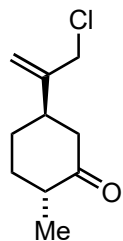


Asymmetric Total Synthesis of (-)-Vinigrol

Long Min, Xiaohong Lin, and Chuang-Chuang Li, *J. Am. Chem. Soc.* **2019**, *141*, 15773-15778



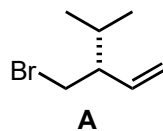
↓ 1-4



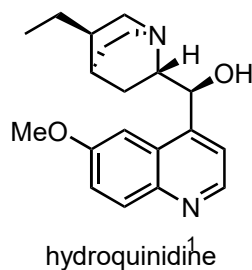
↓ 5-7



- 1) LiHMDS, 2-chloroacetyl chloride
- 2) DIBAL
- 3) **A**, Mg, CuI
- 4) *n*-BuLi, HCHO (gas)



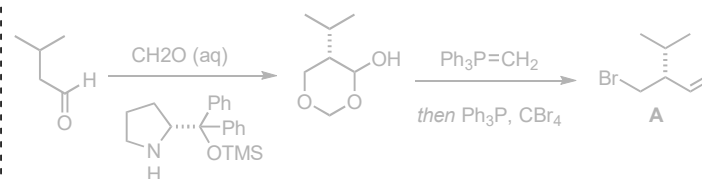
- 5) VO(acac)₂, TBHP
- 6) (Boc)₂O, DMAP
then 2,2,2-trifluoroethanol, AgSbF₆
- 7) hydroquinidine (0.2 equiv.), 170 °C



What is the name of the starting material?

Chloro-dihydrocarvone

Step 3: How would you synthesize the building block **A**?

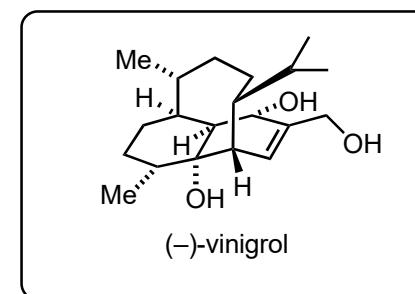


Step 5: Name? Please propose the mechanism.

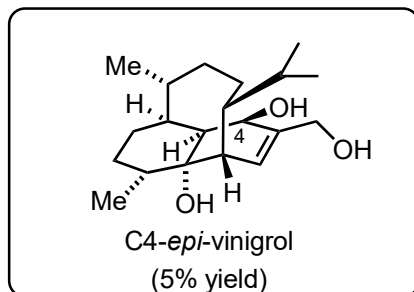
Achmatowicz reaction; see below

Step 7: Please provide a mechanism of the reaction.

see below



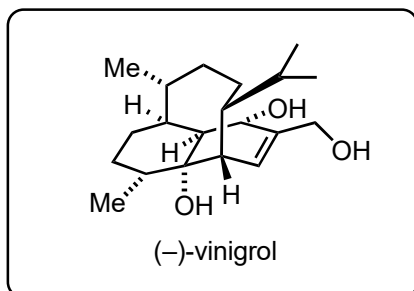
8-13



+



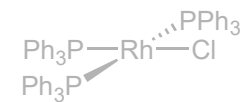
14



- 8) Wilkinson's catalyst, H₂
then BH₃·THF, NaOH, H₂O₂
- 9) IBX, DMSO, 80 °C,
then quenched by NaHCO₃/Na₂S₂O₃
- 10) Sml₂
- 11) LiHDMS, Mander's reagent
- 12) PhSeBr, py
- 13) DIBAL, LDA

14) ¹O₂, hν, NaHCO₃ then PMe₃

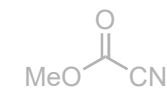
Step 8: What is the structure of the Wilkinson's catalyst?



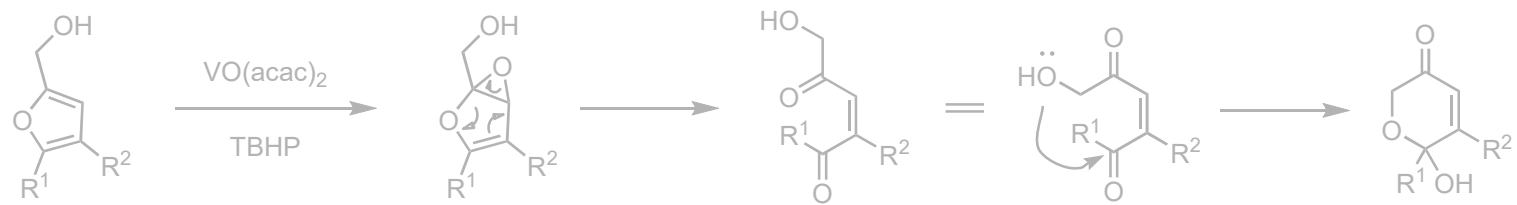
Step 9: Please provide the mechanism of the reaction.

See below

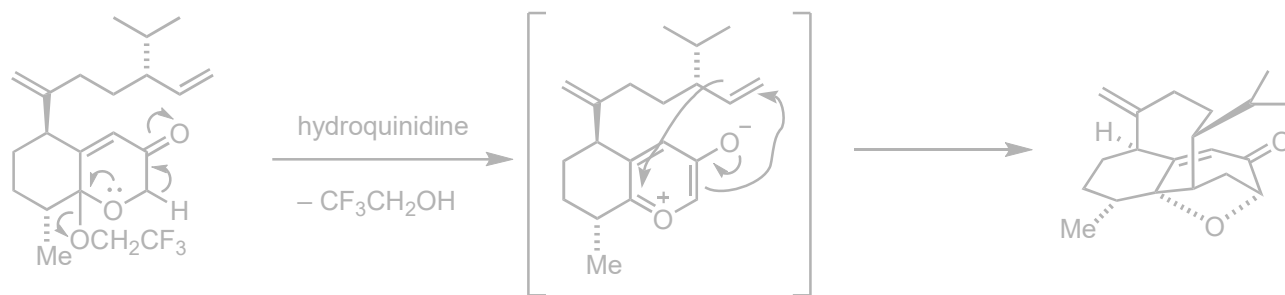
Step 11: What is the structure of the Mander's reagent?



Step 5



Step 7



Step 9

