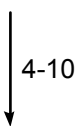
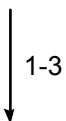
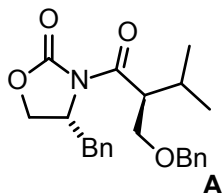


Asymmetric Total Synthesis of *ent*-(–)-*Roseophilin*: Assignment of Absolute Configuration

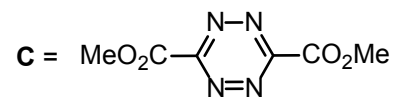
Hong, J.; Boger, D. L., *J. Am. Chem. Soc.* **2001**, *123*, 8515-8519.



- 1) LAH (3 eq.), 0 °C
- 2) TPAP (0.05 eq.), NMO (1.5 eq.), DCM
- 3) CH₃OCHPPH₃, (1.5 eq.), NaHMDS (1.5 eq.)

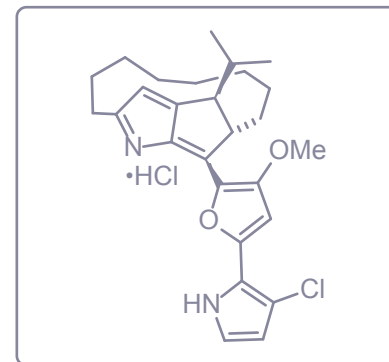
- 5) **C**, 25 °C
- 6) Zn, TFA, 25 °C
- 7) 10 % Pd-C, H₂, 1 atm
- 8) CSA (10 mol %), benzene

How would you prepare **A**?

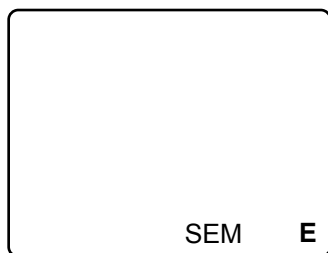


Classify the reaction in step 5.

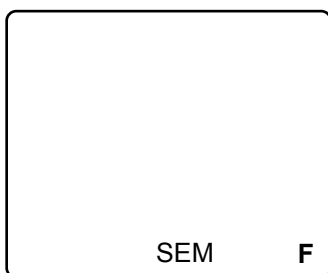
Step 5 and 6: Mechanism?



9-14



15-20



21-25

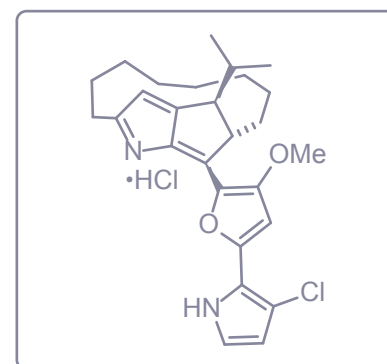


- 9) SEMCl (3 eq.)
- 10) LiI, DMF, 130 °C
- 11) ethyl chloroformate (2.5 eq.), Et₃N,
then NaBH₄ (5 eq.)
- 12) MnO₂ (4 eq.), DCM, 25 °C
- 13) BnO(CH₂)₄PPh₃Br (6 eq.), NaHMDS (6 eq.)
- 14) 10 % Pd-C, H₂, 1 atm

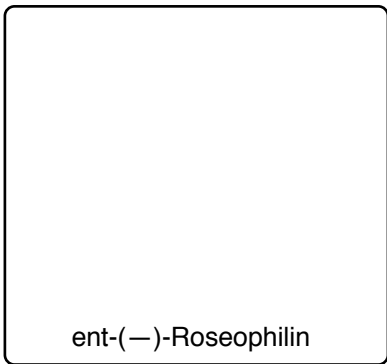
- 15) TPAP (0.1 eq.), NMO (1.5 eq.), DCM
- 16) CH₃PPh₃Br (2.5 eq.), NaHMDS (2.5 eq.)
- 17) aq. LiOH (1M)
- 18) TMSCHN₂
- 19) TPAP (0.1 eq.), NMO (1.5 eq.), DCM
- 20) CH₂CH(CH₂)₂PPh₃Br (2.5 eq.),
NaHMDS (2.5 eq.)

- 21) Grubbs I (10 mol %), DCM, 40 °C
- 22) NaOH, EtOH, H₂O, reflux
- 23) (EtO)₂P(O)Cl (7 eq.), PhSeNa (3.5 eq.)
- 24) Bu₃SnH, AIBN
- 25) PtO₂, H₂, 25 °C

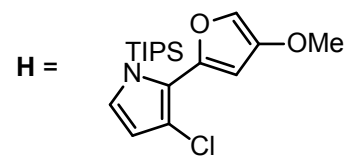
Step 23 and 24: Mechanism?



↓
26, 27



26) **H**, *n*-BuLi, CeCl₃, -55 °C, then **G**
27) Bu₄NF, aq. HCl



How would you prepare **H**?

