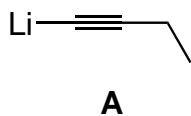
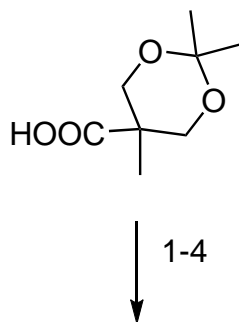


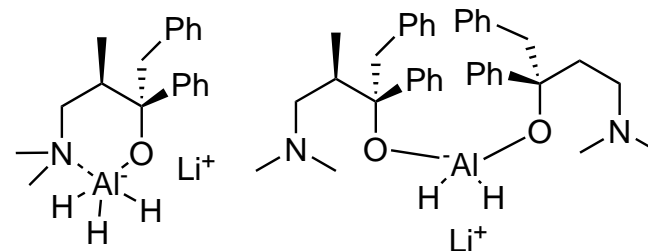
Asymmetric Total Synthesis of (-)-Secodaphniphylline

Jeffrey A. Stafford and Clayton H. Heathcock, *J. Org. Chem.* **1990**, 55, 5433-5434

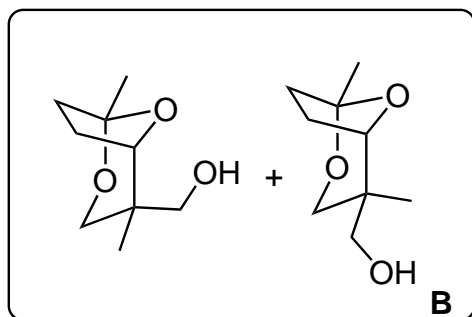


- 1) CDI, MeONHMe, **A**
- 2) LiAlH_4 , Darvon alcohol, -80°C
- 3) K , $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$, -15°C
- 4) HgSO_4 , H_2SO_4 , then NaBH_4 , NaOH

Suggest a reaction mechanism for step 2.
(*S*)-alcohol is obtained

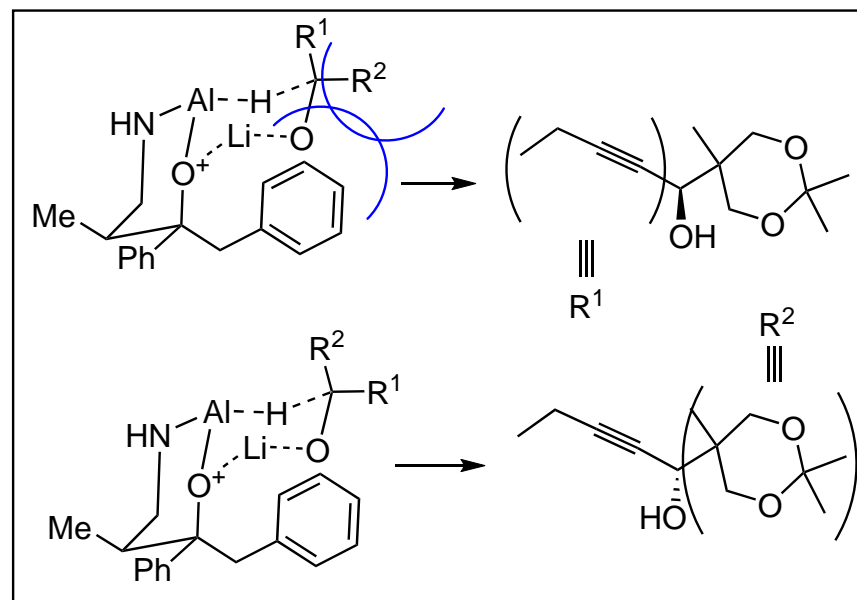


Active species are not well known

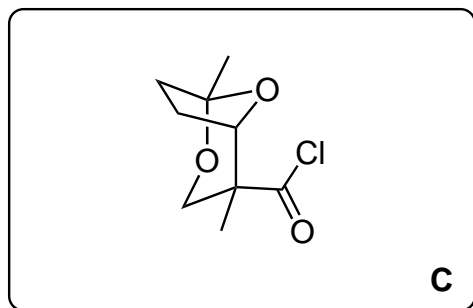


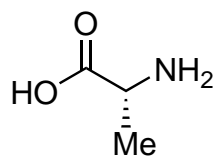
Name the reaction of step 3
Alkyne-Zipper reaction

