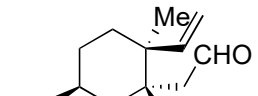
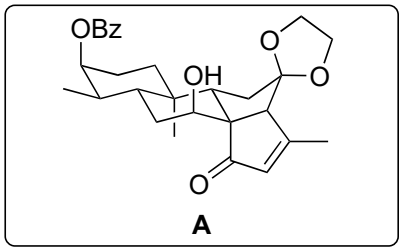
Total Synthesis of (−)-Rhodomollanol A

J. Gao, P. Rao, K. Xu, S. Wang, Y. Wu, C. He, H. Ding, *J. Am. Chem. Soc.* **2020**, *142*, 4592.

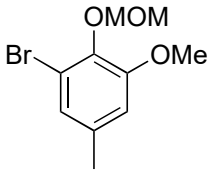


1-4



A

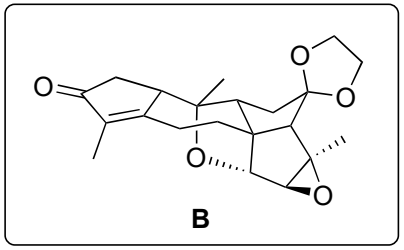
1) **1**, *n*-BuLi
2) DHP, *p*-TsOH
3) PIFA, Na_2CO_3, Na_3PO_4, *then* TFA
4) $(TMSOCH_2)_2$, TMSOTf



1

3) Mechanism?
4) Mechanism?
Hint: 3 Reactions in step 4

5-12

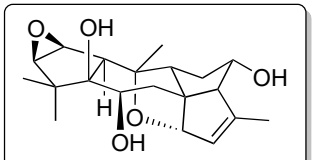


B

5) NaH, CS_2, MeI
6) AIBN, *n*-Bu_3SnH
7) DIBAL-H
8) $VO(acac)_2$, TBHP
9) $(PhSeO)_2O$, pyridine
10) $NaBH_4$, $CeCl_3$
11) LiHMDS, TMSCl
12) hν (254 nm), AcOH

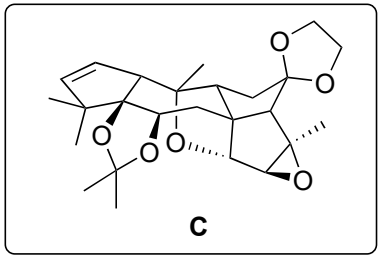
5) + 6) Name of the reaction?
Barton-McCombie deoxygenation

12) Mechanism?



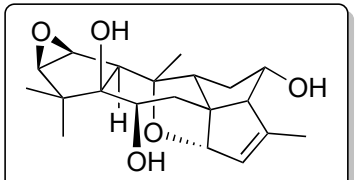
(–)-Rhodomollanol A

13-18



C

19-24



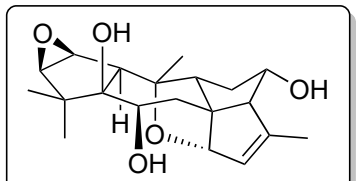
(–)-Rhodomollanol A

13) $MeSOCH_2Na$, MeI
14) OsO_4, pyridine
15) 2,2-Dimethoxypropane, PPTS
16) LiHMDS, NIS, *then m*-CPBA
17) $TsNHNH_2$,PPTS
18) $NaBH_3CN$, *then* NEt_3

19) Cp_2TiCl_2, Zn
20) NaH, CS_2, MeI
21) 150 °C
22) *p*-TsOH
23) $VO(acac)_2$
24) $NaBH_4$

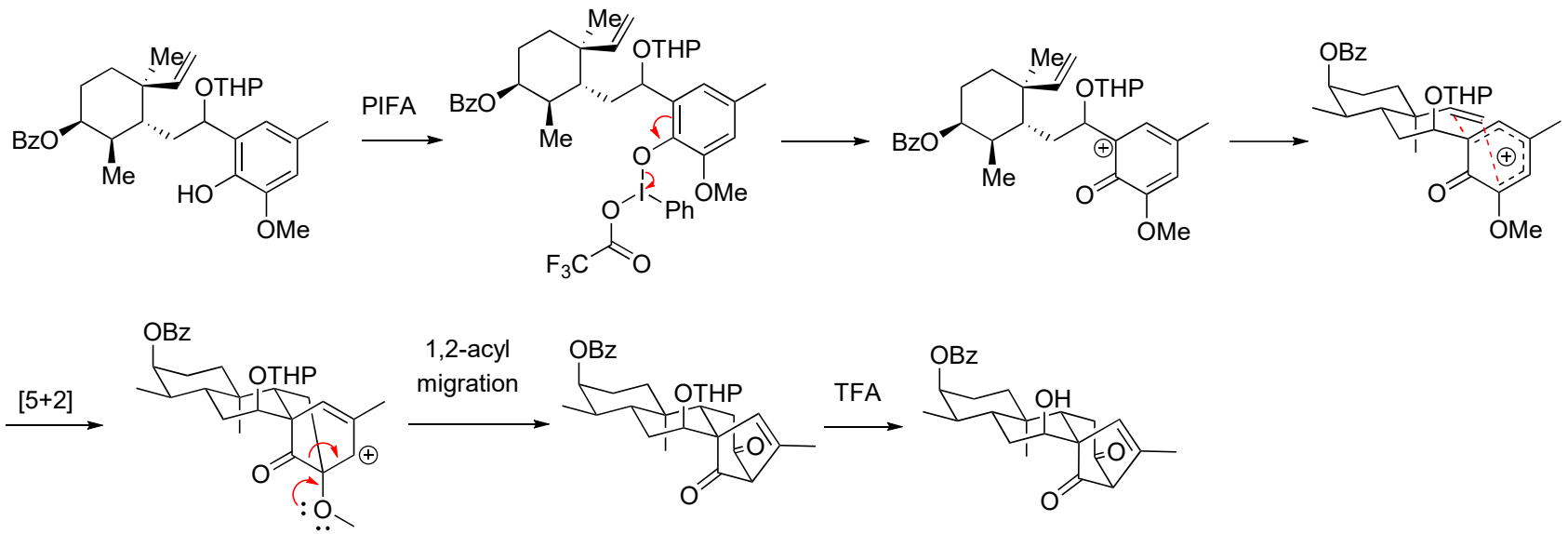
14) Name of the reaction?
Upjohn dihydroxylation

22) Name of the reaction?
Chugaev elimination

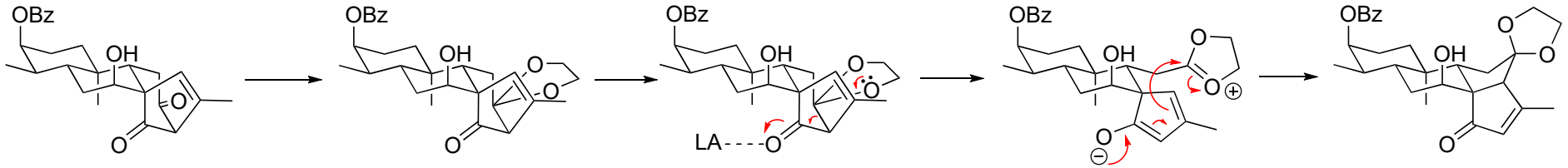


(–)-Rhodomollanol A

Step 3:



Step 4:



Step 12: