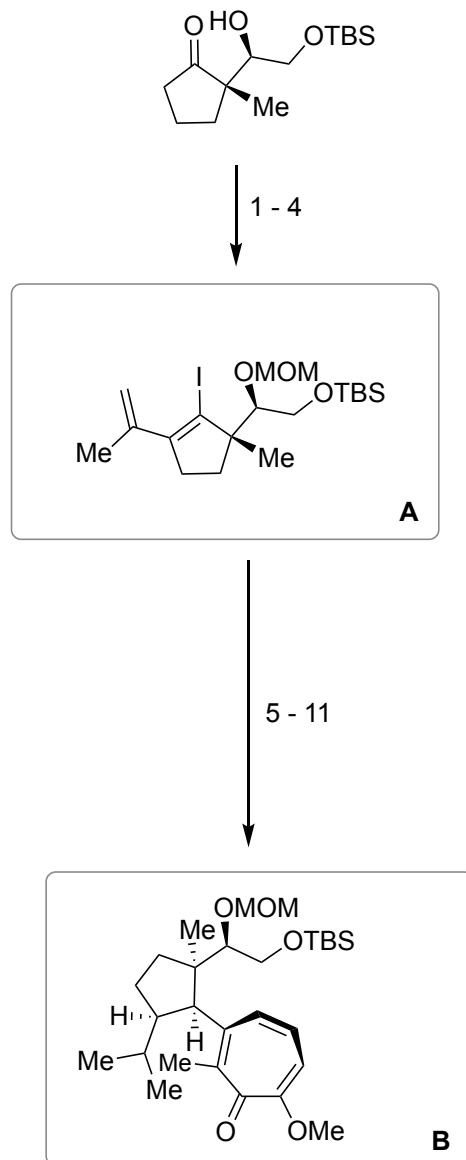


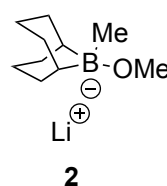
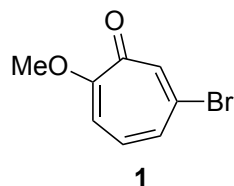
Total Synthesis of Gukulenin B via Sequential Tropolone Functionalizations

K. C. Nicolaou, Ruocheng Yu, Zhaoyong Lu, and Fernando G. Alvarez *J. Am. Chem. Soc.* **2022**, *144*, 5190-5196.

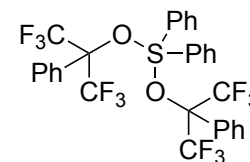


- 1) MOMCl
- 2) TsNHNH₂, MgSO₄
- 3) *n*-BuLi then acetone then *n*-BuLi then I₂
- 4) Martin sulfurane

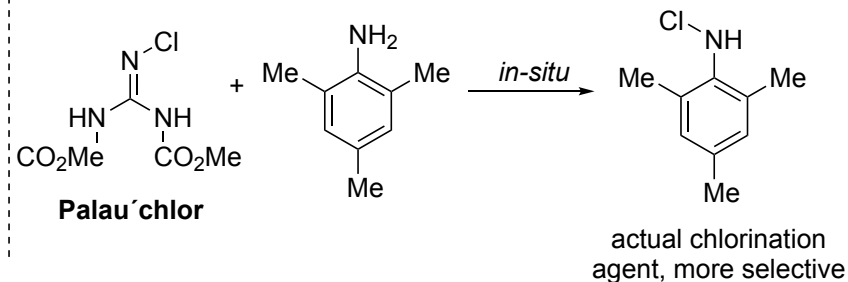
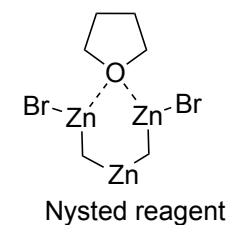
- 5) *t*-BuLi, ZnCl₂ then **1**, Pd₂(dba)₃, RuPhos, LiCl
- 6) OsO₄, NaIO₄, 2,6-lutidine
- 7) H₂, Pd(OH)₂/C
- 8) Nysted reagent,
- 9) H₂, Crabtree's catalyst BAr_F analogue
- 10) Palau'chlor,
- 11) **2**, SPhos-Pd-G4



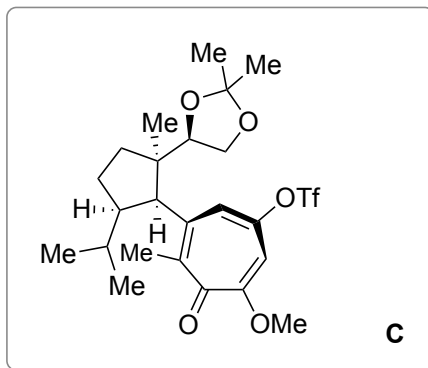
- 2) + 3) Name of the reaction?
Shapiro reaction
- 4) Martin sulfurane structure?



- 5) Name of the reaction?
Negishi coupling
- 7) Name of the catalyst?
Pearlman's catalyst
- 8) Structure of Nysted reagent?
- 9) Structure of Crabtree's catalyst
[Ir(PCy₃)(py)(cod)]PF₆
- 10) Structure of Palau'chlor?
Role of the 2,4,6-trimethylaniline?

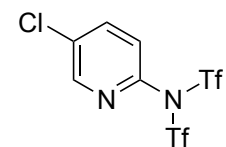


12-16



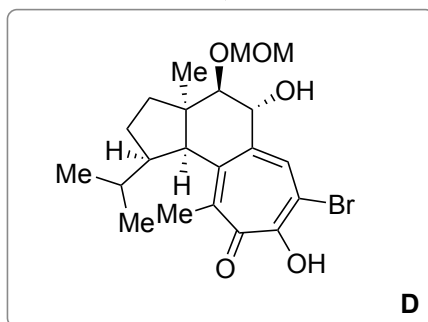
- 12) HCl, MeOH
- 13) TsOH, Me₂C(OMe)₂
- 14) [Ir(cod)(OMe)]₂, dtbpy, B₂pin₂
- 15) NaBO₃
- 16) Comins' reagent, Et₃N

16) Structure of Comins' reagent?

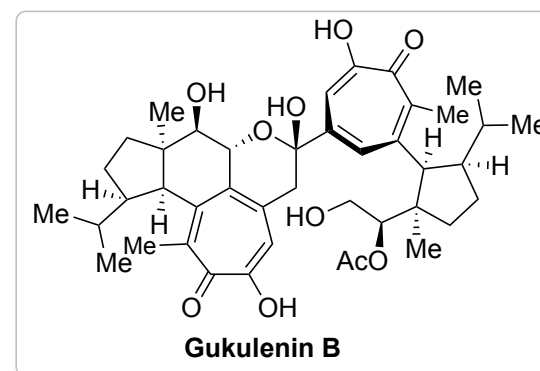
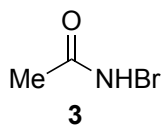


B

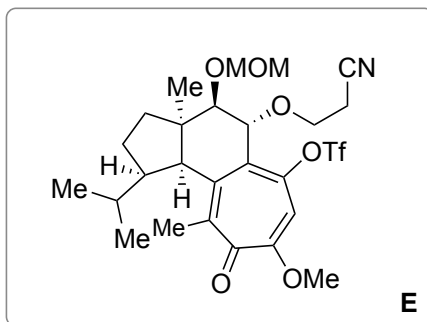
17-20



- 17) HCl, MeOH
- 18) DMP
- 19) MgBr₂, THF, reflux
- 20) **3**

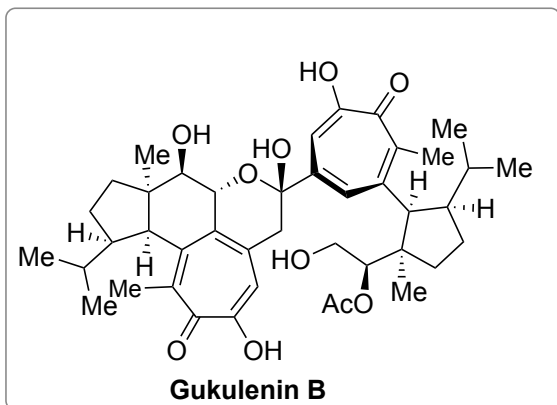


21-25

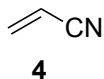


C

26-31



- 21) NaOBn (excess)
- 22) MeI
- 23) **4**, Cs₂CO₃
- 24) 1,4-cyclohexadiene, Pd/C
- 25) Et₃N, Comins' reagent



- 21) *hint* - 4 things happen
2x deprotonation - Br elimination - OBn addition
- 22) *hint* - selective mono-methylation

- 26) **5**, Pd(PPh₃)₄, CuDPP
- 27) **E**, Pd(Pt-Bu₃), *n*-Bu₃SnF
- 28) KHMDS
- 29) Me₂BBr, DIPEA
- 30) Yb(OTf)₃, MeC(OMe)₃ then H₂O
- 31) MgI₂

