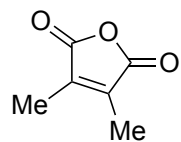


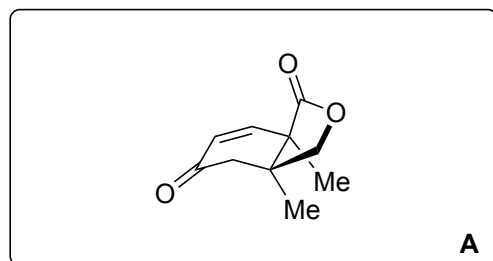
# Total Synthesis of (±)-11-O-Debenzoyltashironin

Jie Tong, Tianrun Xia, and Bo Wang

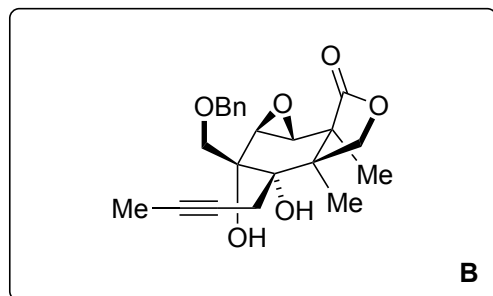
*Org. Lett.* **2020**, *22*, 2730–2734.



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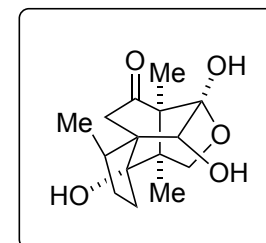


6-10

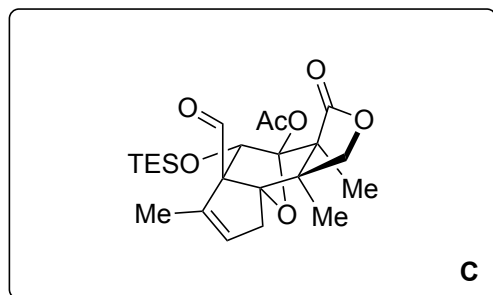


- 1) Danishefsky diene, toluene, 150 °C  
then 4 M HCl
- 2) NaOMe, MeOH
- 3) methyl chloroformate  
then NaBH<sub>4</sub> (excess)
- 4) PIDA, TEMPO
- 5) DBU

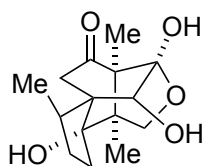
- 6) DBU, *t*-BuOOH
- 7) Pb(OAc)<sub>4</sub>, benzene, reflux
- 8) BOMCl, Mg, HgCl<sub>2</sub>  
then K<sub>2</sub>CO<sub>3</sub>, MeOH
- 9) IBX
- 10) Zn, 1-bromo-2-butyne



11-15



16-19



- 11) NaHMDS
- 12) DMP
- 13) Ac<sub>2</sub>O, NEt<sub>3</sub>, DMAP
- 14) TESOTf, 2,6-lutidine, CH<sub>2</sub>Cl<sub>2</sub>, reflux
- 15) [Pd(dppe)(PhCN)<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub>, toluene, 90 °C

- 16) Cp<sub>2</sub>TiCl<sub>2</sub>, Mn
- 17) aq. HBF<sub>4</sub>, MeOH
- 18) H<sub>2</sub>, Pd/C
- 19) Sml<sub>2</sub>, HMPA

11) Name of the reaction?

Payne rearrangement

13) hint: one new ring is formed

14) hint: one ring is cleaved

15) Classify the reaction.

5-endo ene-yne cycloisomerization

