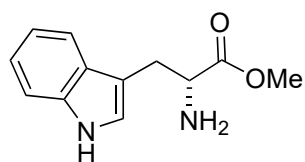
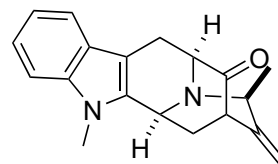


1 Please provide plausible mechanisms.



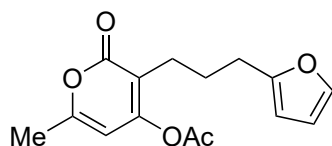
1-1

1. **A** (1.5 eq), K_2CO_3 (2.5 eq), CH_3CN , $65\text{ }^\circ\text{C}$, 85%
2. **B** (1.5 eq), TFA (2.5 eq), CH_2Cl_2 , rt, 89%
3. NaH (1.1 eq), CH_3I (1.1 eq), DMF $-10\text{ }^\circ\text{C}$ to rt, 96%
4. NaH (3 eq), MeOH (6 eq), toluene $110\text{ }^\circ\text{C}$, 80%
5. AcOH/conc. HCl aq/ H_2O (7/10/3) $110\text{--}130\text{ }^\circ\text{C}$, 82%
6. TBAF (1.5 eq), THF, $0\text{ }^\circ\text{C}$ to rt, 90%
7. I-B(Cy) $_2$ (2.5 eq), CH_2Cl_2 , $0\text{ }^\circ\text{C}$ to rt; AcOH (11 eq), $0\text{ }^\circ\text{C}$ to rt; NaOH (18 eq), H_2O_2 (3 eq) $0\text{ }^\circ\text{C}$ to rt, 79%
8. $Pd_2(dba)_3$ (0.05 eq), DPEPhos (0.07 eq) Na t -BuO (2 eq), THF, $70\text{ }^\circ\text{C}$, 68%



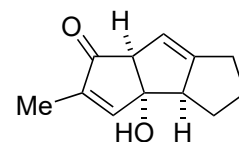
1-2

2 Please provide plausible mechanisms.

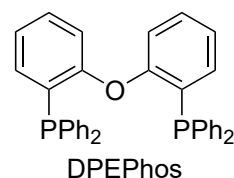
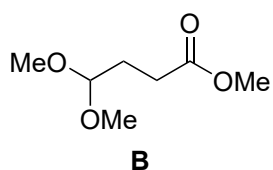
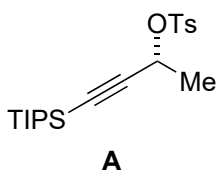


2-1

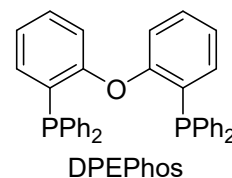
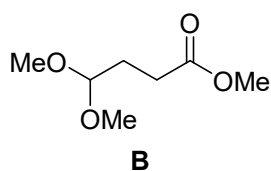
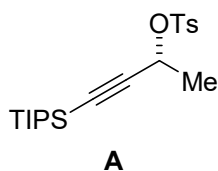
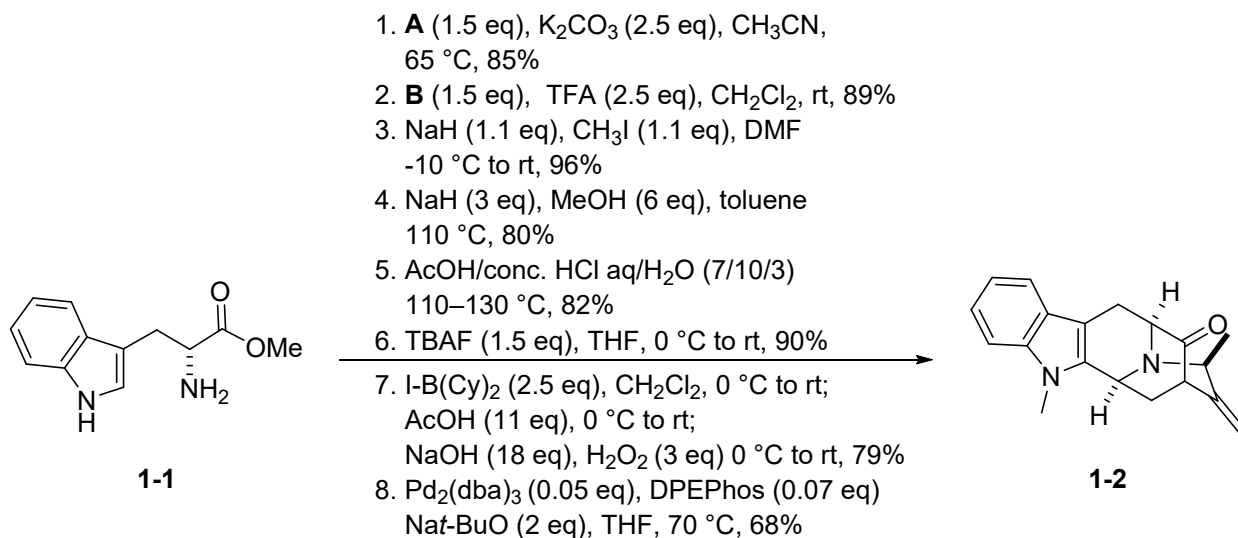
1. $h\nu$, MeOH, $10\text{ }^\circ\text{C}$
2. $55\text{ }^\circ\text{C}$, 60% (2 steps)
3. MeLi (2.1 eq), Et_2O , $-78\text{ }^\circ\text{C}$ to reflux, 63%



