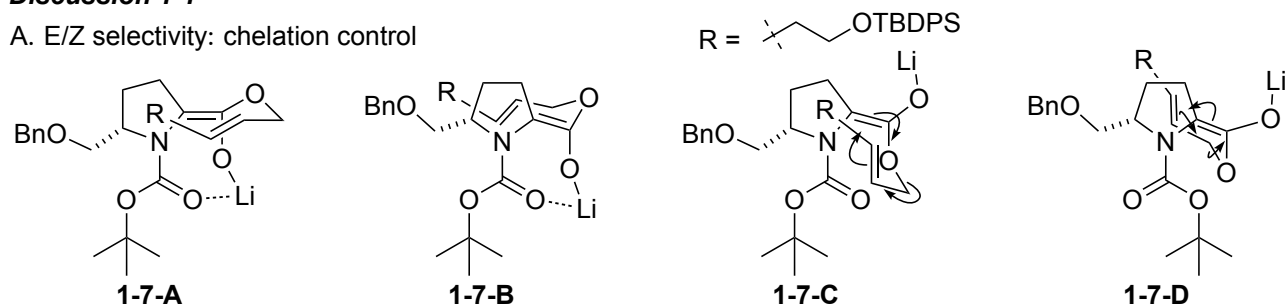
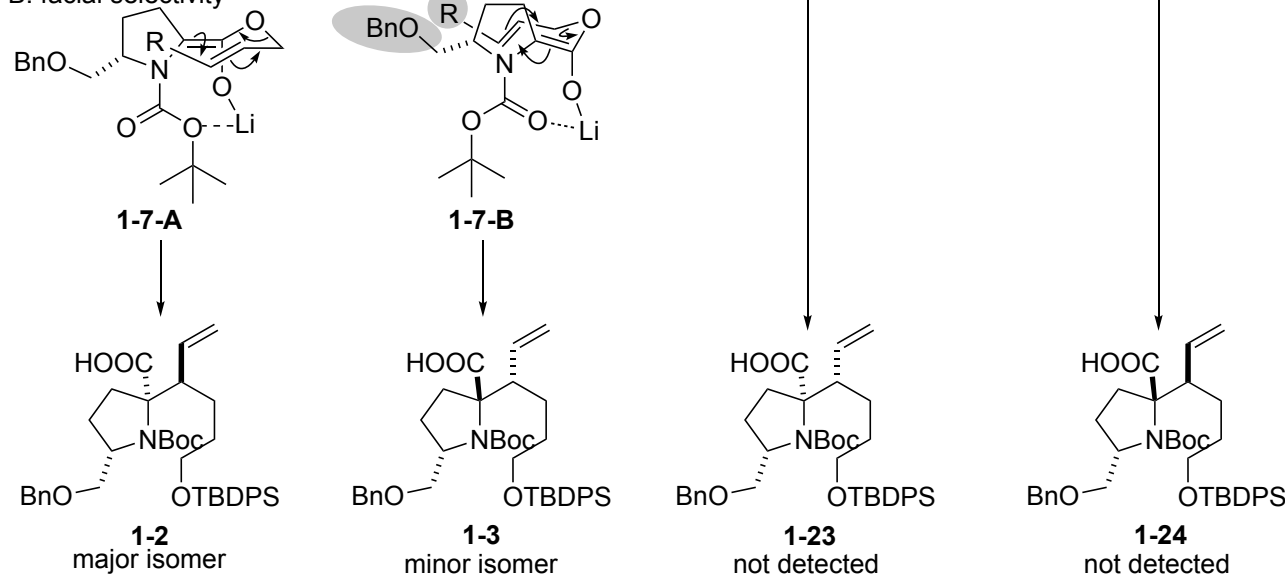


Discussion 1-1

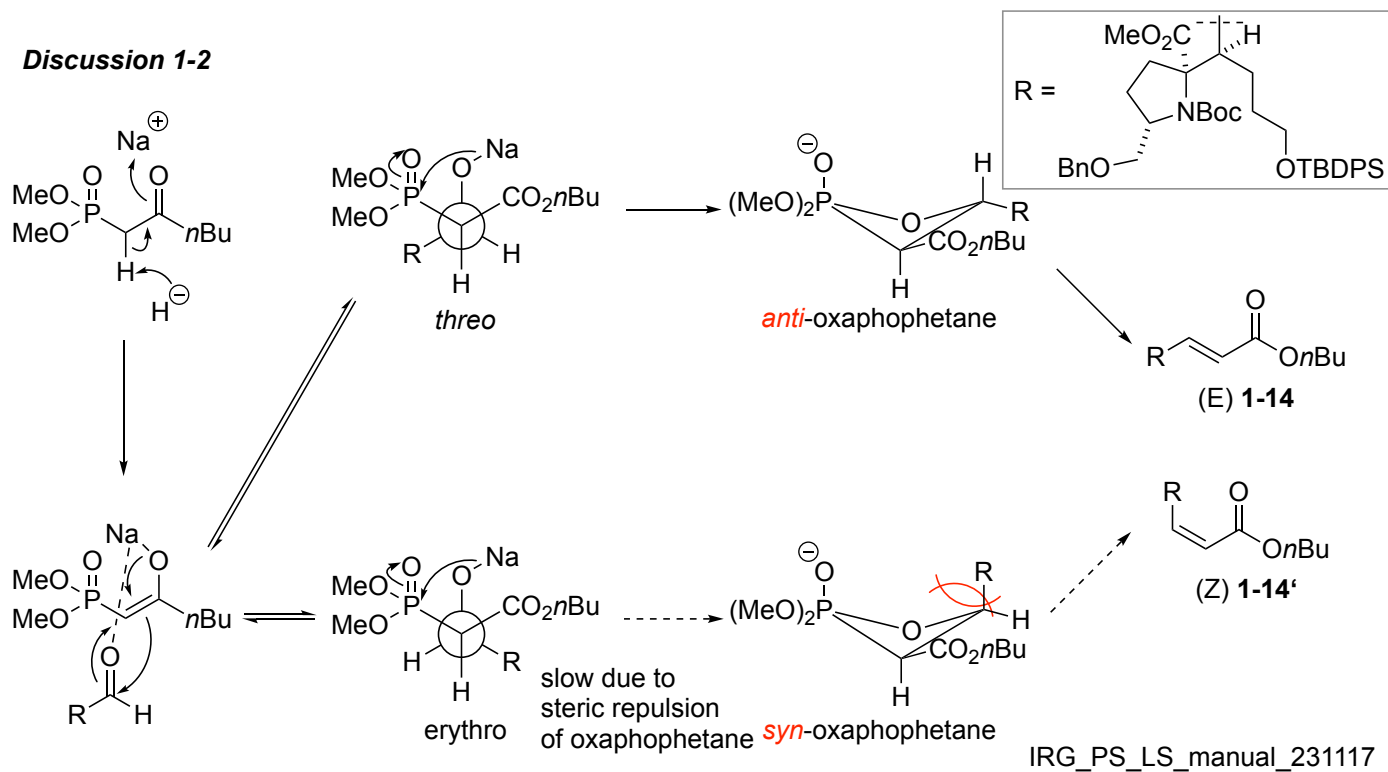
A. E/Z selectivity: chelation control



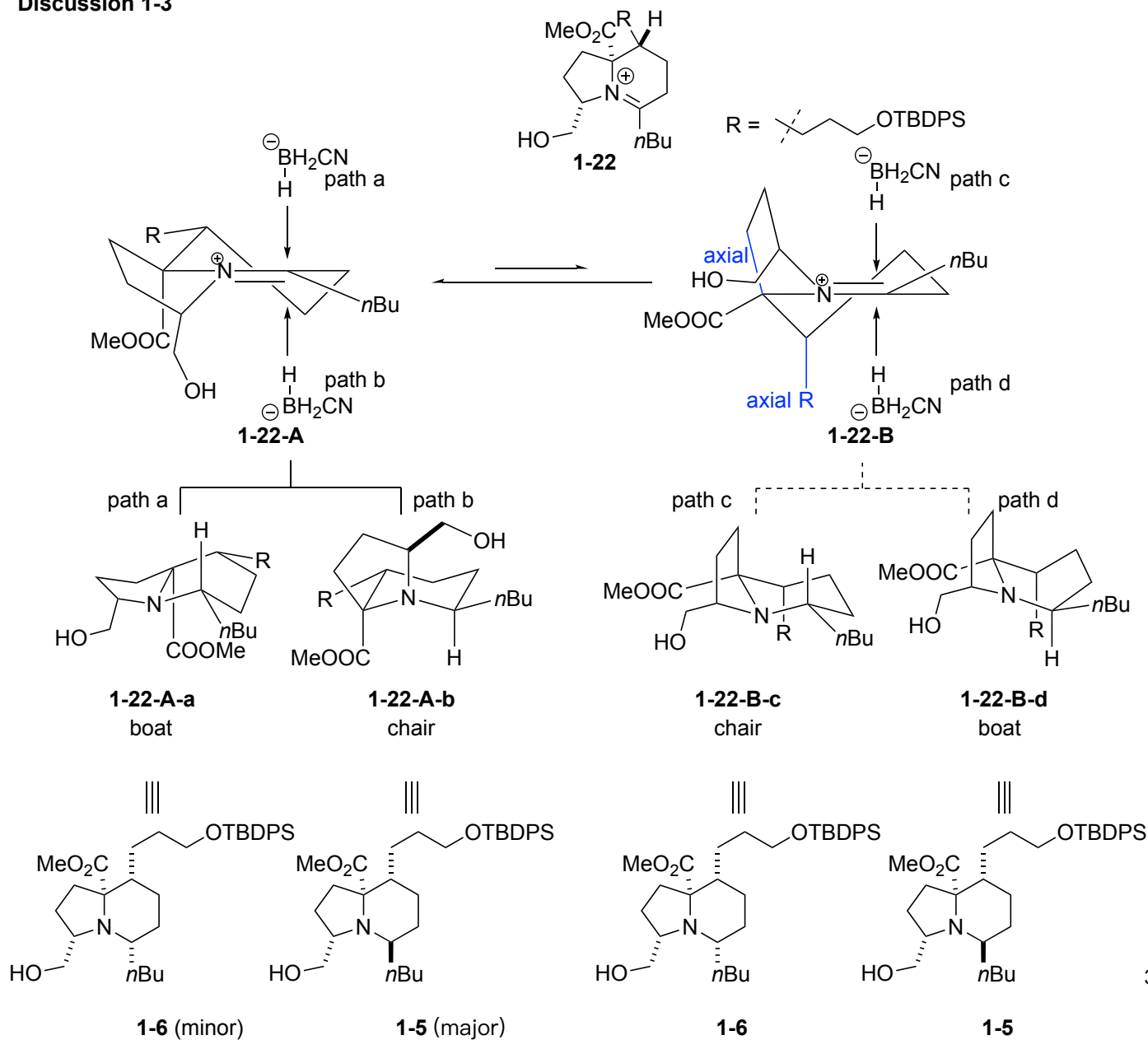
B. facial selectivity



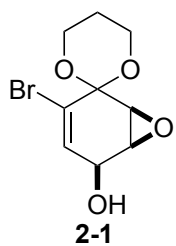
Discussion 1-2



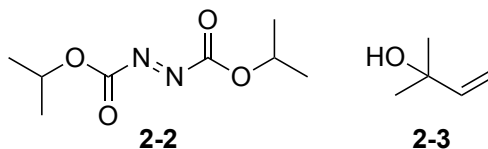
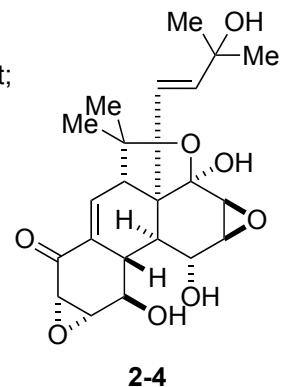
Discussion 1-3



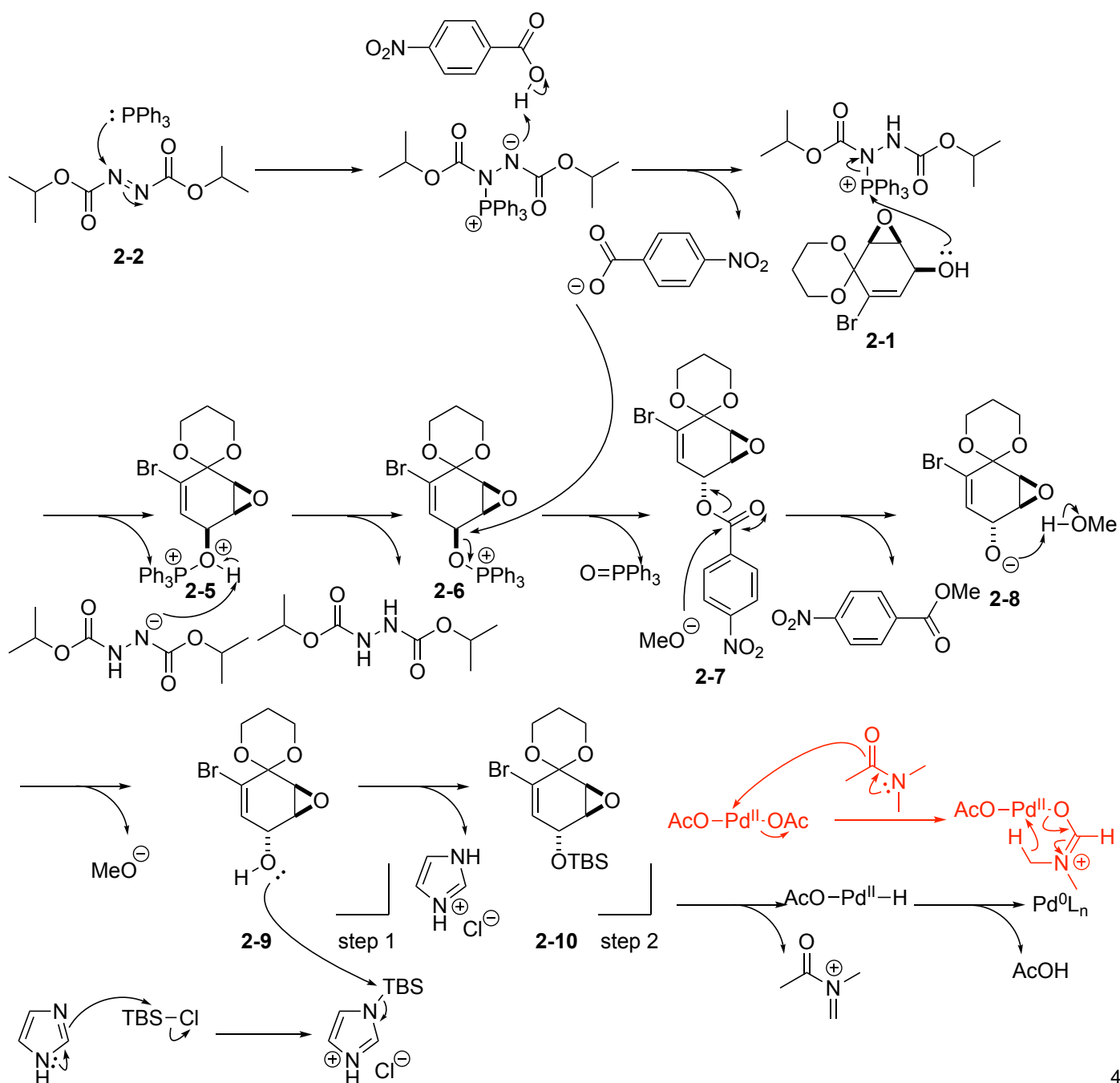
problem 2



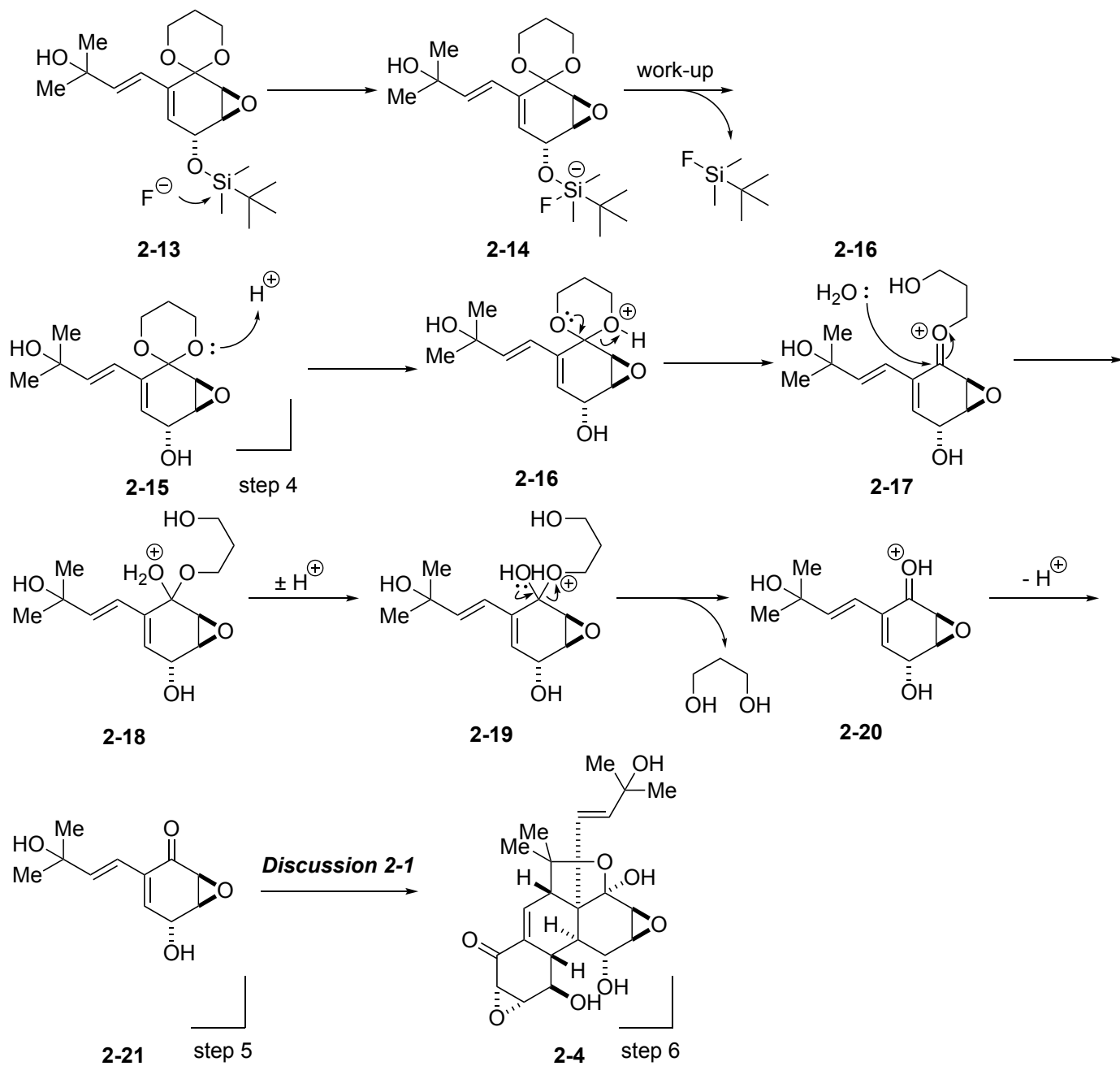
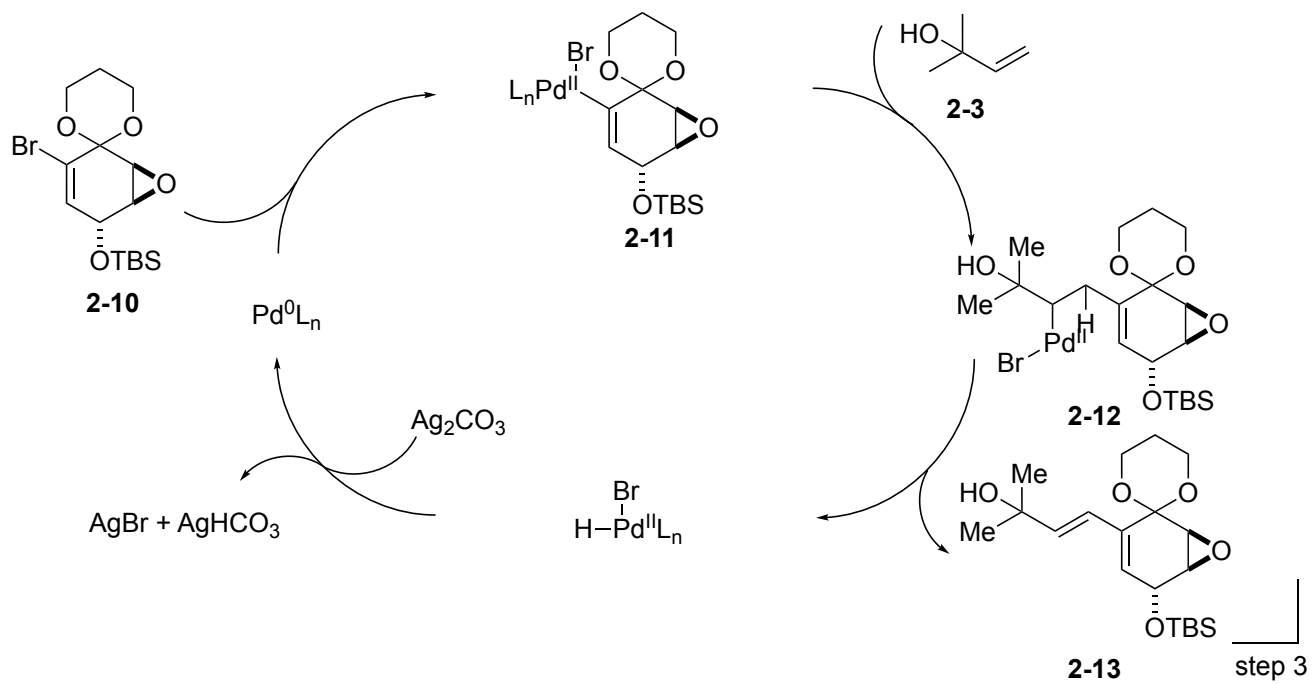
1. PPh_3 (1.3 eq), **2-2** (1.3 eq), 4-nitrobenzoic acid (1.3 eq), THF, -78°C to rt; NaOMe (1.1 eq), MeOH, rt, 80%
2. TBSCl (1.5 eq), imidazole (1.5 eq), DMF, rt, 90%
3. $\text{Pd}(\text{OAc})_2$ (0.09 eq), Ag_2CO_3 (2.0 eq), **2-3** (6.0 eq), DMF, 90°C , 80%
4. TBAF (1.2 eq), THF, rt, 98%
5. HCl (1.0 M, 2.2 eq), $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1/1), 0°C to rt, 95%
6. neat, rt, 80%.



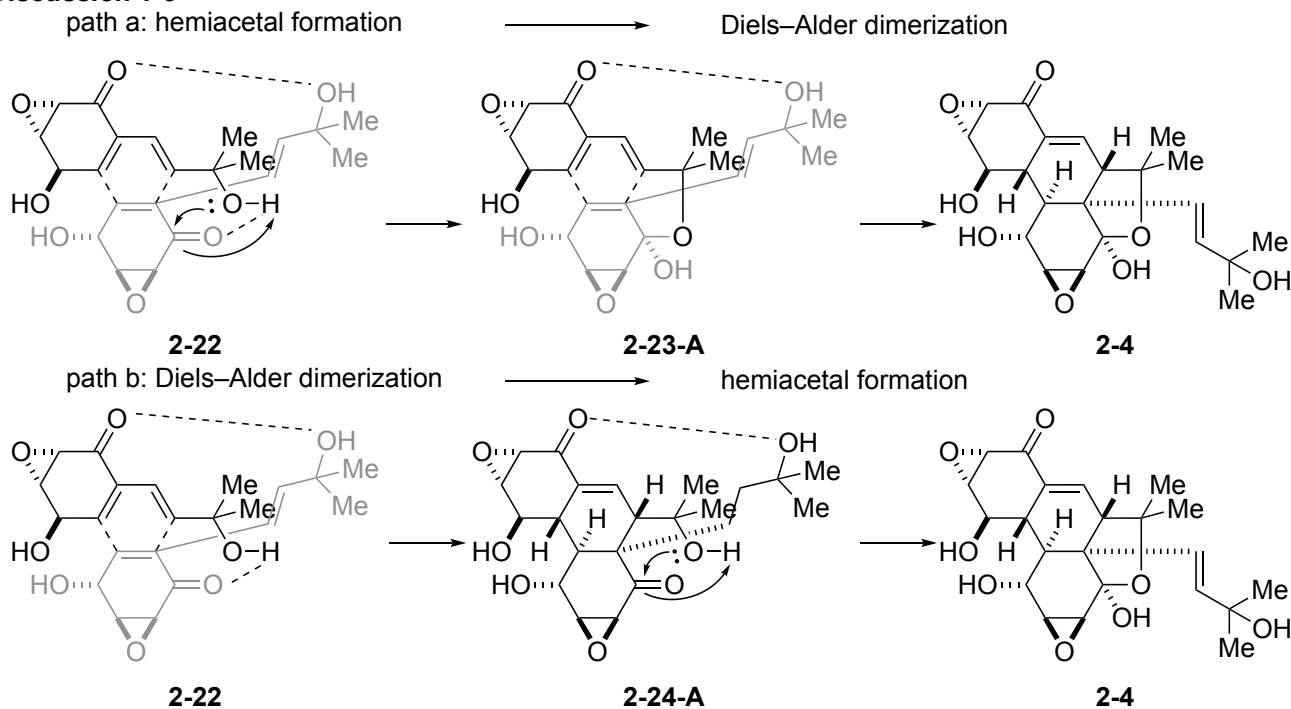
Lei, X.; Johnson, R. P.; Porco, J. A. *Angew. Chem.* **2003**, *115*, 4043.



