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

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

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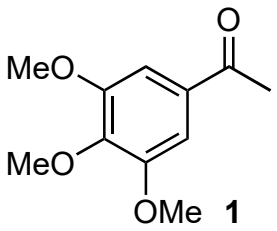

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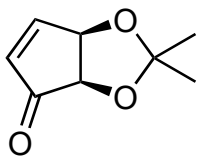


2

1-7

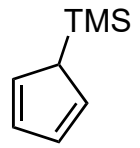
8-10

A **B**

11-14

C

1. 1,2-Ethanediol, *p*-TsOH
2. 9-BBN, PhMe, 110 °C, then H_2O_2, NaOH, H_2O
3. MsCl, Et_3N
4. NaN_3, DMF
5. H_2O_2, HCO_2H
6. **3**, **4**, TfOH
7. PMe_3
8. TMSOTf, $Pd(OAc)_2$, TMS-TMS, then NaOAc, AcOH
9. LHMDS, Comins' reagent
10. **5**, $Pd(PPh_3)_2Cl_2$, LiCl



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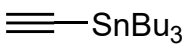

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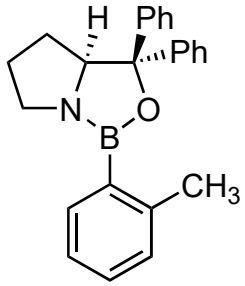


4

11. **A**, CH_3OTf, then **B**•Li
12. PhMe, 135 °C
13. Bu_3SnH, $Pd(PPh_3)_4$
14. TBAF

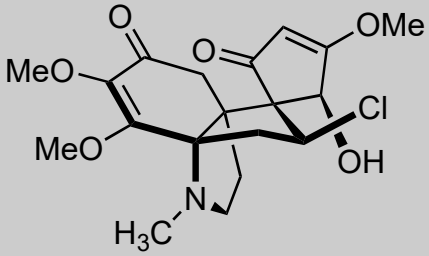
Please propose a synthesis of acetonide **2** from D-ribose.

2. Please provide a mechanism

7. Name of the reaction:

8. Hint: in situ cleavage of the resulting enoxysilane.
Please provide a mechanism for the formation of this intermediate.

14. Name of the reaction:

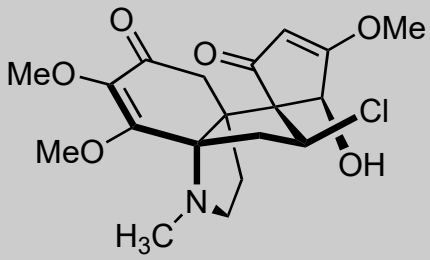


(–)-acutumine

15-20

D

21-24



(–)-acutumine

15. $CuCl_2$
16. PTSA, H_2O, MeOH
17. TFAA, DMSO, DIPEA, then $NaSCH_3$
18. CH_2N_2
19. NIS, HCO_2H
20. DIPEA, CH_3CN, 100 °C

21. NH_4OH, CH_3OH
22. DMP
23. $NaBH_4$
24. $Rh(nbd)(dppb)BF_4$, H_2 (300 psi)
(H_2, Pd/C for Dechloroacutumine)

20. Please classify the reaction: