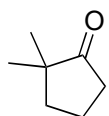
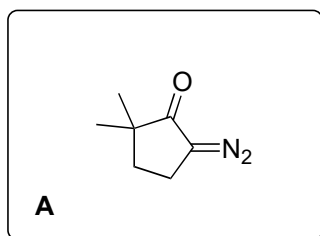


Enantioselective Total Synthesis of (+)-Psiguadial B

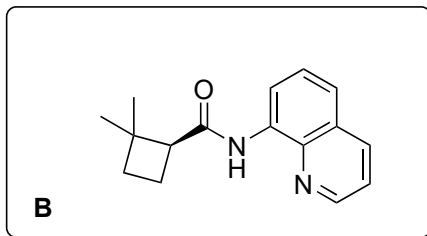
L. M. Chapman, J. C. Beck, L. Wu, S. E. Reisman, *J. Am. Chem. Soc.* **2016**, *138*, 9803-9806.



1) ethyl formate, NaH
2) TsN₃, NEt₃

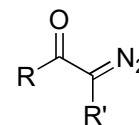


3) $h\nu$ (254 nm)
1, 2

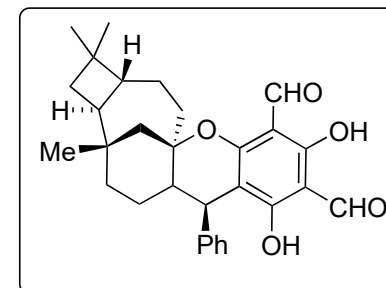
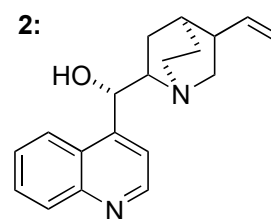
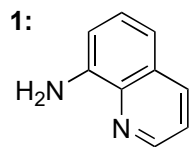


provide a Mechanism for step 2

Name the reaction in step 3 (first part), provide the two competing mechanisms on a general substrate, name every heterocycle and explain which mechanism is taking place in step 3

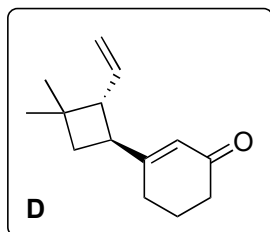
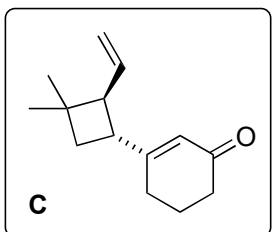


general substrate

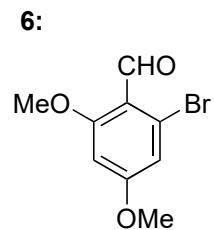
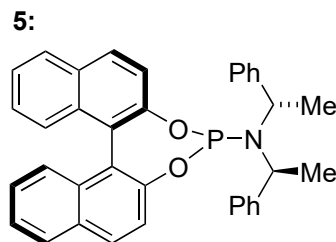
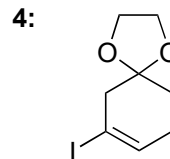
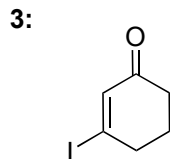
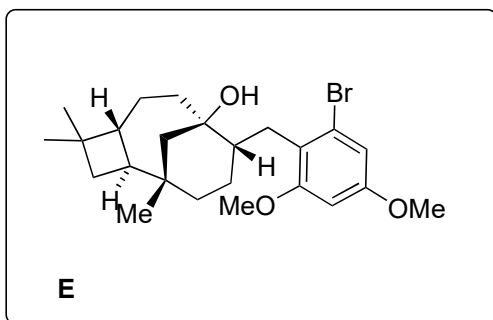


4) Pd(OAc)₂,
Ag₂CO₃, **3**
5) DBU
6) ethylene glycol
CH(OMe)₃,
p-TsOH
7) Cp₂ZrHCl
then PhP=CH₂
then 5 M HCl

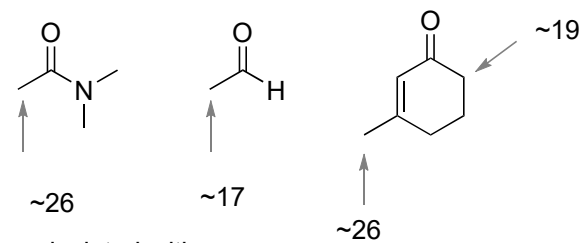
4') Pd(OAc)₂,
Ag₂CO₃, **4**
5') Cp₂ZrHCl
6') KOH, MeOH
7') PhP=CH₂
then 5 M HCl



