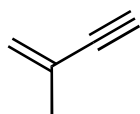


Divergent Synthesis of 17-nor-Cephalotane Diterpenoids through Developed Ynol-diene Cyclization

Sun, Z.; Shu, X.; Ma, F.; Li, A.; Li, Y.; Jin, S.; Wang, Y.; Xiangdong, H.
Angew. Chem. Int. Ed. **2024**, e202407757.

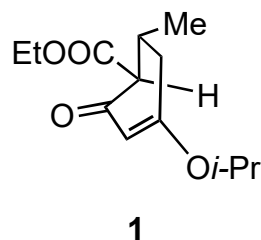


1-7



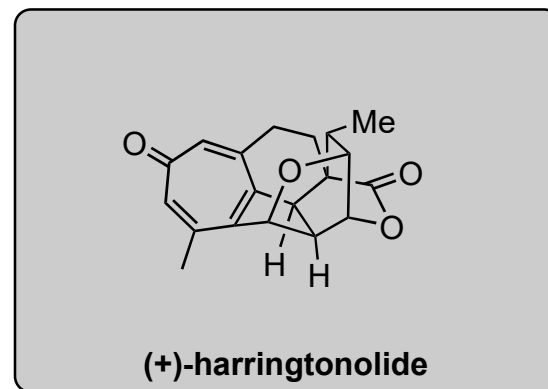
8-11

- 1) *n*-BuLi then Br(CH₂)₂CHO
- 2) TBDPSCI, imidazole
- 3) Cs₂CO₃, NaI, **1**
- 4) LAH then HCl
- 5) Et₃N, TMSOTf then NCS then citric acid
- 6) DMP
- 7) CH(OMe)₃, *p*-TsOH then NaBH₄ then HCl

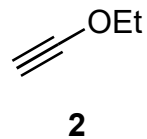
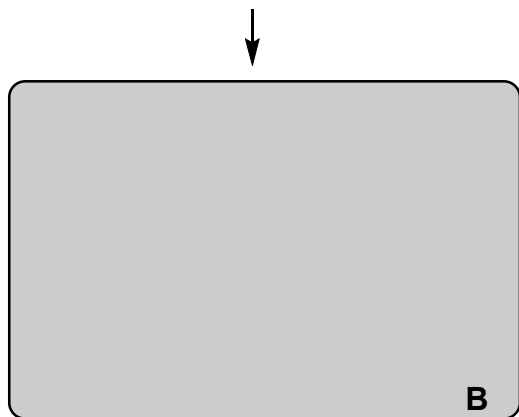


- 8) Cu(OTf)₂ (cat), CH(*i*-Pr)₂OH
- 9) TBAF
- 10) NaClO, KBr (cat.), TEMPO (cat.)
- 11) Co₂(CO)₈

- 3) HINT: Consider the conformation of **1** that I have provided.
- 4) HINT: ¹H NMR shift at 6.6 ppm
- 5) Structure of NCS?
HINT: no ¹H NMR shift below 1 ppm
- 6) Who reported the crystal structure of DMP?



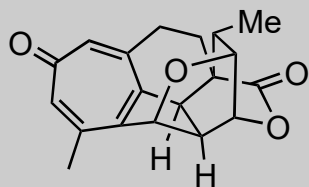
11) Name of the reaction?



12-15

- 12) **2**, *n*-BuLi then **B**
- 13) Ti(*O*-i-Pr)₃ then NaClO, KBr (cat.), TEMPO (cat.)
- 14) *t*-BuNH₂•BH₃
- 15) AgBF₄

13) Name of the ring system formed?



(+)-harringtonolide