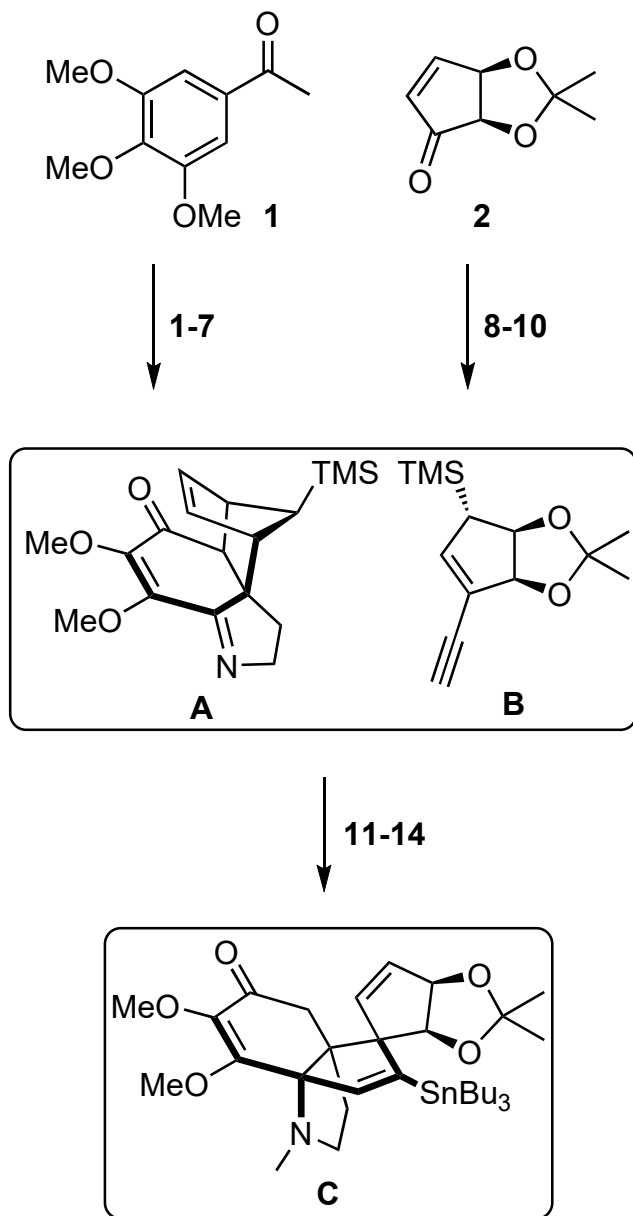


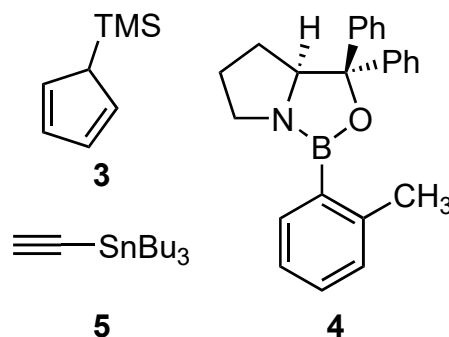
Total Syntheses of (–)-Acutumine and (–)-Dechloroacutumine

Sandra M. King, Nicholas A. Calandra, and Seth B. Herzon

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- 1,2-Ethanediol, *p*-TsOH
- 9-BBN, PhMe, 110 °C, then H₂O₂, NaOH, H₂O
- MsCl, Et₃N
- NaN₃, DMF
- H₂O₂, HCO₂H
- 3**, **4**, TfOH
- PMe₃
- TMSOTf, Pd(OAc)₂, TMS-TMS, then NaOAc, AcOH
- LHMDS, Comins' reagent
- 5**, Pd(PPh₃)₂Cl₂, LiCl



- A**, CH₃OTf, then **B**•Li
- PhMe, 135 °C
- Bu₃SnH, Pd(PPh₃)₄
- TBAF

Please propose a synthesis of acetonide **2** from D-ribose.

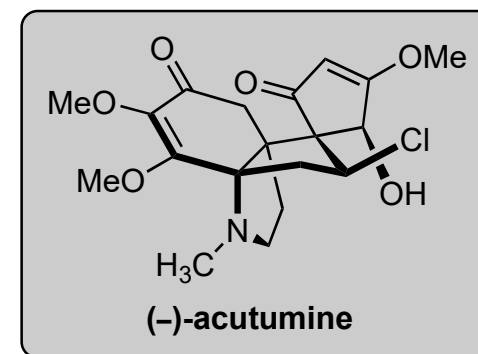
2. Please provide a mechanism

7. Name of the reaction: Staudinger reduction

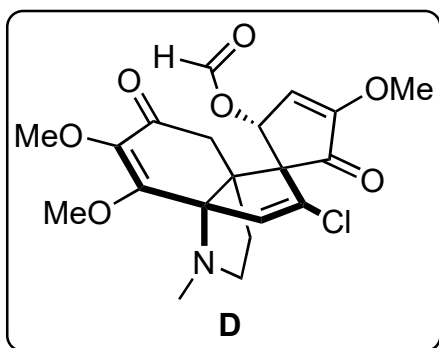
8. Hint: in situ cleavage of the resulting enoxysilane.

Please provide a mechanism for the formation of this intermediate.

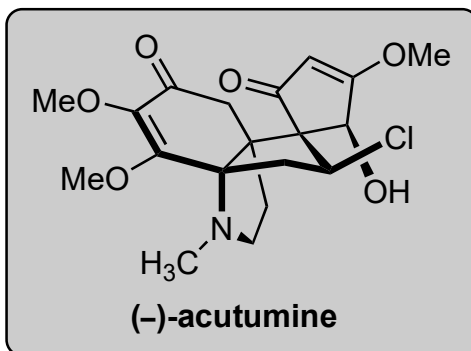
14. Name reaction: Hosomi–Sakurai allylation



15-20



21-24

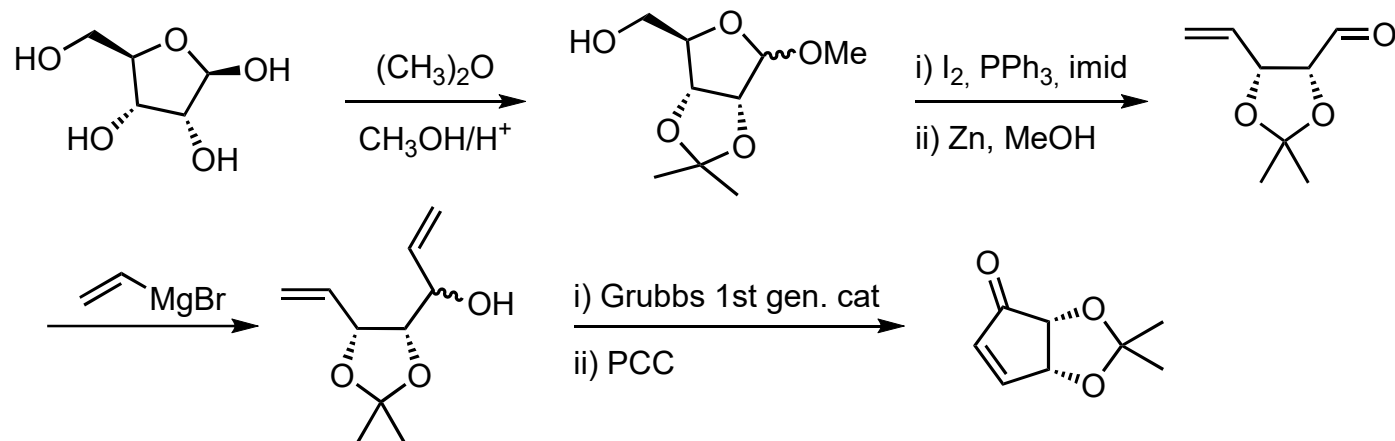


15. CuCl_2
16. PTSA, H_2O , CH_3OH
17. TFAA, DMSO, DIPEA, then NaSCH_3
18. CH_2N_2
19. NIS, HCO_2H
20. DIPEA, CH_3CN , $100\text{ }^\circ\text{C}$

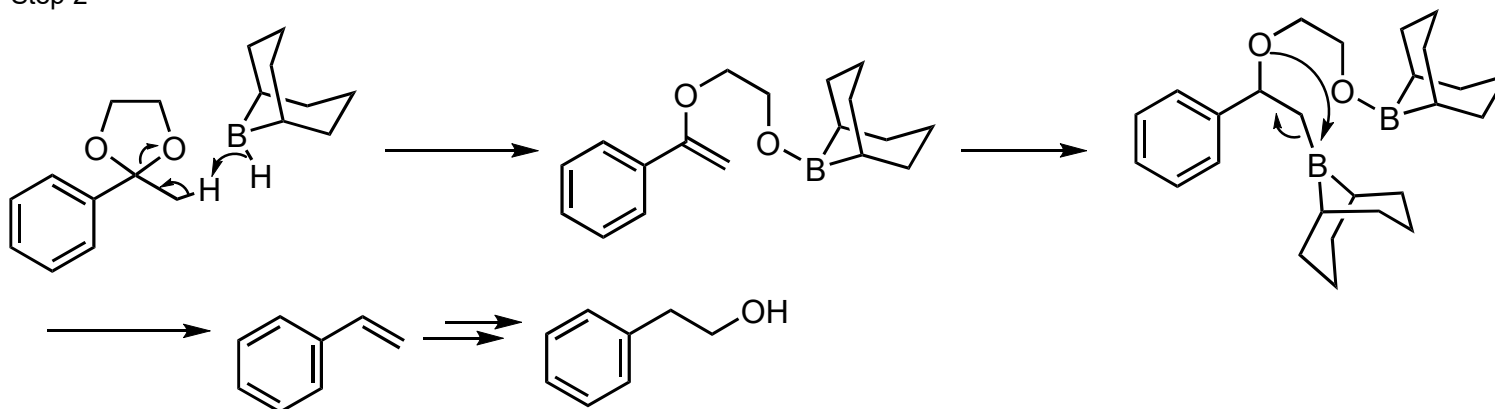
21. NH_4OH , CH_3OH
22. DMP
23. NaBH_4
24. $\text{Rh}(\text{nbd})(\text{dppb})\text{BF}_4$, H_2 (300 psi)
(H_2 , Pd/C for Dechloroacutumine)

20. Please classify the reaction: [3,3]-
sigmatropic rearrangement.

Synthesis of acetonide **2** from D-ribose.



Step 2



Step 8