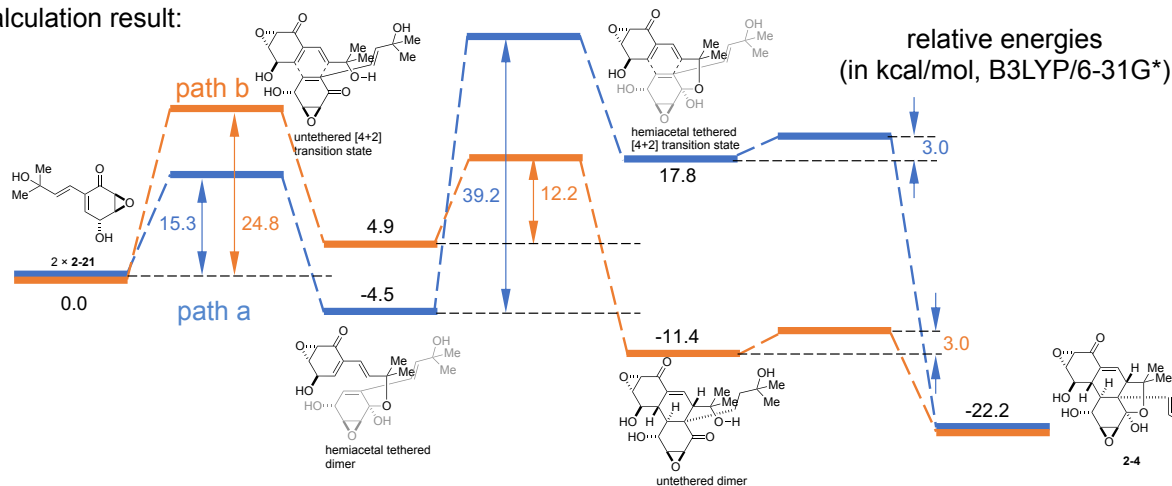
- Molina de la Torre, J. A.; Espinet, P.; Albeniz, A. C. *Organometallics* **2013**, *32*, 5428.
- Sherwood, J.; Clark, J. H.; Fairlamb, I. J.; Slattery, J. M. *Green Chem.* **2019**, *21*, 2164.



Discussion 1-3

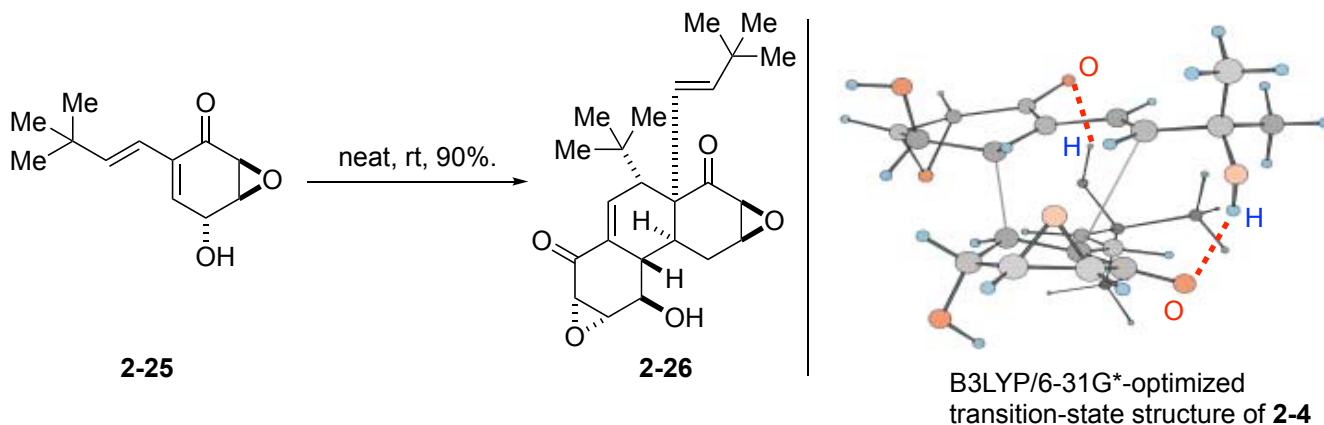


calculation result:



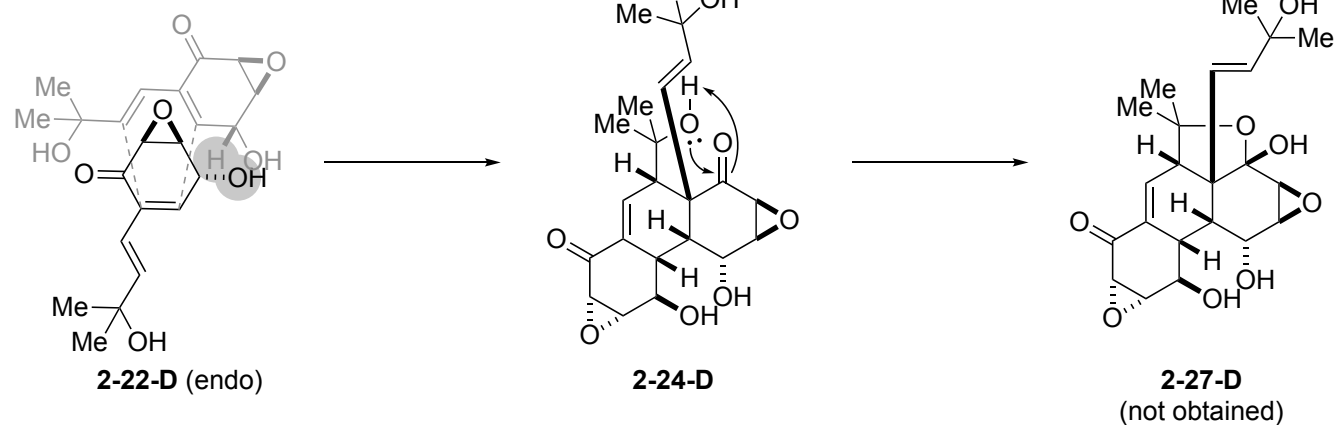
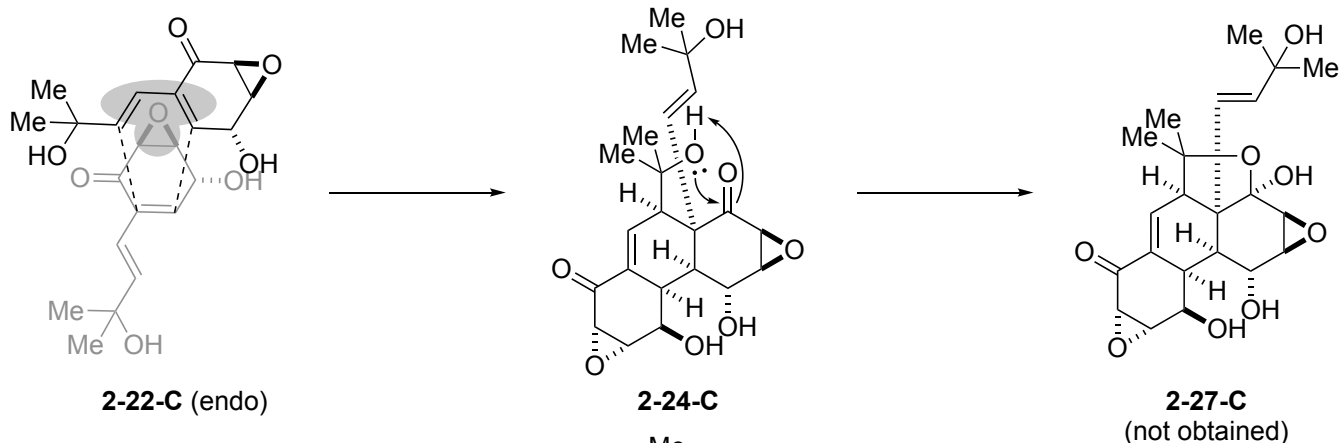
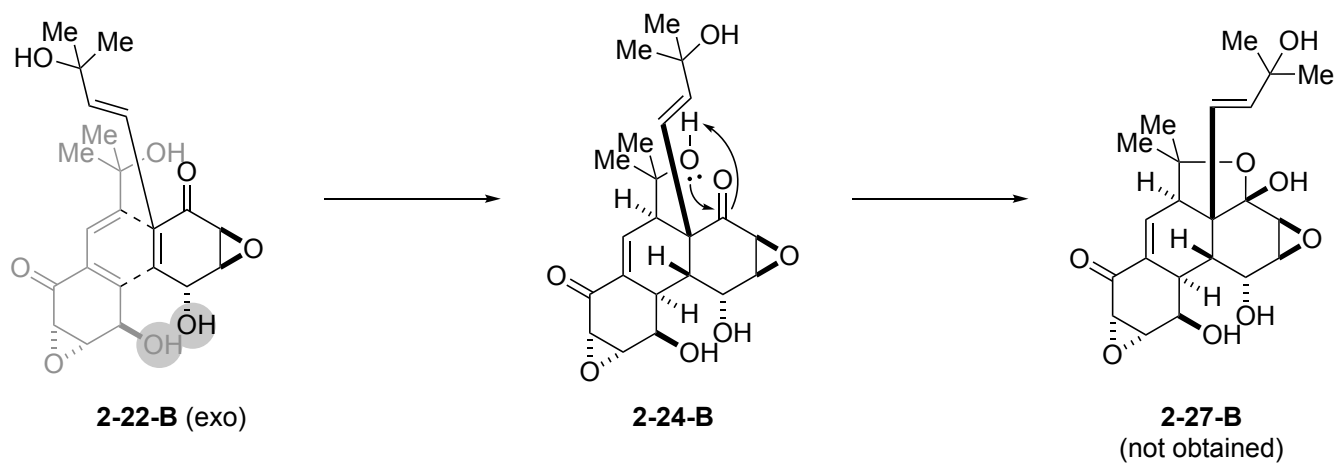
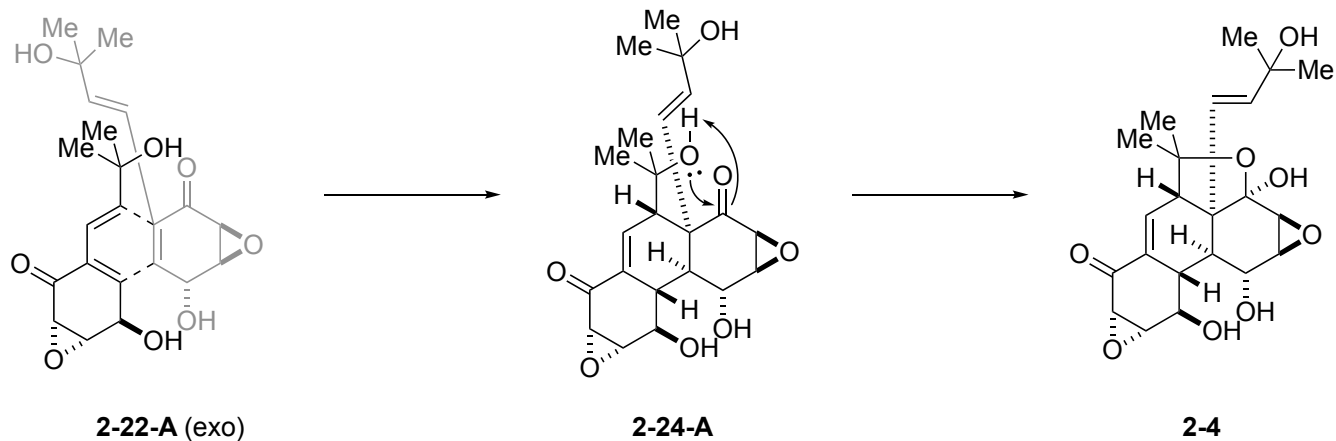
From the calculation result, although the initial formation of the hemiacetal link provided the advantage of an intramolecular [4+2] reaction, the dienophile became much less reactive because it was no longer an enone. So path b is more preferable.

