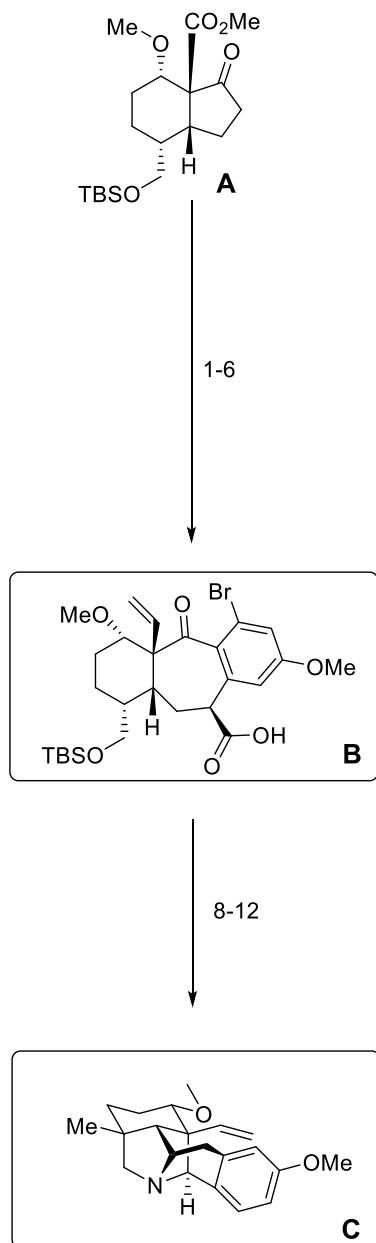


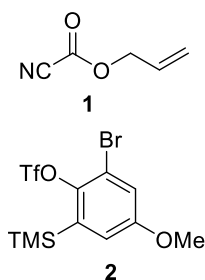
A Benzyne-Insertion Approach to Hetsisine-Type Diterpenoid Alkaloids: Synthesis of Cossonidine (Davisine)

Kevin G. M. Kou, Jason J. Pflueger, Toshihiro Kiho, Louis C. Morrill, Ethan L. Fisher, Kyle Clagg, Terry P. Lebold, Jessica K. Kisunzu, and Richmond Sarpong*

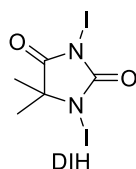
JACS, 2018, 140, 8105



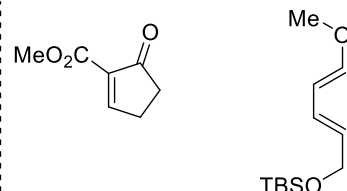
- 1) LAH
- 2) TPAP, NMO
- 3) Rh(PPh₃)₃Cl, TMSCH₂N₂, PPh₃, iPrOH
- 4) LiHMDS, then **1**
- 5) **2**, MeCN, CsF, 70 °C
- 6) Pd(PPh₃)₄, PhSiH₃



- 8) *hν*, DIH
- 9) TBAF
- 10) TEMPO, PhI(OAc)₂, NH₄OAc
- 11) LiHMDS, then MeI



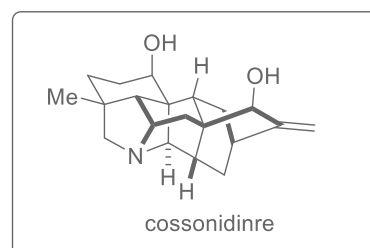
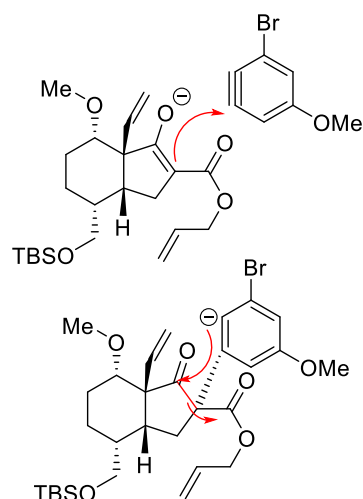
how could you synthesis A



name step 2
Ley Oxidation

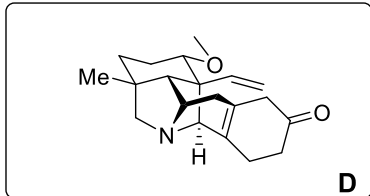
what is the alternative method for step 3
Wittig reaction (gives very poor yield)

name the intermediate generated by compound **2** of step 5, draw the mechanism of step 5
Benzyne intermediate

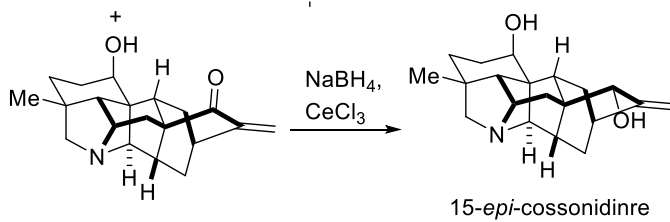
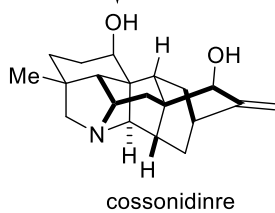


C

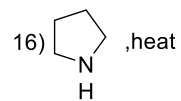
12-15



16-22



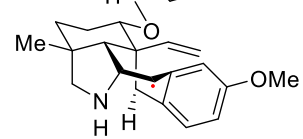
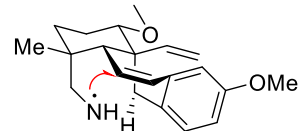
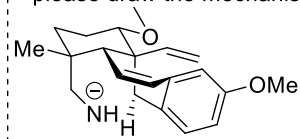
- 12) $\text{Co}_2\text{B}, \text{BH}_3 \cdot t\text{BuNH}_2, \text{MeOH}, \text{heat}$
- 13) LAH
- 14) $n\text{-BuLi}, h\nu$
- 15) $\text{Na}, \text{NH}_3(\text{l}), \text{then HCl}$



- 17) HBr, AcOH
- 18) $\text{K}_2\text{CO}_3, \text{MeOH}$
- 19) $\text{Ph}_3\text{P}=\text{CH}_2$
- 20) $\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf}, \text{ABNO}, \text{NMI}, \text{MeO}^i\text{ppy}, \text{air}, 50^\circ\text{C}$
- 21) LAH
- 22) SeO_2

hint: That the author used sequence step 12-13 is because a global reduction method failed by LAH

step 14 is a photoredox reaction, please draw the mechanism



Name the reaction that would take place after addition of pyrrolidine
Intramolecular Diels Alder addition

using step 17-18 sequence is because direct attempt failed.

what is the function of step 20-21 sequence?

correct the configuration of equatorial OH