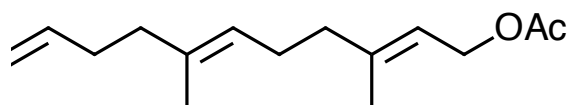


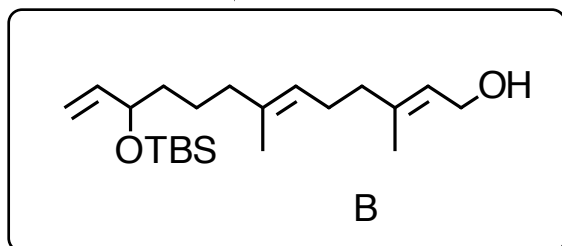
Synthesis Challenge # 33

"Asymmetric Total Synthesis of Mycolectodiscin A", S. Zhou, H. Chen, Y. Luo, W. Zhang, A. Li,
Angew. Chem. Int. Ed. **2015**, ASAP, DOI: 10.1002/anie.201501021
30.04.2015



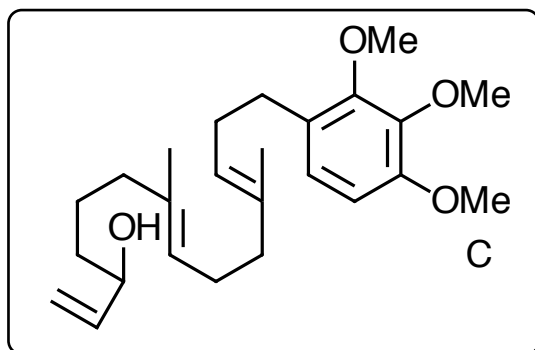
A

1-4



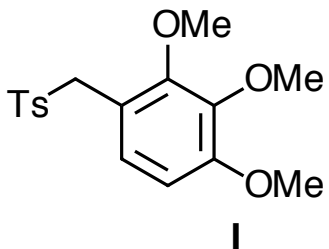
B

5-8



C

- 1) 9-BBN (1.05 equiv), then aq. NaHCO₃, aq. H₂O₂ (30 wt %)
- 2) DMP (1.2 equiv), CH₂Cl₂,
- 3) vinylmagnesium bromide
- 4) TBSCl, imidazole, DMF; K₂CO₃ (1.0 equiv), MeOH,
- 5) MsCl, Et₃N, LiBr, THF
- 6) **I**, KHMDS (1.05 equiv), THF, -78°C, then product of step 5), -78°C
- 7) Na(Hg), Na₂HPO₄, MeOH, -20°C
- 8) HF·py/ THF (1:10),



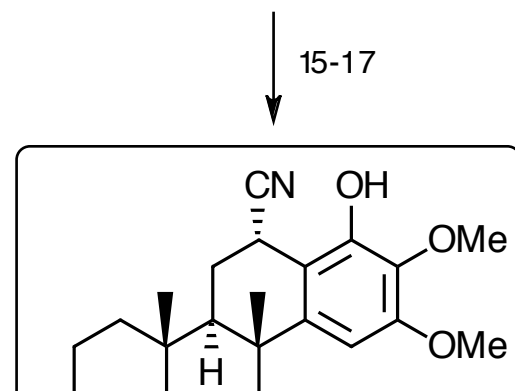
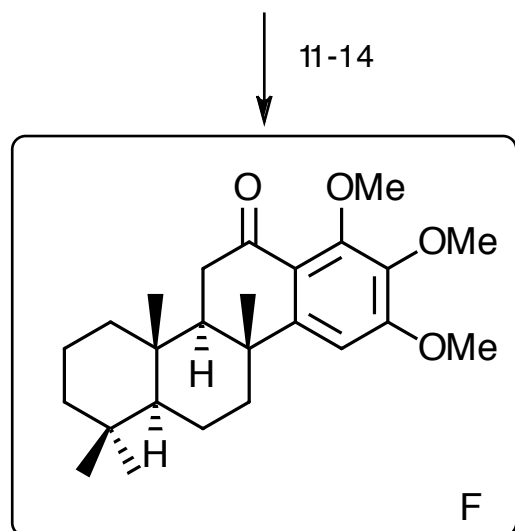
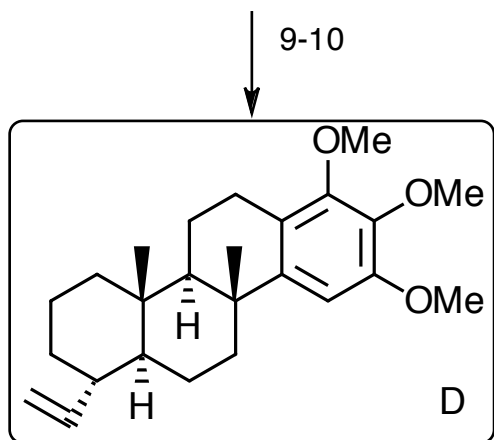
I

Please design a synthesis of A starting from farnesol.

S. Yildizhan, J. vanLoon, A. Sramkova, M. Ayasse, C. Arsene, C. ten Broeke, S. Schulz, *ChemBioChem* **2009**, *10*, 1666.

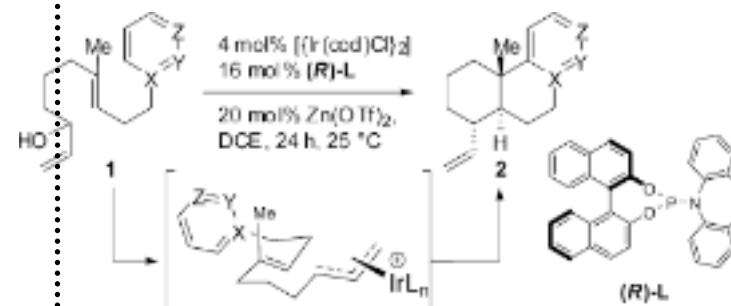
Please, provide a detailed mechanism for step 1.

Hydroboration



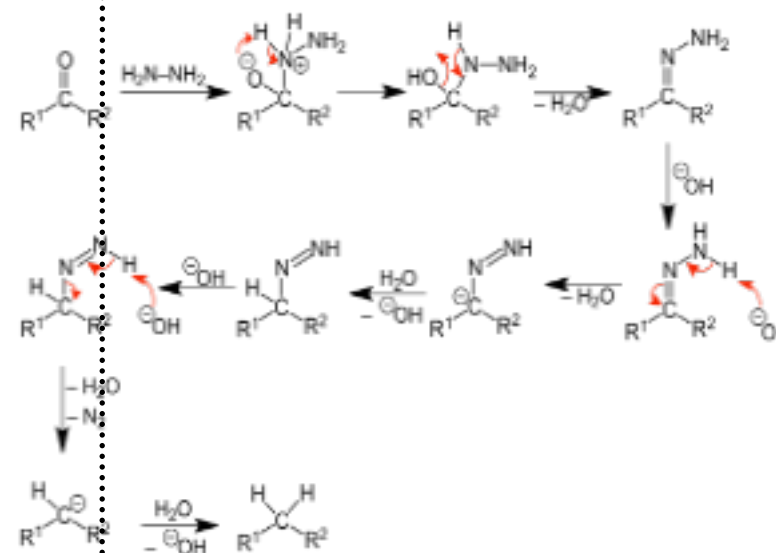
- 9) $[\text{Ir}(\text{cod})\text{Cl}]_2$ (4 mol%), *R*-II (16 mol%),
 $\text{Zn}(\text{OTf})_2$ (20 mol%), DCE, 22 °C
 10) $\text{BF}_3 \cdot \text{OEt}_2$ (2.5 equiv), CH_2Cl_2 , 0 °C,

Step 9 and 10 promote the same transformation. Please, provide a detailed mechanism.



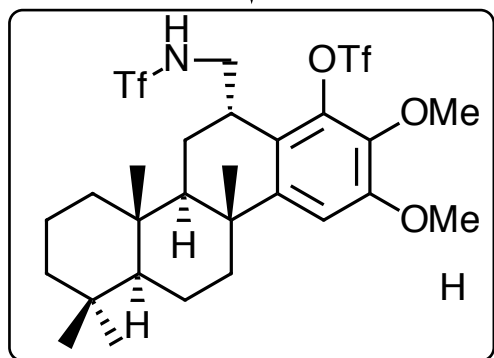
Please, provide a detailed mechanism for step 13).

- 11) $\text{K}_2\text{OsO}_2(\text{OH})_2$ (10 mol %),
 2,6-lutidine (1.0 equiv), Na_2IO
 (3.0 equiv), acetone/water (3:1)
 12) tBuOK , MeI (10 equiv), tBuOH
 13) $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, diethylene glycol,
 160 °C, 2 h, then KOH , 180 °C
 14) 3,5-dimethylpyrazole, CrO_3

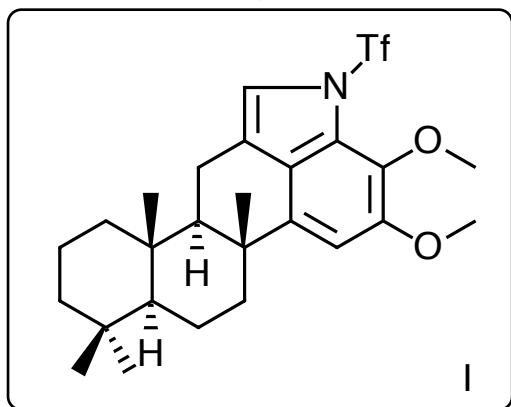


- 15) AlCl_3 (1.1 equiv), CH_2Cl_2
 16) NaBH_4 , $\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1:1)
 17) TMSBr (20 mol %), InCl_3 (10 mol %),
 TMSCN (1.2 equiv), MeCN

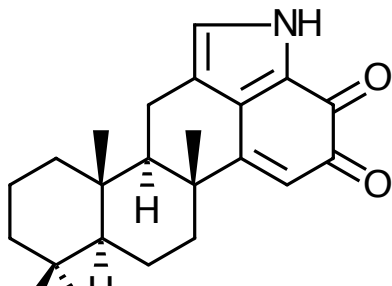
18-19



20-21



22-23



- 18) $\text{BH}_3 \cdot \text{THF}$, THF, 50 °C
19) Tf_2O , Et_3N , 4-DMAP (10 mol %)

- 20) CuI (4.0 equiv), CsOAc , NMP, 160°C, 4 h
21) DDQ (5.0 equiv), toluene, 110°C,

- 22) BBr_3 (10.0 equiv), CH_2Cl_2 , -78-22°C,
23) Mg (10.0 equiv), NH_4Cl (2.0 equiv), MeOH, sonication, 5 min, then work up under an air atmosphere,