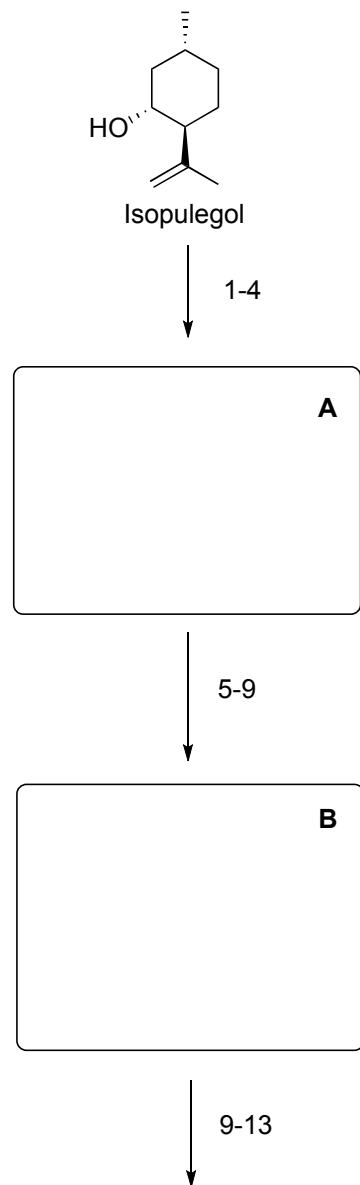


Total Synthesis of 4-Desmethyl-3 α -hydroxy-15-rippertene

Henning, R., Metz, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 1157–1159



- 1) TMSCl, imidazole, DMAP
- 2) Et₂BH, Et₂O
- 3) Et₂Zn, CuCN•2LiBr, then methallyl bromide.
HCl wash
- 4) PCC, DCM

- 5) TMSCHN₂, Me₃Al, DCM, then 1M HCl
- 6) K₂OsO₂(OH)₄ (cat.), NaIO₄, pyridine, THF/H₂O
- 7) *t*-BuOK, *t*-BuOH, THF, 65 °C
- 8) LiHMDS, then allyl iodide

- 9) PdCl₂, p-benzoquinone, DMA/H₂O
- 10) *t*-BuOK, *t*-BuOH, THF, MW, 40 °C, 5 min
- 11) LiAlH₄, Et₂O, -78 °C
- 12) Propargyl bromide, TBAI, 50% aq. KOH/PhMe
- 13) *t*-BuOK, *t*-BuOH, THF, MW, 150°C, 15 min

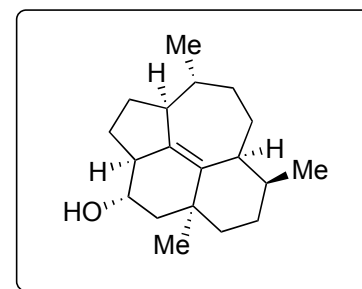
Explain the stereochemical outcome in step 2

What is the reactive species in step 3?

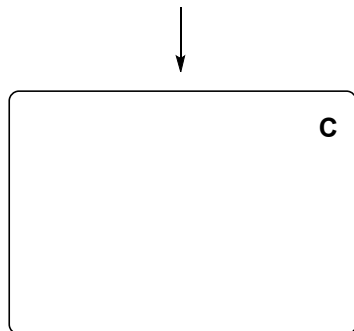
Mechanism of 5. What is the role of AlMe₃?

Name the reaction in step 9

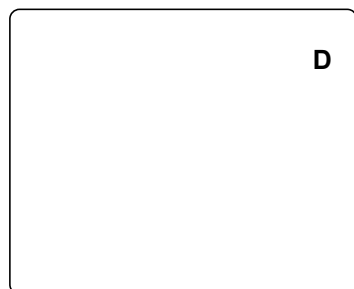
Provide a mechanism for step 13



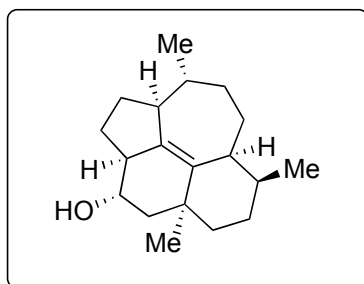
4-Desmethyl-3 α -hydroxy-15-rippertene



↓
14-18



↓
19-23



4-Desmethyl-3 α -hydroxy-15-rippertene

- 14) TsOH, THF, H₂O
- 15) TPAP (cat.), NMO, 4A molsieves
- 16) LiHMDS, THF, -78 °C, then MoOPH
- 17) 50% aq. KOH, THF
- 18) LiAlH₄
- 19) NaIO₄, THF, H₂O

- 20) Me₄NBH(OAc)₃, AcOH, MeCN/THF
- 21) MOMCl, DIPEA, TBAI, -40°C
- 22) *n*-BuLi, THF, then CS₂, then MeI
- 23) Bu₃SnH, AIBN, PhMe, reflux
- 24) 6N HCl, THF

Name the reaction in step 15

Structure of MoOPH? Hint: Molybdenum (VI)

Explain the stereochemical outcome in step 20