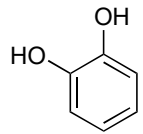
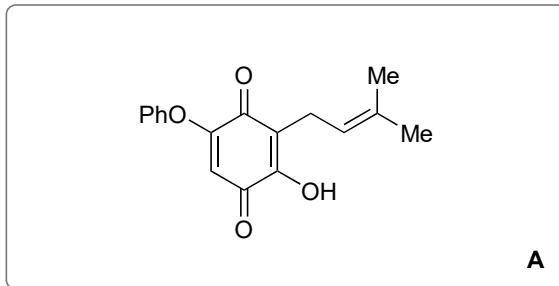


Enantioselective Synthesis of Azamerone

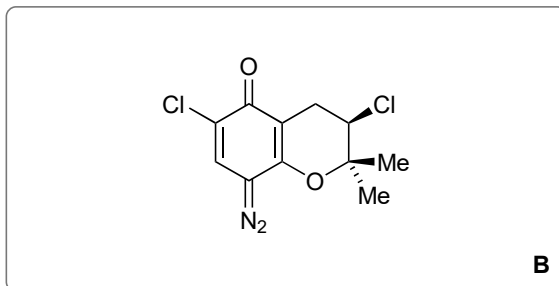
Matthew L. Landry, Grace M. McKenna, and Noah Z. Burns
J. Am. Chem. Soc. **2019**, *141*, 2867-2871.



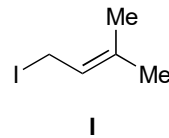
1 - 4



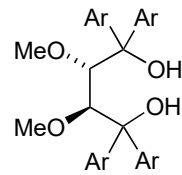
5 - 8



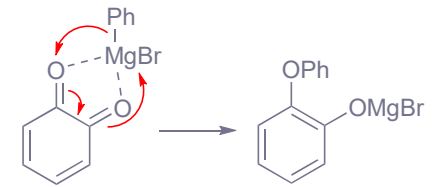
- 1) NaIO₃, MeOH, 60 °C
- 2) PhMgBr
- 3) BBr₃, then air, aq. CuSO₄
- 4) Proton Sponge, **I**



- 5) CITi(O*i*-Pr)₃, **II**, *t*-BuOCl, quinoline
- 6) aq. HClO₄
- 7) (COCl)₂, DMF
- 8) TsNHNH₂, then NaOH

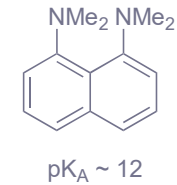


II
Ar = 2-naphthyl



2) *hint*: formal etherification

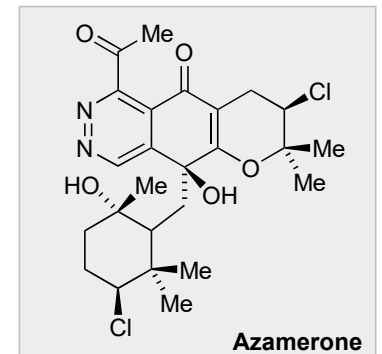
4) Structure and pK_A of Proton Sponge?



pK_A ~ 12

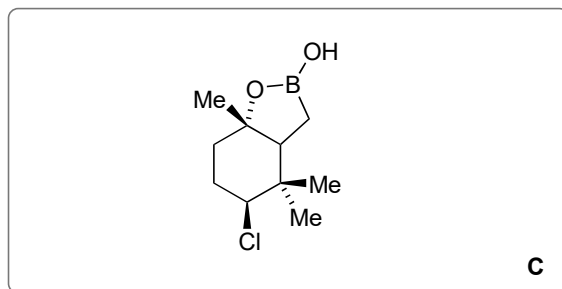
5) Please provide a mechanism and name the ligand class.

TADDOL

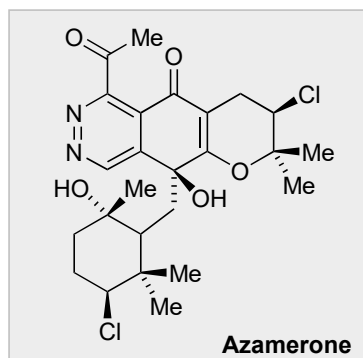


geranyl acetate

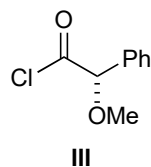
9 - 14



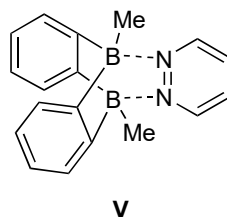
15 - 19



- 9) $\text{Hg}(\text{OTFA})_2$, then aq. NaCl, then Cl_2 , LiCl, pyridine
- 10) K_2CO_3 , MeOH
- 11) **III**, pyridine
- 12) K_2CO_3 , MeOH
- 13) Tf_2O , 2,6-lutidine, then DBU
- 14) $\text{BH}_3\text{-SMe}_2$

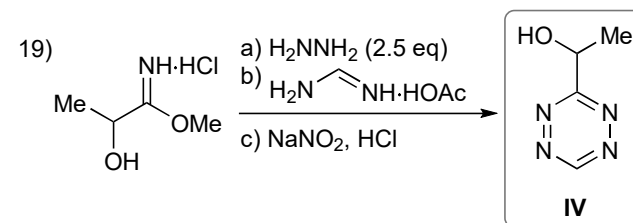


- 15) **B**, SPhos-Pd G3, K_3PO_4
- 16) SPhos-Pd G3, K_2CO_3 , *i*-PrOH
- 17) TBSOTf, DIPEA (excess), then NaOH
- 18) $\text{PhI}(\text{OTFA})_2$, MeCN / H_2O
- 19) **IV**, **V**, 110 °C, air, then HCl



- 11) What chiral acid is **III** derived from?
Mandelic acid

- 14) Name the heterocycle in **C**.
1,2-oxaborolan-2-ol



- 19) Name the heterocycle in **IV** and classify the reaction(s).
1,2,4,5-tetrazine
[4+2]-cycloaddition, cycloreversion

Name the heterocycle in Azamerone.
Pyridazine

