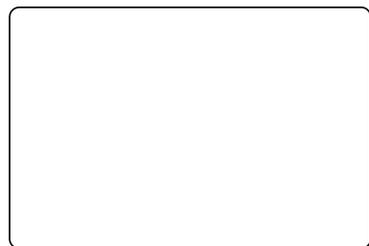
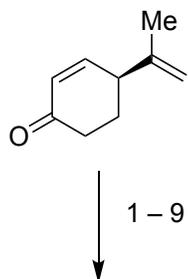


Total Synthesis of Isorosthin L and Isodenolin I

Ao, Junli; Sun, Chao; Chen, Bolin; Yu, Na; Liang, Guangxin
Angew. Chem. Int. Ed. **2022**, *65*, e202114489.

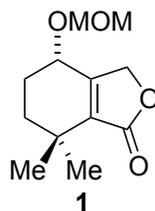


10 – 16



1. LiHMDS, Mander's reagent, THF, -78 °C
2. Raney Nickel, THF, 0 °C
3. NaBH₄, EtOH, 0 °C
4. SO₂Cl₂, Na₂CO₃, CH₂Cl₂, 0 °C
5. IBX, EtOAc, 80 °C
6. K₂CO₃, NaI, acetone, 60 °C
7. KHMDS, DIBAL-H, Et₂O, -78 °C
8. TrisNHNH₂, THF, 0 to 25 °C
then n-BuLi, I₂, Et₂O, -78 to -40 °C
9. IBX, DMSO, 25 °C

10. **1**, LDA, *then A* THF, -78 to -20 °C
11. AIBN, Bu₃SnH, toluene, 85 °C
then NaOMe, MeOH, 0 to 25 °C
12. LiAlH₄, THF, 65 °C
13. TBSCl, imH, CH₂Cl₂, 0 to 25 °C
14. IBX, DMSO, THF, 25 °C
15. TBAF, THF, 0 °C to 25 °C
16. Pb(OAc)₄, CH₂Cl₂/benzene, 0 to 25 °C



Hint step 2: inert atmosphere

Step 3: Explain why this step could be necessary.

Step 8: Reaction name?

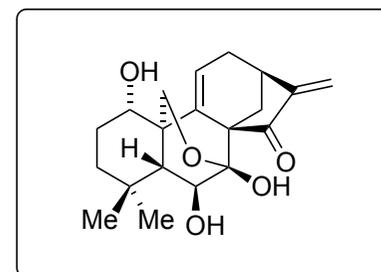
Name of the reaction using NaH instead of *n*-BuLi and with which products can you eventually end up with?

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

Hint step 11: Subsequent Epimerization

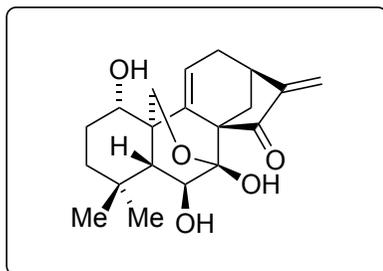
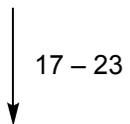
Hint step 14: Single oxidation

Hint step 16: Oxidative laconization, new ¹H-NMR signal : δ 9.92 (s, 1H).

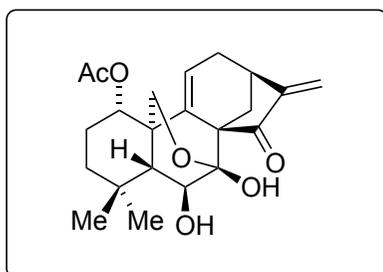


isorosthin L

B



isorosthin L



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

Hint step 17: 2 equivalents of LiBH_4

Hint step 19: 2.1 equivalents of SmI_2 , reductive coupling.