8) CuTC, AlMe₃, **5**
9) KOH, **6**
10) vinylLi (2:1 d.r.)
11) HG-II, 1,4-BQ
12) Crabtree's cat,
H₂ (34 bar)



pK_a



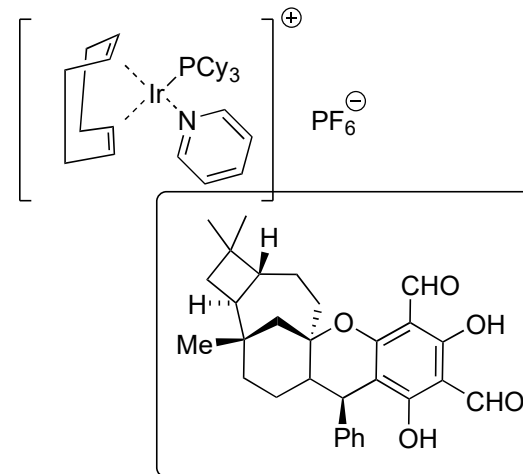
calculated with
<https://ace.chem.illinois.edu/ace/public/pKa.jsp>

C and **D** are enantiomers, explain which sequence 4-7 or 4'-7' forms the desired enantiomer

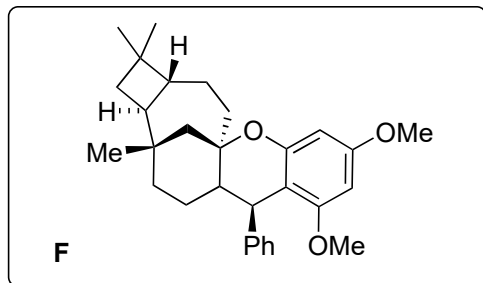
8) ligand class? phosphoramidite

10) Hint: continue with the *S*-enantiomer

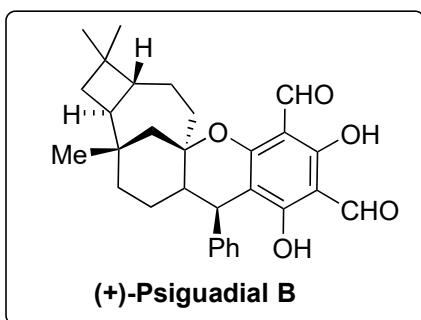
12) Structure of Crabtree's catalyst?



- 13) CuI, 2,2'-bipy, KOtBu
14) DDQ, EtO(CH₂)₂OH
15) Ph₂Cu(CN)Li₂,
BF₃ · OEt

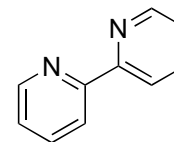


- 16) pyr · HCl
17) MeOCHCl₂, TiCl₄



13) Name the reaction and draw the ligand

Ullmann reaction

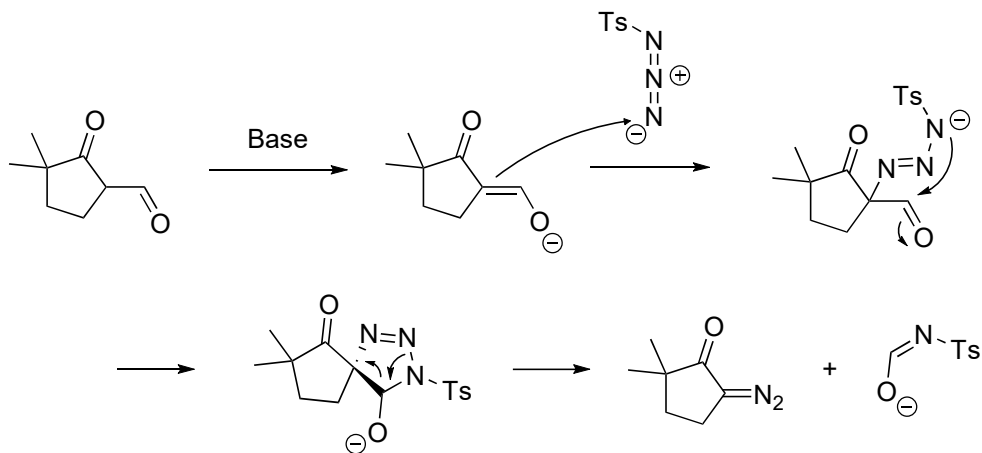


17) Name the reaction

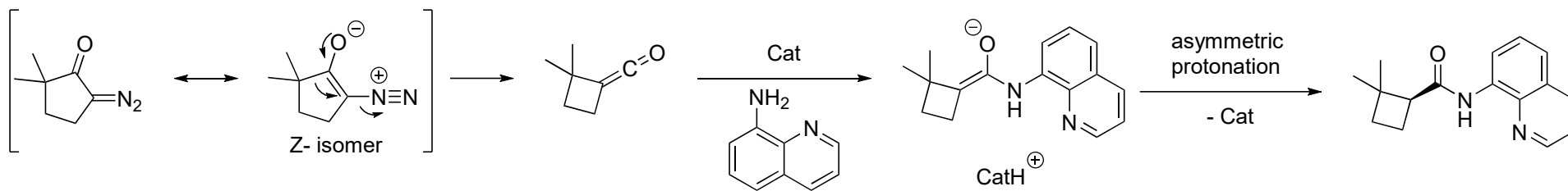
Rieche formylation

Mechanism for step 2

deformylative Regitz diazo transfer



Wolff rearrangement
concerted mechanism



stepwise mechanism

