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

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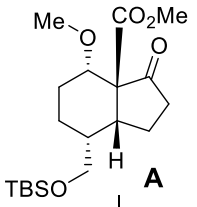



**A**

1-6

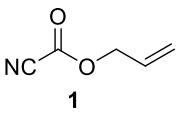
**B**

8-12

**C**

1) LAH
2) TPAP, NMO
3) $Rh(PPh_3)_3Cl$, $TMSCH_2N_2$, $PPh_3$, iPrOH
4) LiHMDS, then **1**
5) **2,** MeCN, CsF, 70 °C
6) $Pd(PPh_3)_4$, $PhSiH_3$

8) *hv,* DIH
9) TBAF
10) TEMPO, $PhI(OAc)_2$, $NH_4OAc$
11) LiHMDS, then MeI



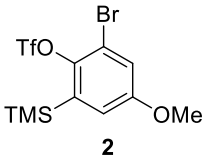

**1**

how could you synthesis A

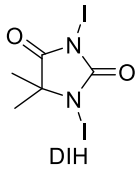
name step 2

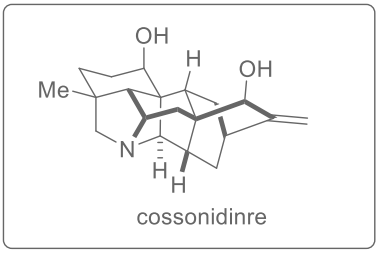
what is the alternative method for step 3

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




**2**



**C**

12-15

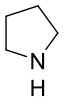
12) $Co_2B,BH_3{\cdot}tBuNH_2$, MeOH ,heat
13) LAH
14) *n*-BuLi, hv
15) Na, $NH_3$(l), then HCl

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

step 14 is a photoredox reaction, please draw the mechanism

**D**

Name the reaction that would take place after addition of pyrrolidine

16)  ,heat

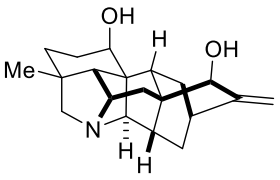
using step 17-18 sequence is because direct attempt failed.

17) HBr, AcOH
18) $K_2CO_3$, MeOH

16-22

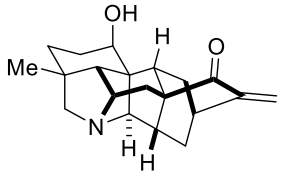
19) $Ph_3P{=}$
20) $Cu(CH_3CN)_4OTf$, ABNO, NMI, $^{MeO}$bpy air, 50 °C
21) LAH
22) $SeO_2$

what is the function of step 20-21 sequence?

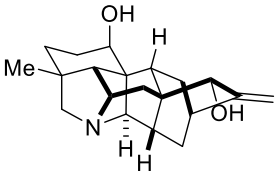


cossonidinre

+



$NaBH_4$, $CeCl_3$



15-*epi*-cossonidinre