- 5) RuO_4 , NaIO_4
- 6) CH_2N_2
- 7) KOH
- 8) $(\text{COCl})_2$

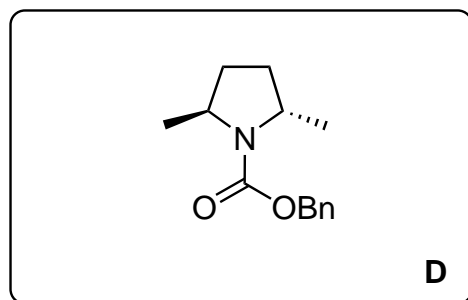


Monomer would lead to (*R*)-alcohol. Mechanism is not clear.

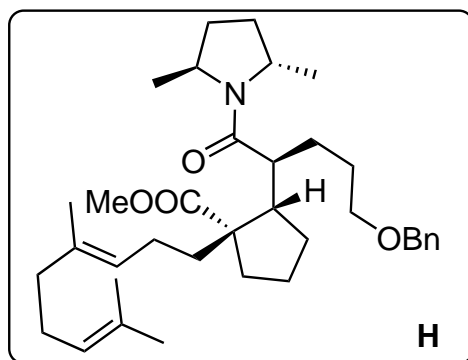




9-14

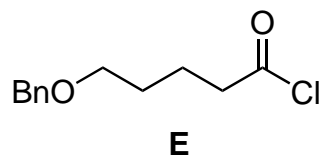


15-18

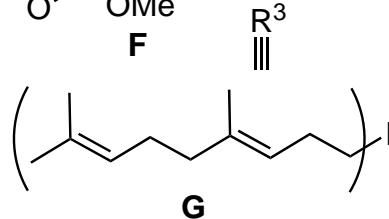
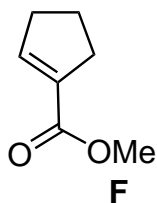


19-20

- 9) LiAlH_4 (2eq)
- 10) NaOH , BnOC(O)Cl
- 11) TsCl
- 12) NaI
- 13) AllylMgCl
- 14) $\text{Hg}(\text{AcO})_2$, then NaBH_4 , NaOH

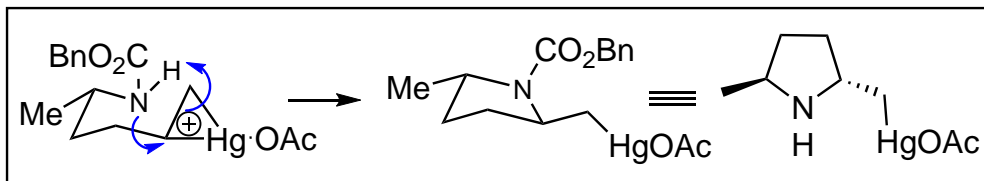


- 15) AcOH , HCl
- 16) NaOH(aq) , extraction
- 17) **E**, NaOH(aq)
- 18) LDA , **F**, **G** in HMPA , -78°C



