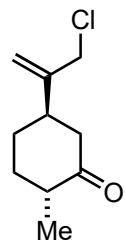
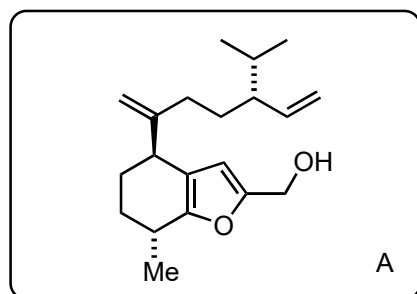


# Asymmetric Total Synthesis of (-)-Vinigrol

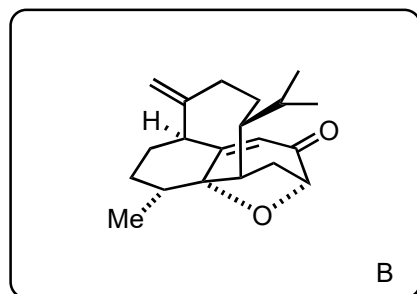
Long Min, Xiaohong Lin, and Chuang-Chuang Li, *J. Am. Chem. Soc.* **2019**, *141*, 15773-15778



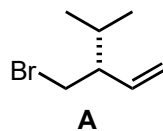
1-4



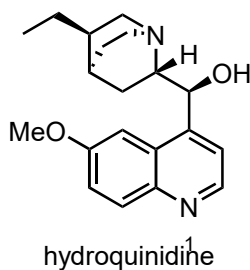
5-7



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



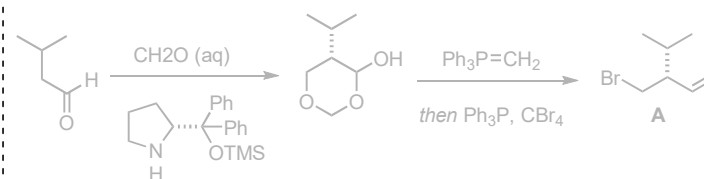
- 5) VO(acac)<sub>2</sub>, TBHP
- 6) (Boc)<sub>2</sub>O, DMAP  
then 2,2,2-trifluoroethanol, AgSbF<sub>6</sub>
- 7) hydroquinidine (0.2 equiv.), 170 °C



What is the name of the starting material?

Chloro-dihydrocarvone

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

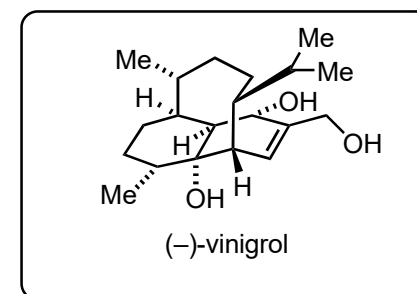


Step 5: Name? Please propose the mechanism.

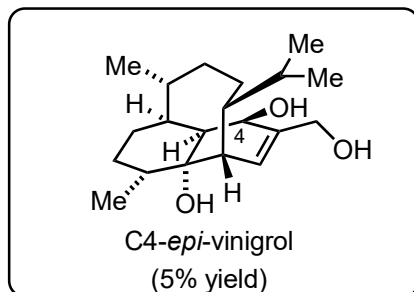
Achmatowicz reaction; see below

Step 7: Please provide a mechanism of the reaction.

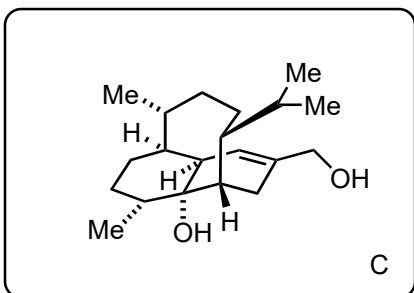
see below



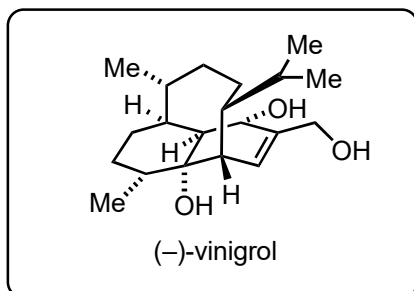
8-13



+



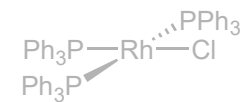
14



- 8) Wilkinson's catalyst, H<sub>2</sub>  
then BH<sub>3</sub>·THF, NaOH, H<sub>2</sub>O<sub>2</sub>
- 9) IBX (5.0 equiv.), DMSO, 80 °C,  
then quenched by NaHCO<sub>3</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>
- 10) SmI<sub>2</sub> (2.2 equiv.)
- 11) LiHDMS, Mander's reagent
- 12) PhSeBr, py
- 13) DIBAL (6.0 equiv.), LDA (1.2 equiv.)

- 14) <sup>1</sup>O<sub>2</sub>, hν, NaHCO<sub>3</sub> then PMe<sub>3</sub>

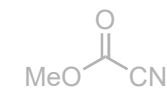
Step 8: What is the structure of the Wilkinson's catalyst?



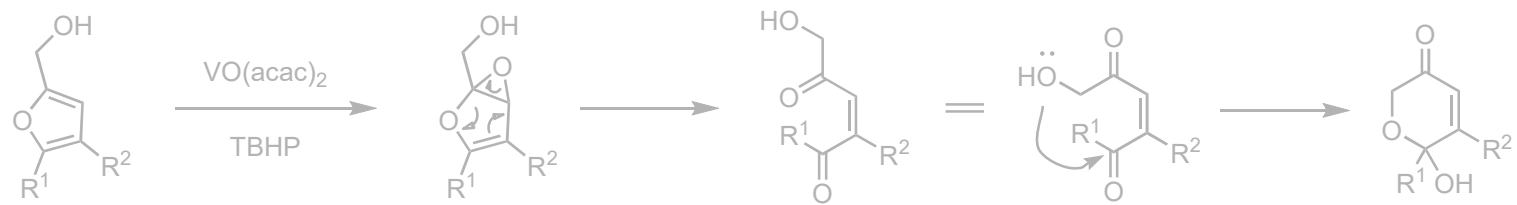
Step 9: Please provide the mechanism of the reaction.

See below

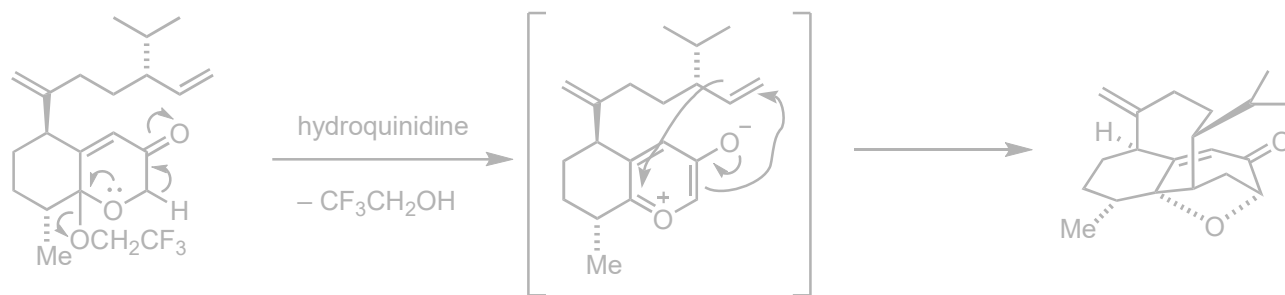
Step 11: What is the structure of the Mander's reagent?



Step 5



Step 7



Step 9