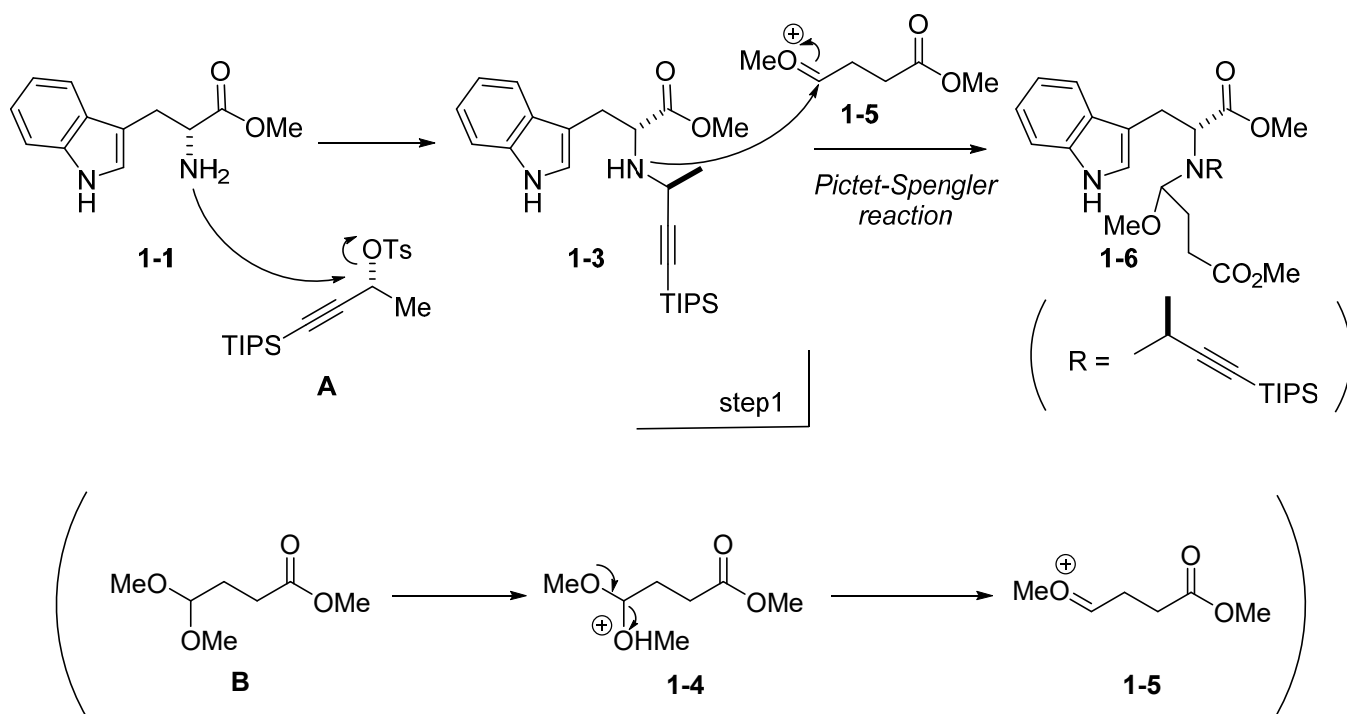
2-2

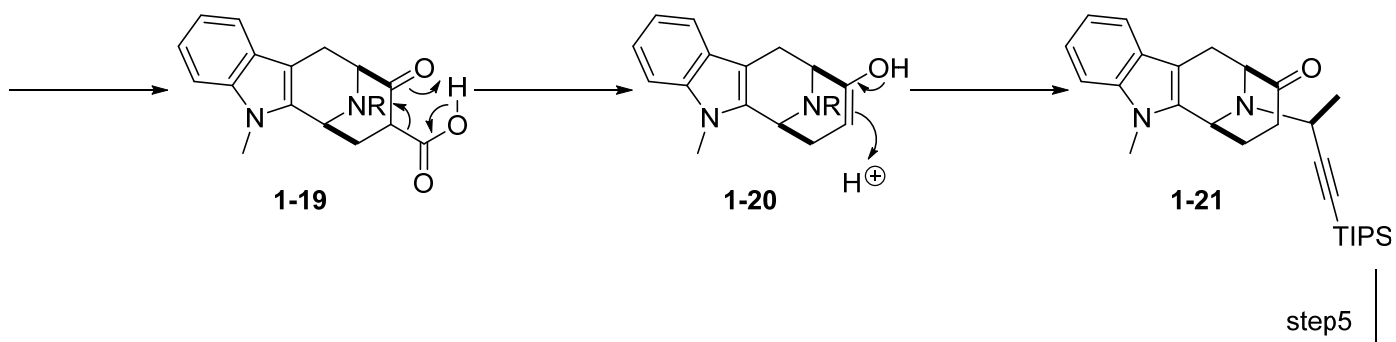
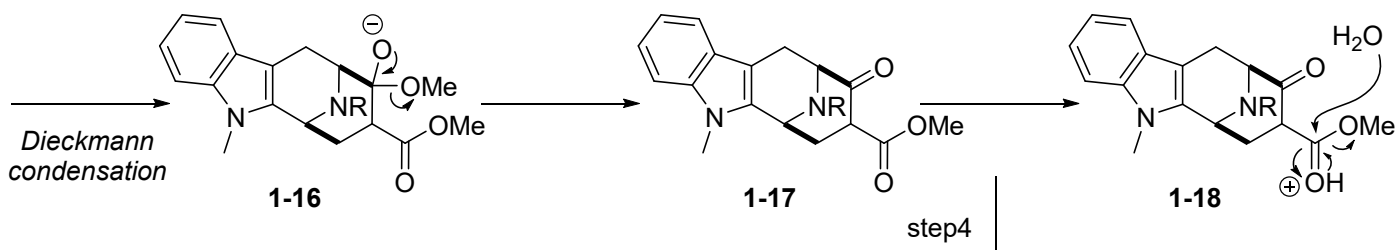
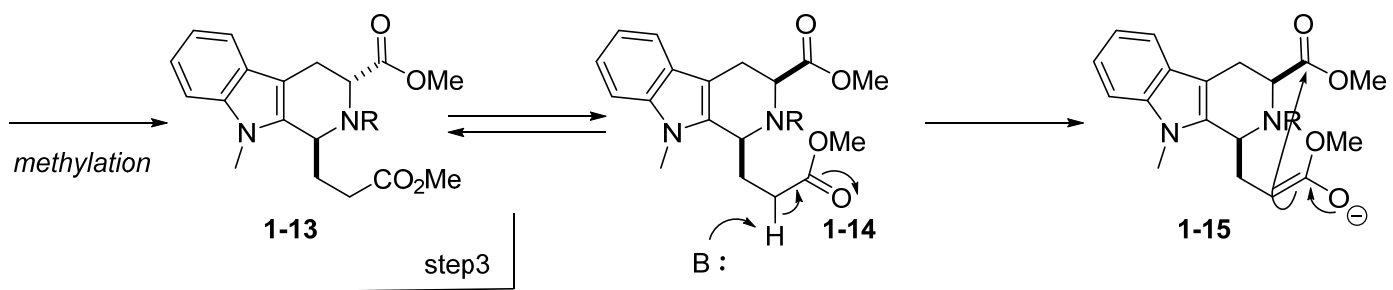
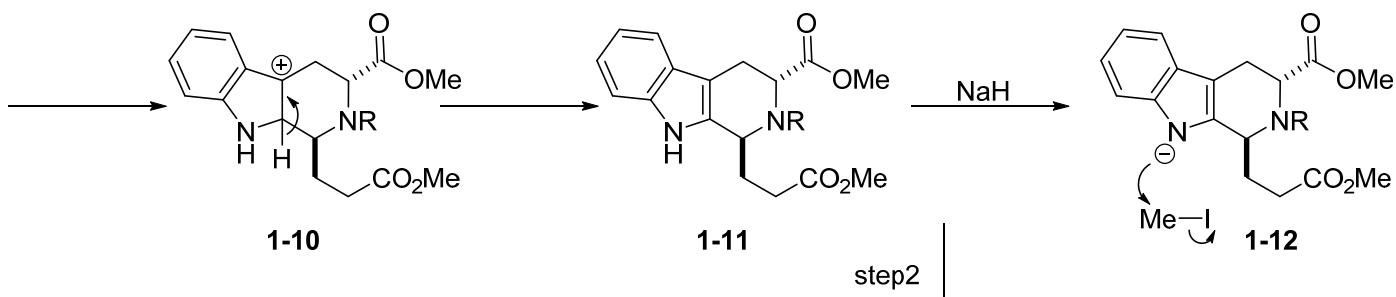
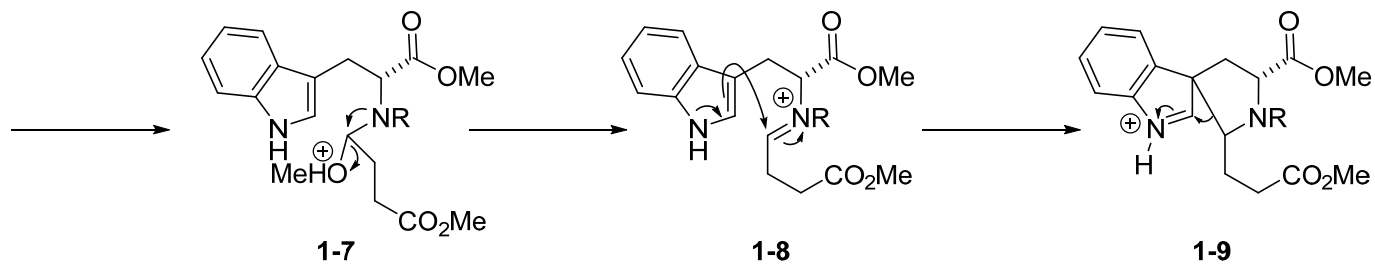


