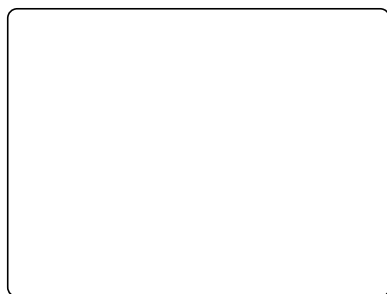
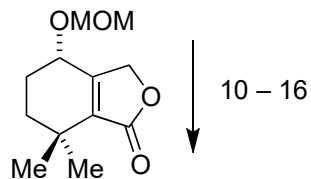
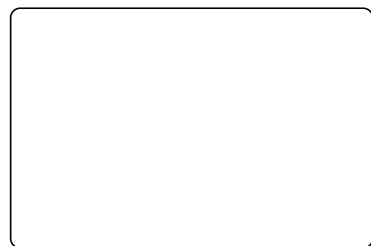
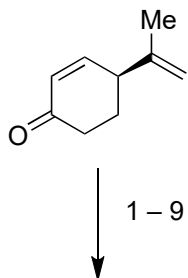


Total Synthesis of Isorosthin L and Isodenolin I

J. Ao, C. Sun, B. Chen, N. Yu, G. Liang, *Angewandte Chemie (International ed. in English)* **2022**, 61, e202114489.



1. LiHMDS, Mander's reagent, THF, $-78\text{ }^{\circ}\text{C}$
2. Raney Nickel, THF, $0\text{ }^{\circ}\text{C}$
3. NaBH_4 , EtOH, $0\text{ }^{\circ}\text{C}$
4. SO_2Cl_2 , Na_2CO_3 , CH_2Cl_2 , $0\text{ }^{\circ}\text{C}$
5. IBX, EtOAc, $80\text{ }^{\circ}\text{C}$
6. K_2CO_3 , NaI, acetone, $60\text{ }^{\circ}\text{C}$
7. KHMDS, DIBAL-H, Et_2O , $-78\text{ }^{\circ}\text{C}$
8. TrisNHNH_2 , THF, 0 to $25\text{ }^{\circ}\text{C}$
then $n\text{-BuLi}$, I_2 , Et_2O , -78 to $-40\text{ }^{\circ}\text{C}$
9. IBX, DMSO, $25\text{ }^{\circ}\text{C}$

10. **A**, LDA, THF, -78 to $-20\text{ }^{\circ}\text{C}$
11. AIBN, Bu_3SnH , toluene, $85\text{ }^{\circ}\text{C}$
then NaOMe, MeOH, 0 to $25\text{ }^{\circ}\text{C}$
12. LiAlH_4 , THF, $65\text{ }^{\circ}\text{C}$
13. TBSCl, imH, CH_2Cl_2 , 0 to $25\text{ }^{\circ}\text{C}$
14. IBX, DMSO, THF, $25\text{ }^{\circ}\text{C}$
15. TBAF, THF, $0\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$
16. $\text{Pb}(\text{OAc})_4$, $\text{CH}_2\text{Cl}_2/\text{benzene}$, 0 to $25\text{ }^{\circ}\text{C}$

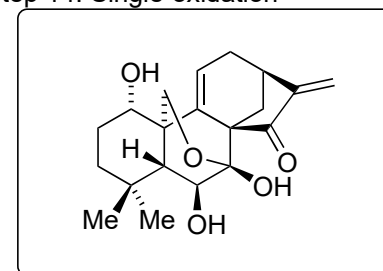
Step 3: Explain why this step could be necessary.

Step 8: Reaction name?
Name of the reaction using NaH instead of $n\text{-BuLi}$ and with which products can you eventually end up with?

Step 10: Only 1 diastereomer is formed, Discuss the stereoselectivity of the two generated stereocenters

Hint step 11: Subsequent Epimerization

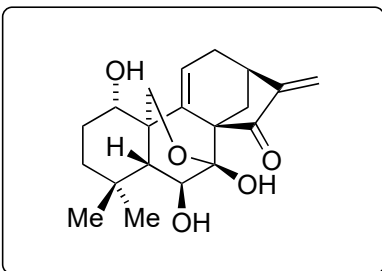
Hint step 14: Single oxidation



isorosthin L

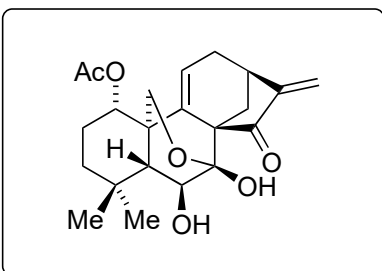
B

17 – 23



isorosthin L

24



isoadenolin I

17. LiBH_4 , THF, 0 to 25 °C
18. DMP, CH_2Cl_2 , 0 to 25 °C
19. SmI_2 , THF, 25 °C
20. MOMCl, DIPEA, NaI, DCE, 25 to 40 °C
21. *t*-BuOOH, SeO_2 , CH_2Cl_2 , 25 °C
22. DMP, NaHCO_3 , CH_2Cl_2 , 0 to 25 °C
23. TFA, 25 °C

24. Ac_2O , NEt_3 , DMAP, CH_2Cl_2 , 0 to 25 °C