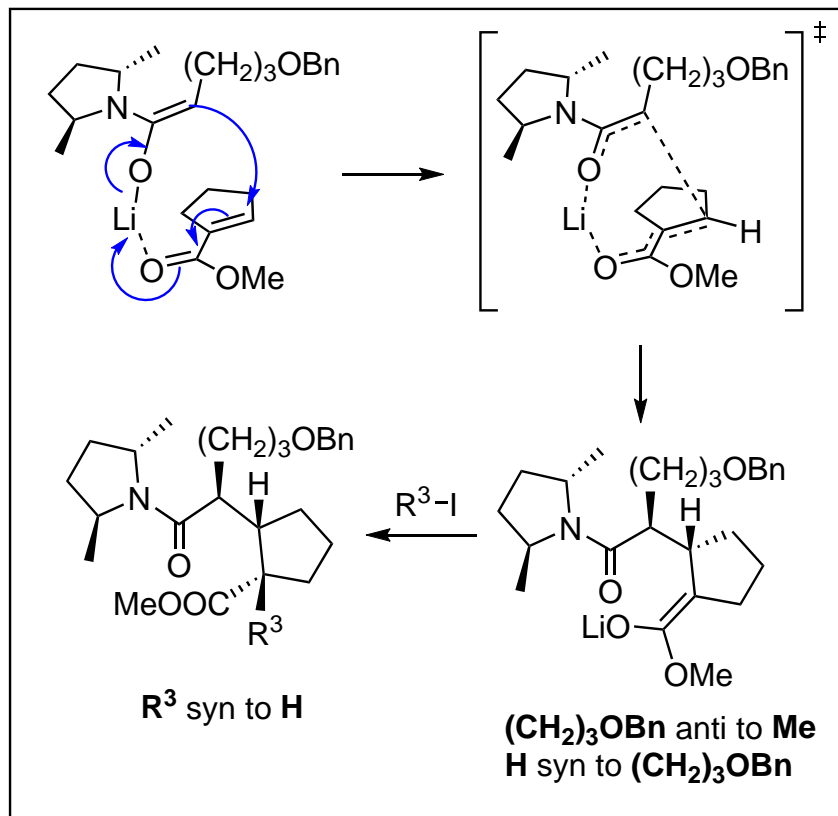
- 19) $i\text{-Bu}_2\text{AlH}$
- 20) KOH 5M, ethylene glycol

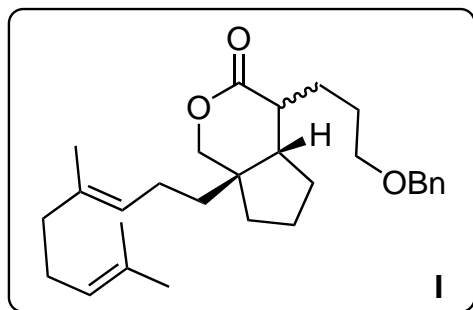
Explain the stereochemistry of step 14



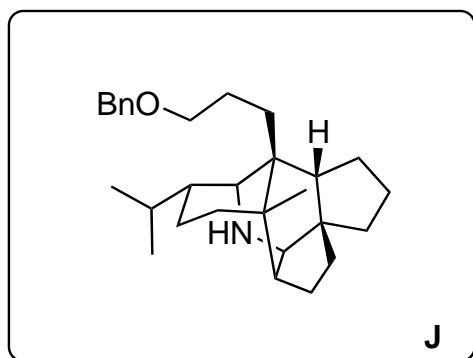
This chair-like intermediate has the lowest steric hindrance.