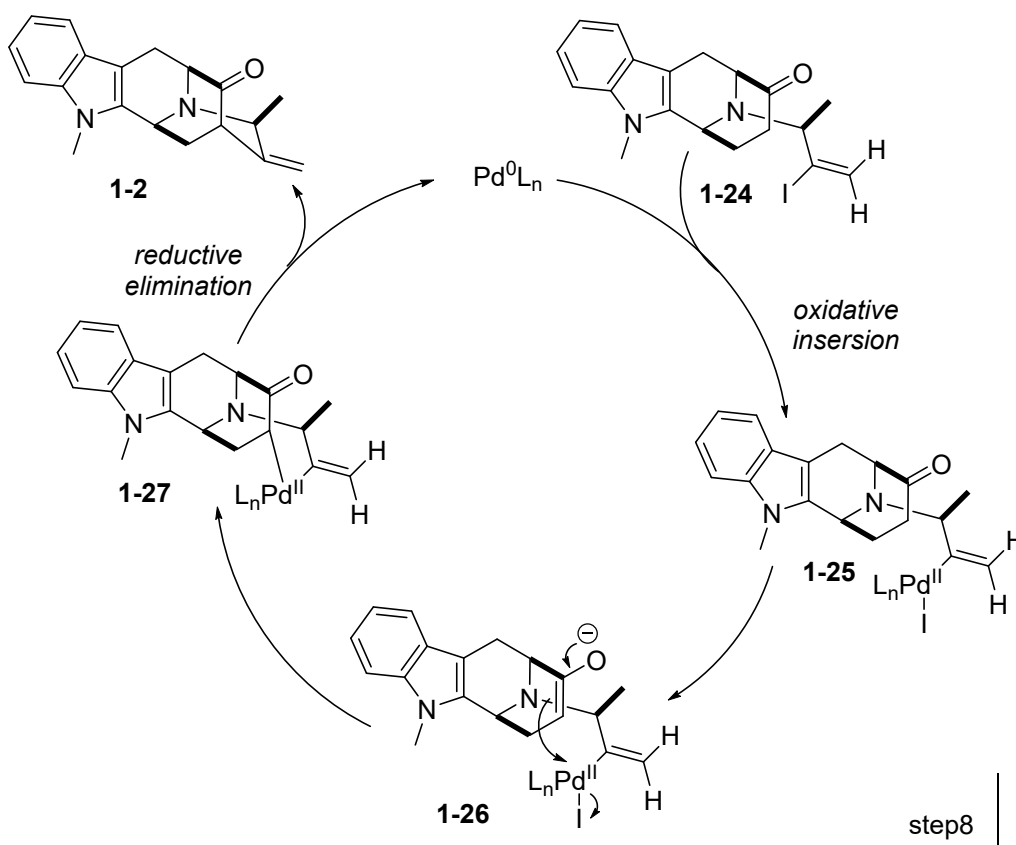
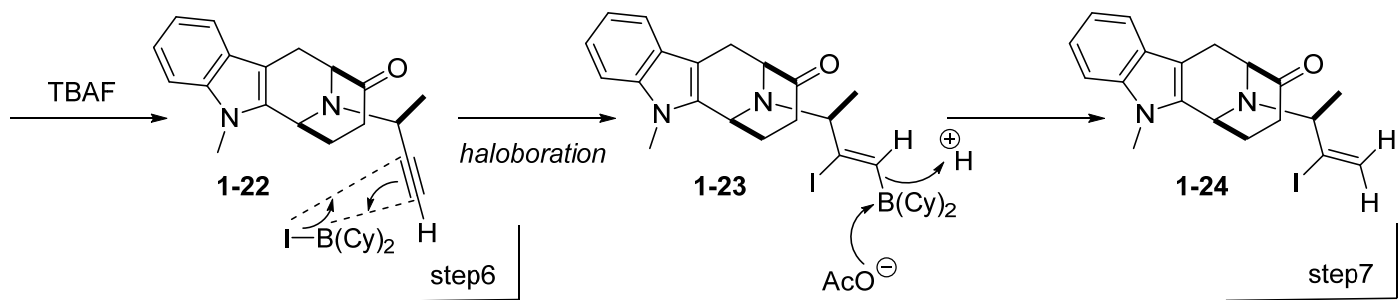
1 Please provide plausible mechanisms.



Rahnam, M. T.; Deschamps, J. R.; Imler, G. H.; Cook, J. M. *Chem Eur. J.* **2018**, *24*, 2345.