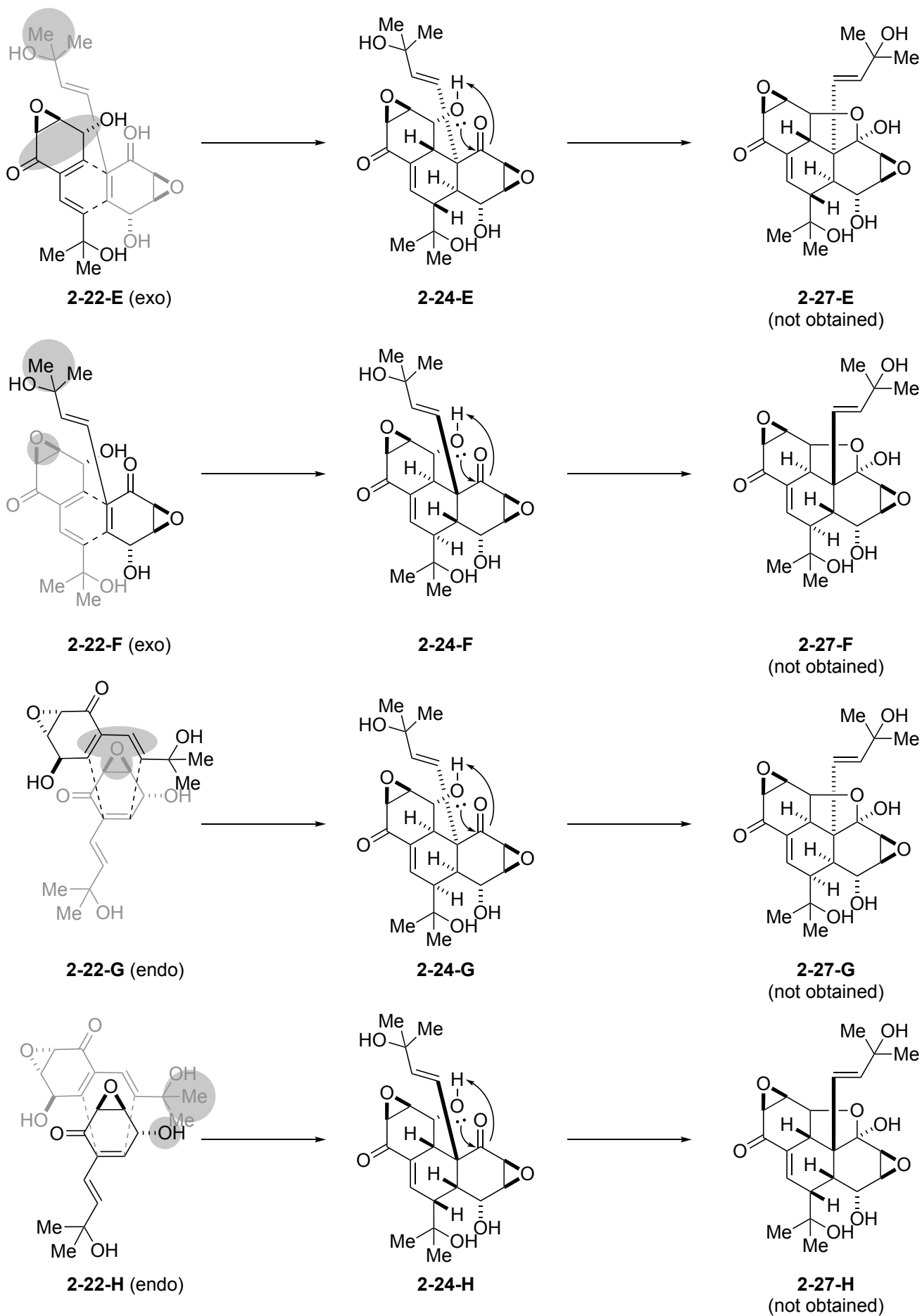
model experiment:



Production of dimer **2-26** confirms that that tertiary hydroxy group of monomers **2-22** and hydrogen-bond organization

is not essential for successful Diels–Alder dimerization. Furthermore, from the calculated transition-state structure of **2-4**, the marked hydrogen bond may not work well.





Steric interactions were major reasons for this stereoselective Diels–Alder dimerization.