Explain the stereochemistry of step 18

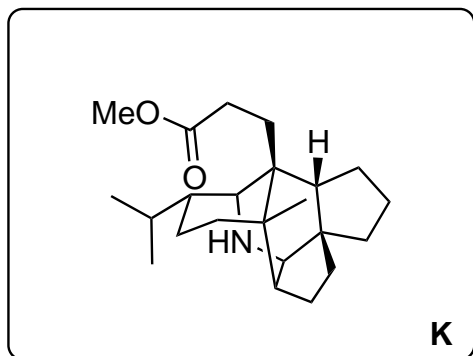




21-24



25-27

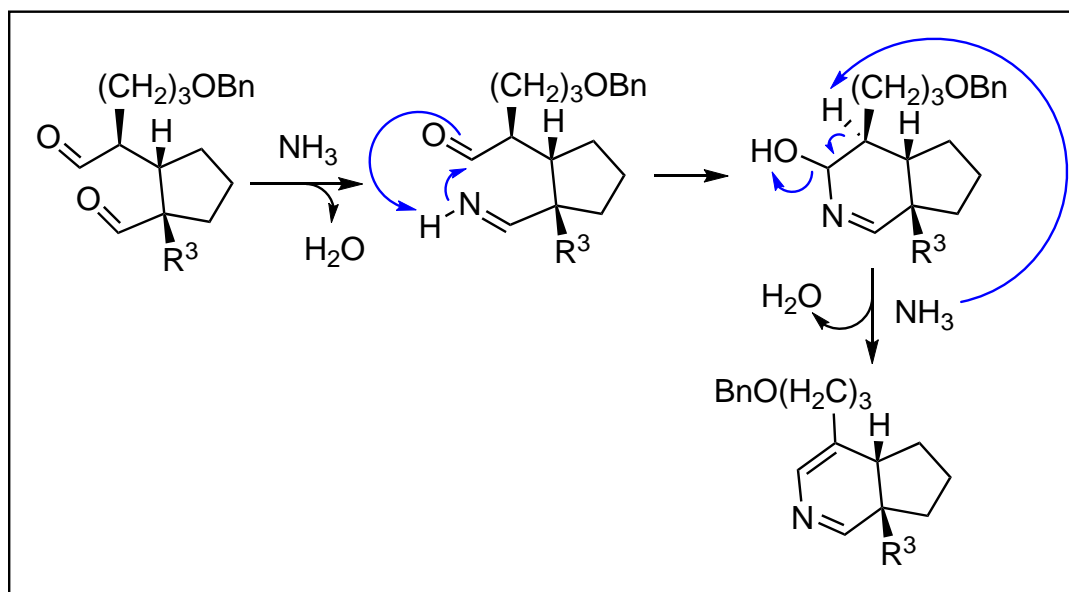


21) LiAlH_4
22) Swern
23) NH_3
24) HOAc

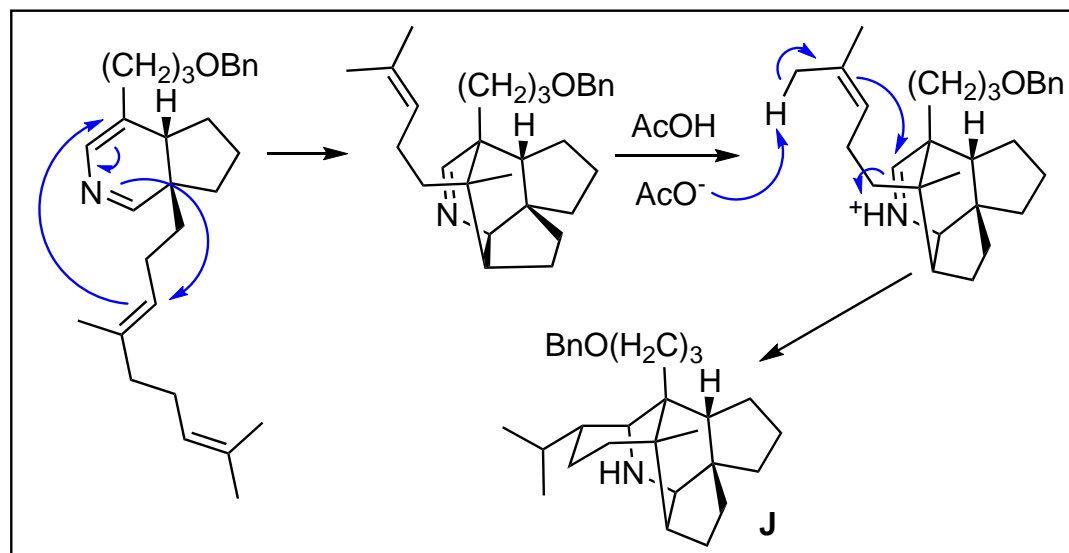
25) H_2/Pd
26) Jones
27) MeOH, H^+

28) $n\text{-BuLi}, \text{C}, -78^\circ\text{C}$
29) $\text{NaCN}, \text{DMSO}, 150^\circ\text{C}$

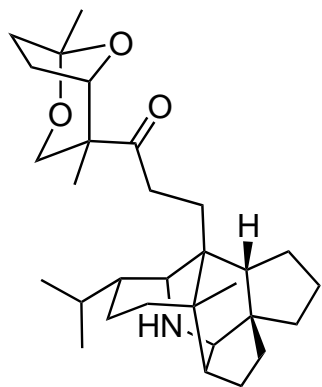
Suggest a reaction mechanism for step 23



Key step (step 24)



Name the reaction of step 29
Krapcho decarboxylation



(-)-Secodaphniphylline