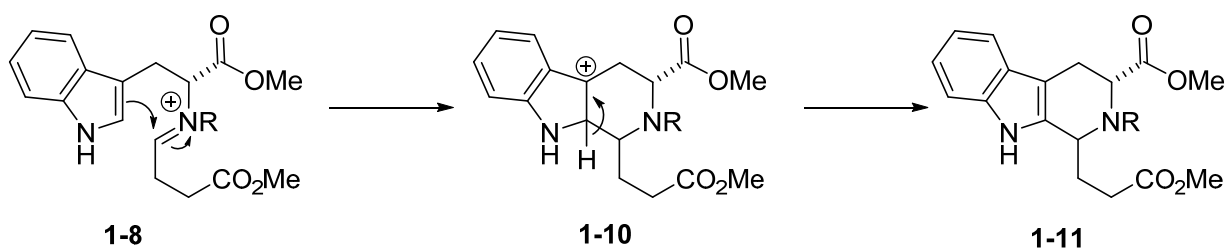




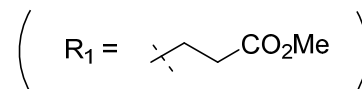
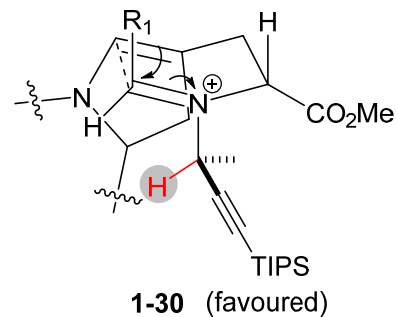
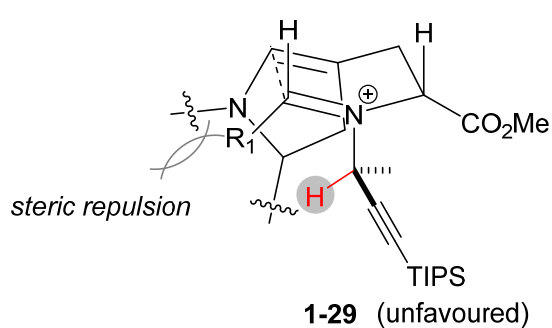
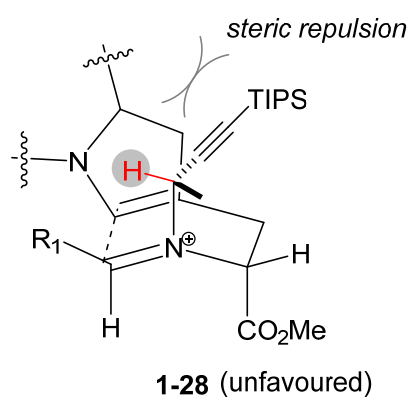
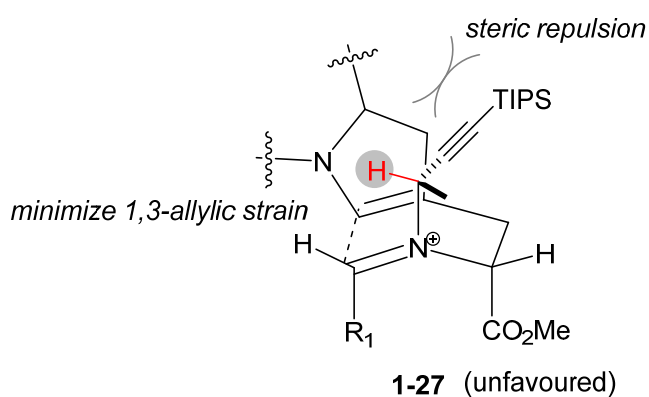
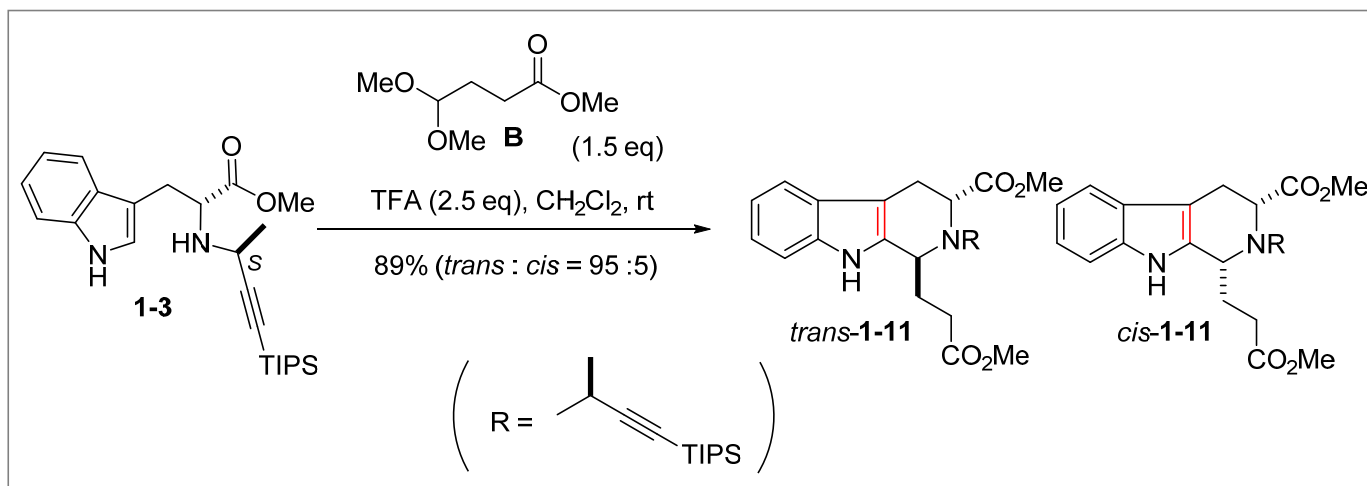


Discussion

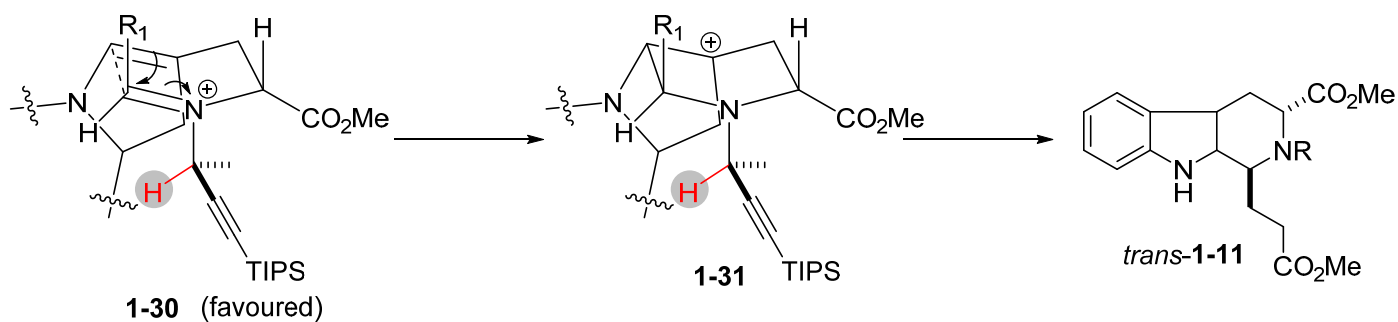
- Another pathway for Pictet-Spengler reacton

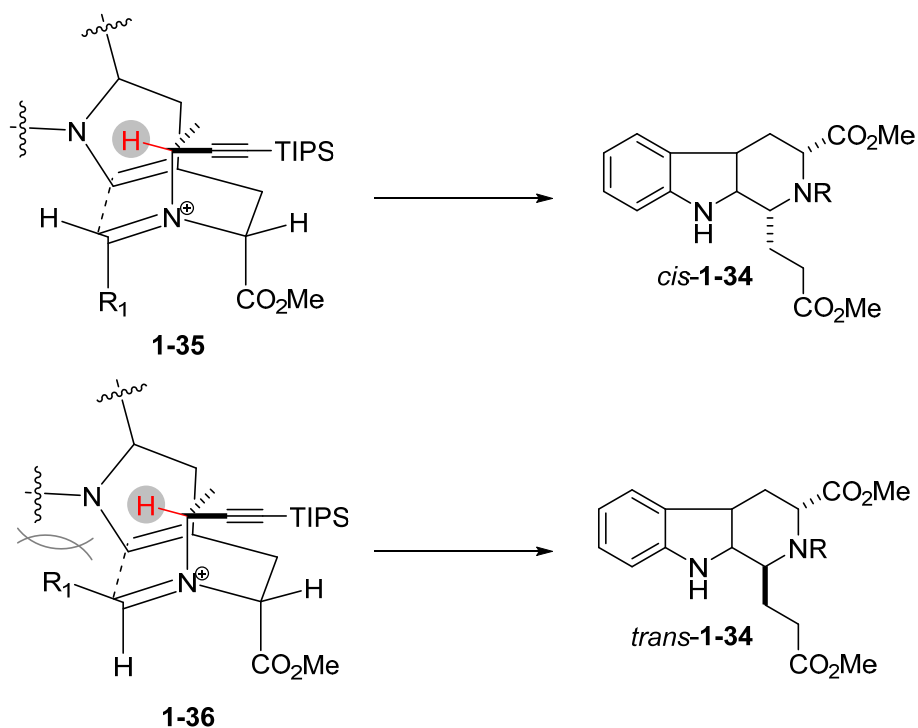
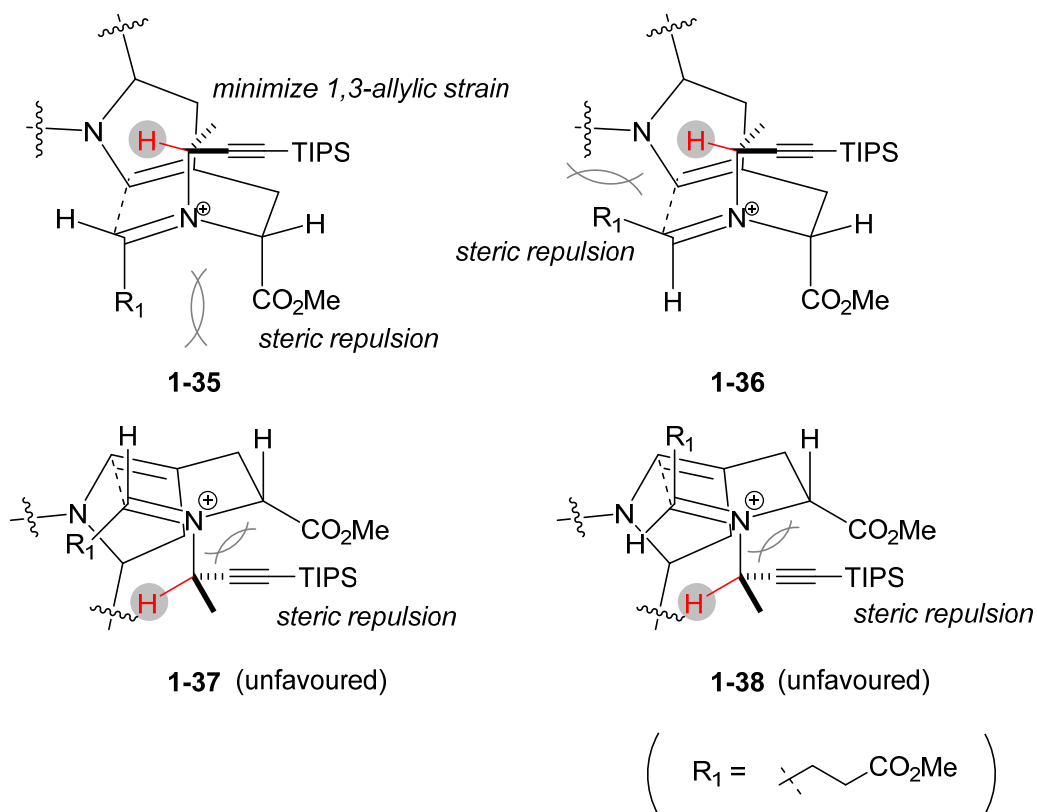
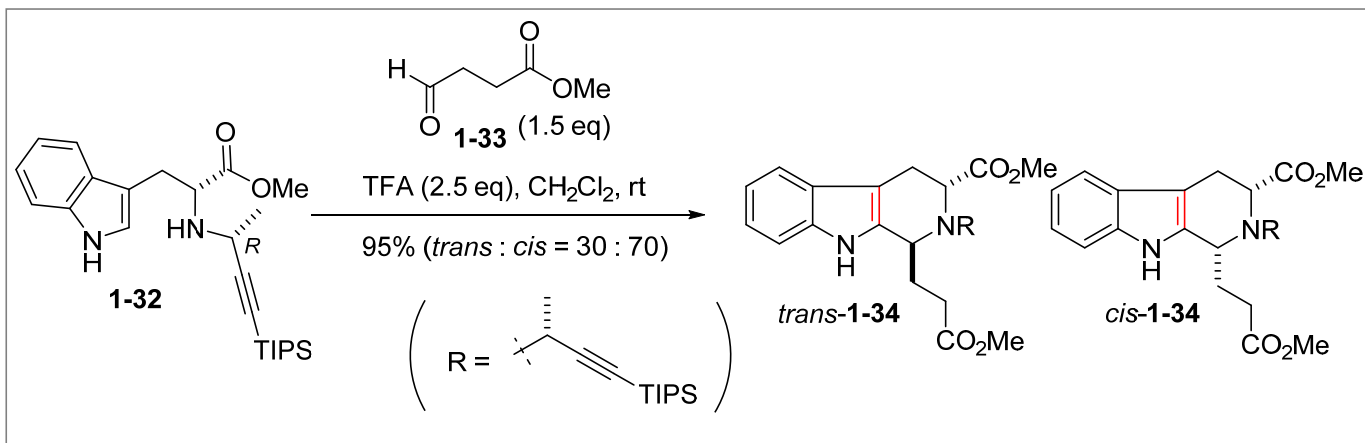


• Diastereoselectivity of Pictet-Spengler reaction

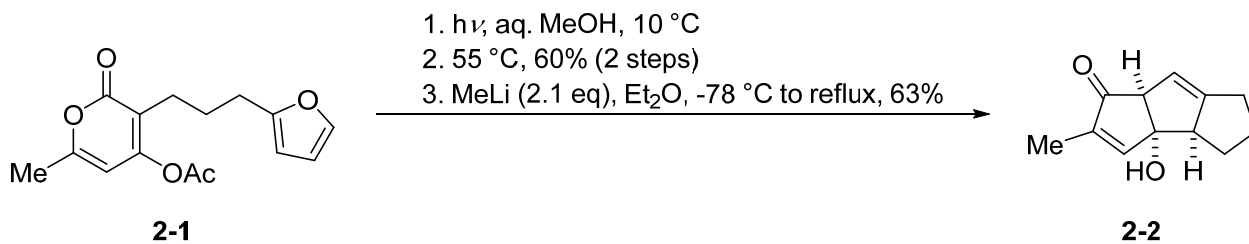


from **1-30**, pictet-spengler reaction occurs

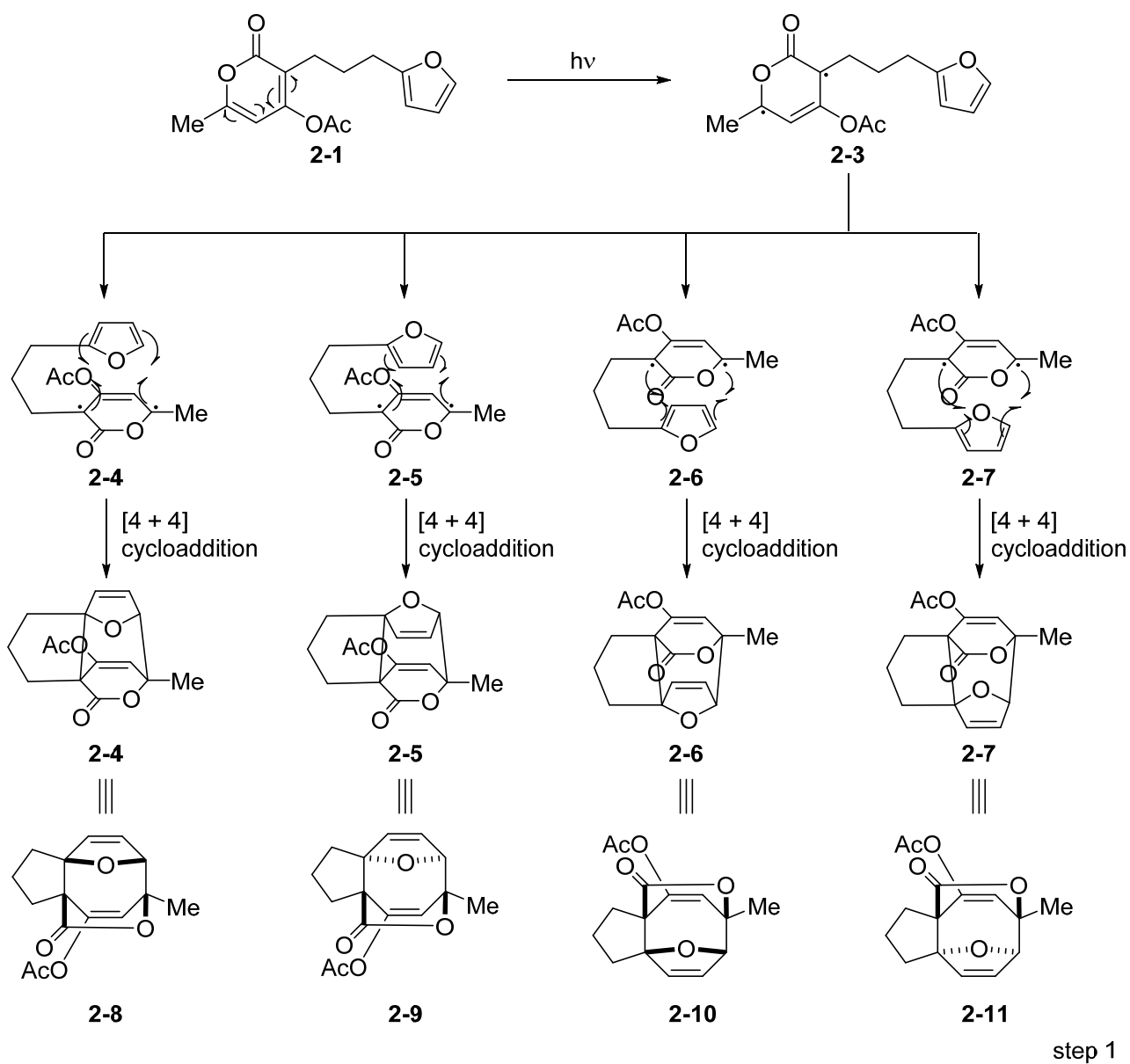


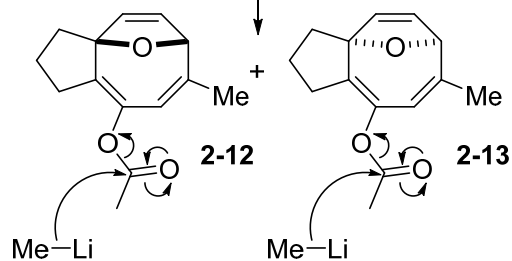
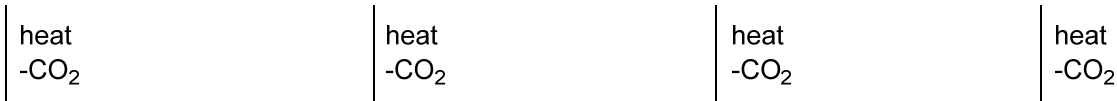
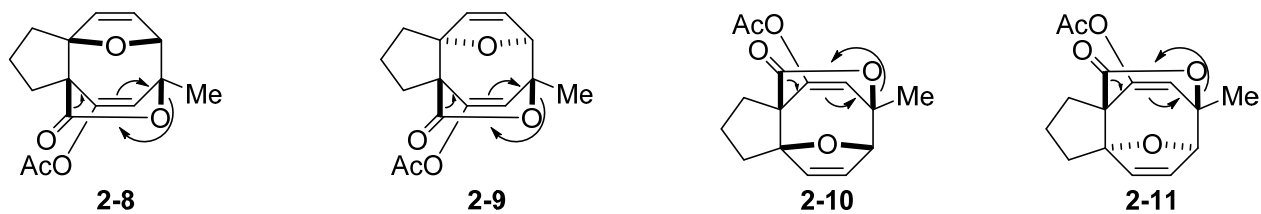


2 Please provide plausible mechanisms.

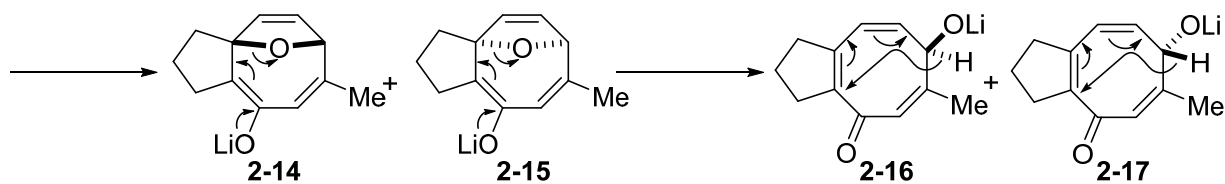


Li, L.; McDonald, R.; West, F. G. *Org. Lett.* **2008**, *10*, 3733.



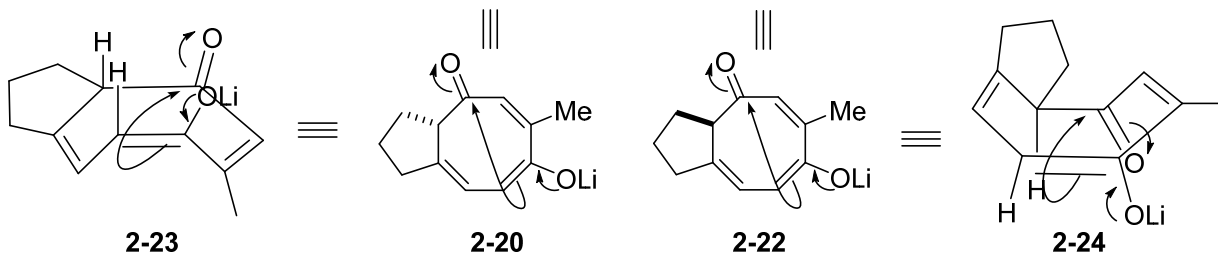
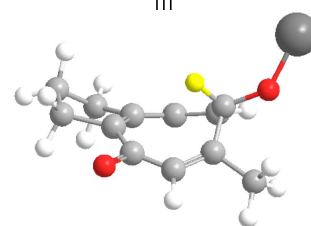
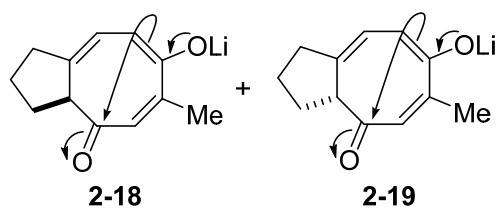


step2

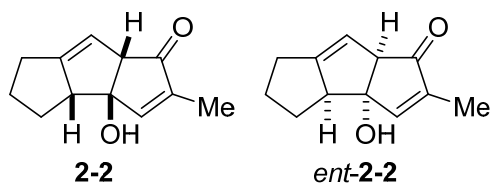


III

1,5-sigmatropic
rearrangement



transannular aldol reaction

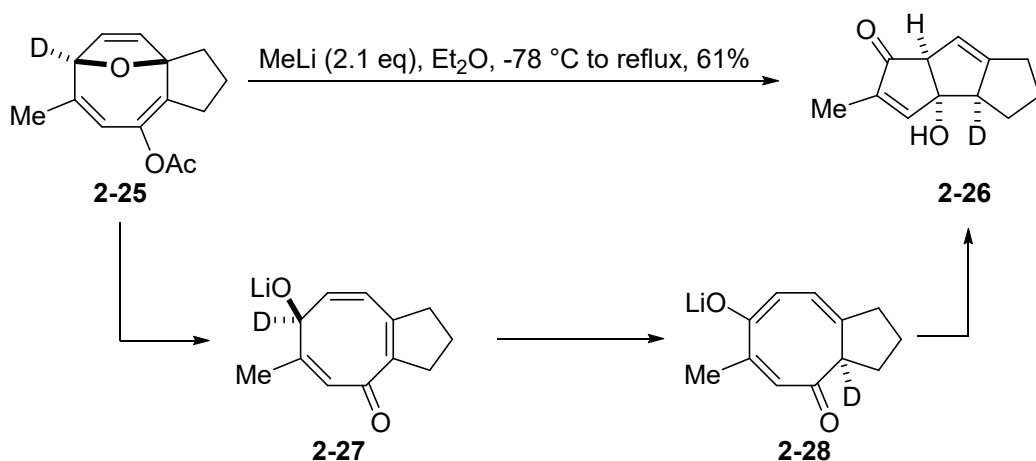


step3

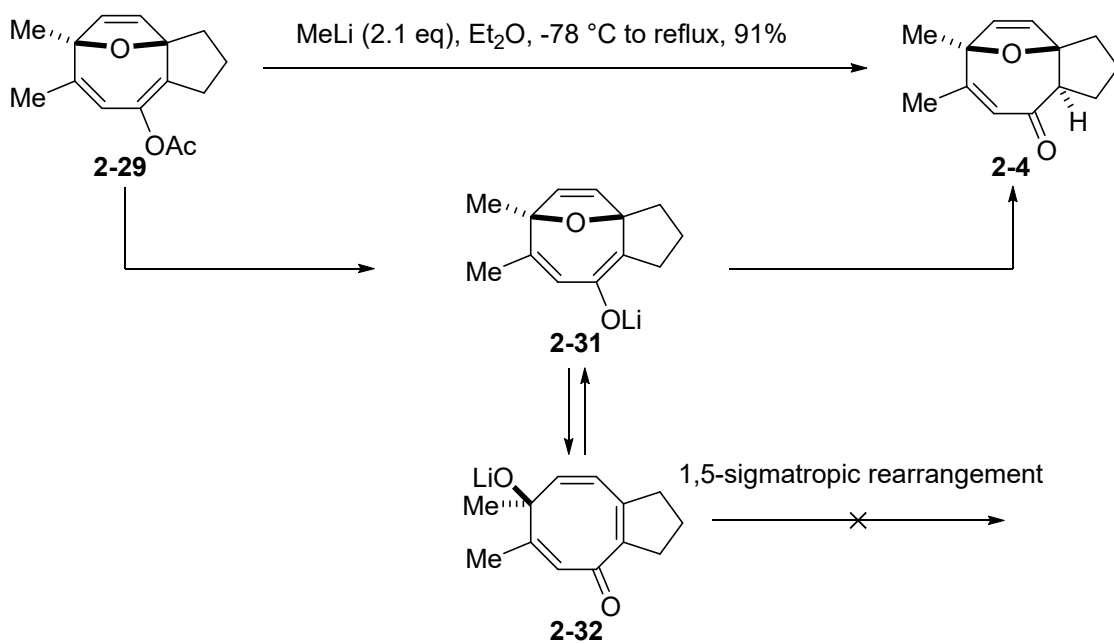
Discussion

- 1,5-sigmatropic rearrangement

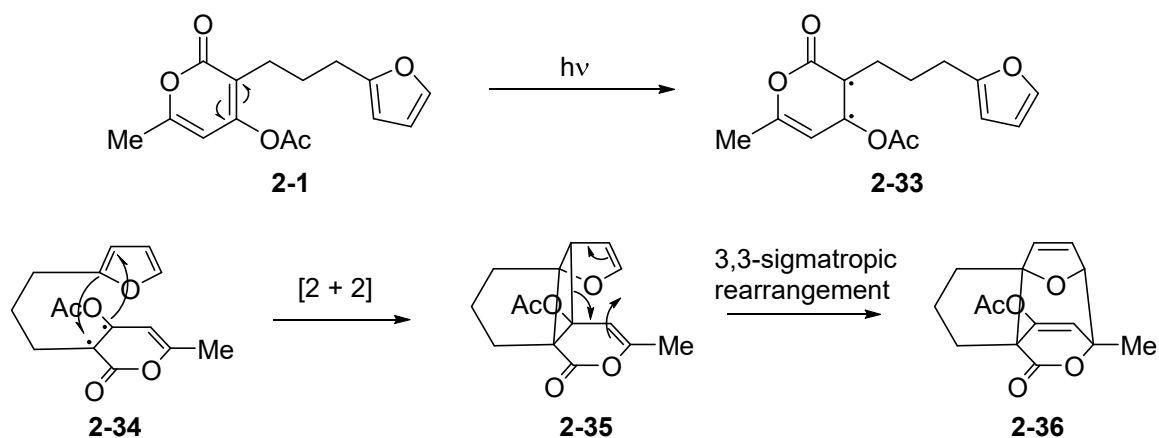
Dauterium labeling experiment

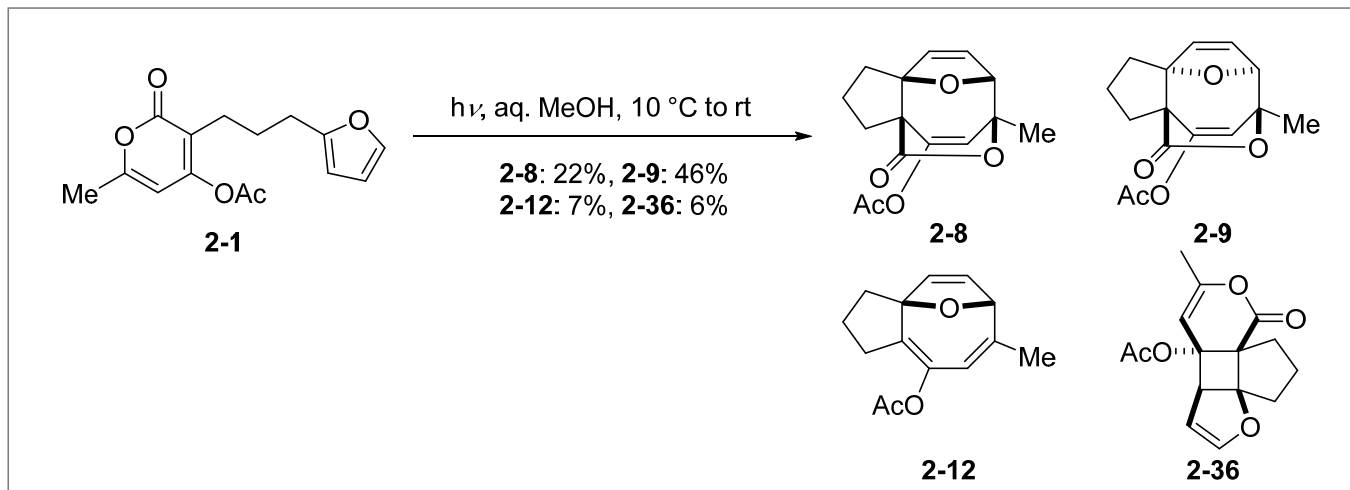


Another evidence

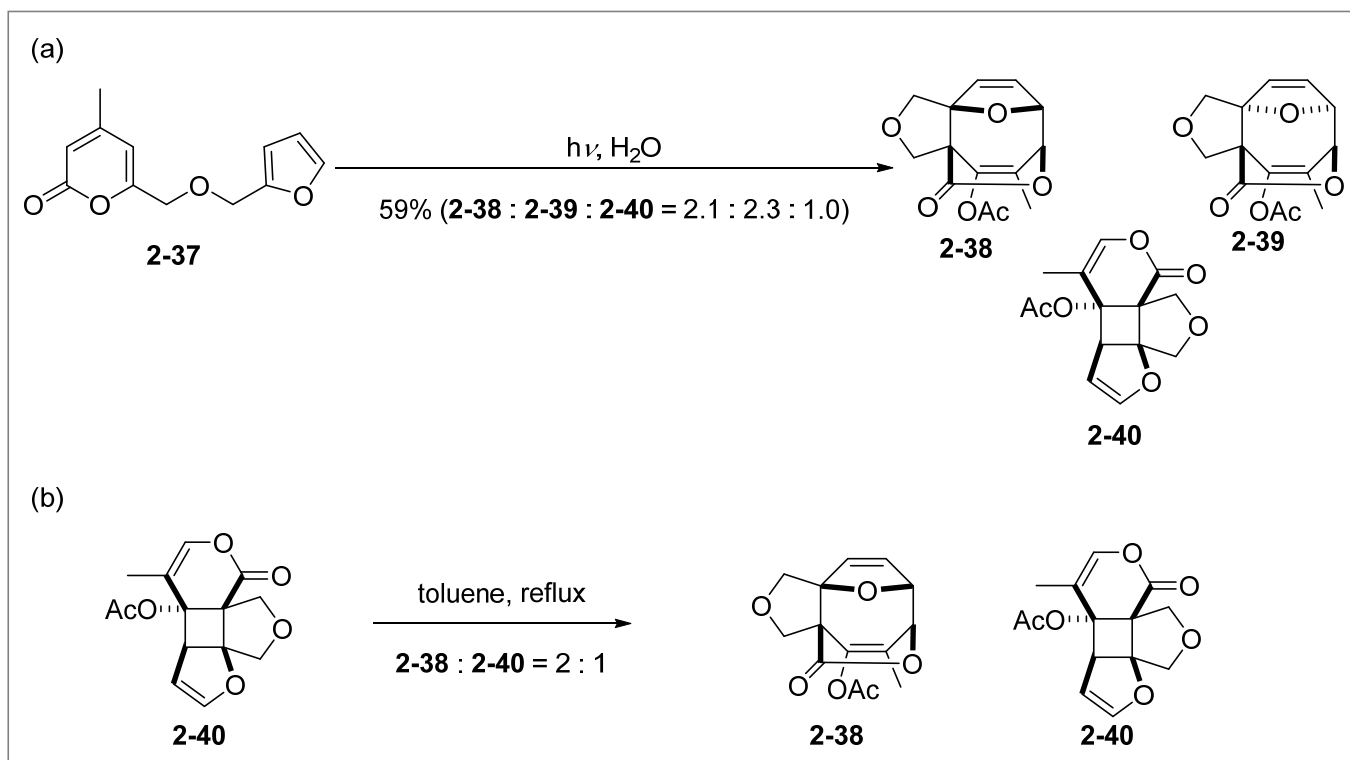


- Another possible pathway





Chase, C. E.; Bender, J. A.; West, F. G. *Synlett*. **1996**, 1173.



West, F. G.; Chase, C. E.; Arif, A. M. *J. Org. Chem.* **1993**, 58, 3794.