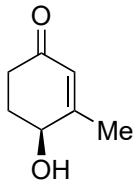
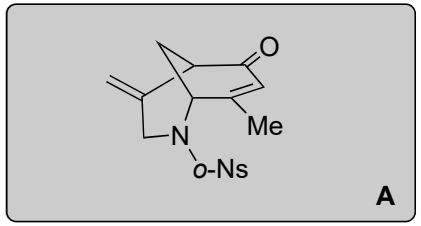
# Total Synthesis of Daphenylline, Daphnipaxianine A, and Himalenine D

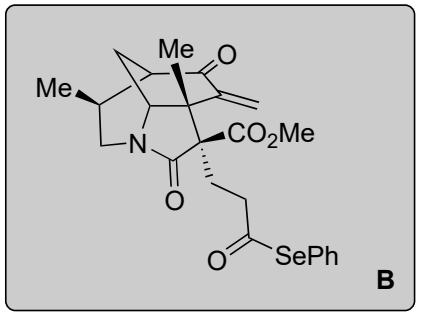
Y. Chen, W. Zhang, L. Ren, J. Li, A. Li, *Angew. Chem. Int.* **2018** *130*, 964–968.



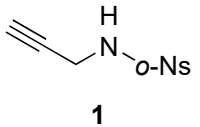

1 – 3



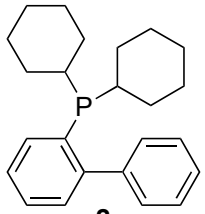

4 – 9




1) **1**, $PPh_3$, DIAD
2) TBDPSOTf, 2,6-lutidine
3) $AgNTf_2$, 2,4,6-tri-*tert*-butylpyrimidine, **2**

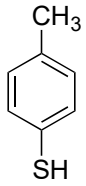



**1**

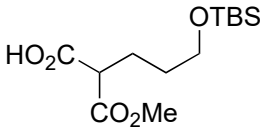



**2**

4) $H_2$, $[Rh(cod)Cl]_2$, $PPh_3$, $AgBF_4$
5) **3**, $K_2CO_3$
6) **4**, EDC, HOBt, $Et_3N$
7) DBU, $(CH_2O)n$
8) $CrO_3$, $H_2SO_4$
9) $SOCl_2$ *then* PhSeH, py




**3**

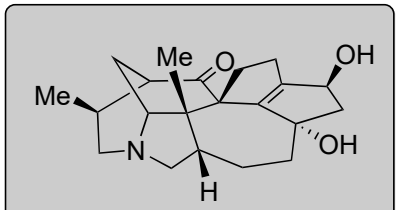



**4**

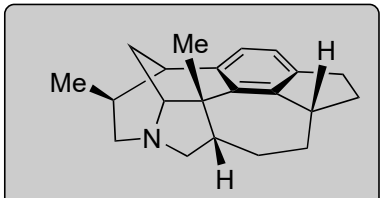
3) Name the ring closure using Baldwin's rules. *6-exo-dig*

3) What is the role of 2,4,6-tri-tert-butylpyrimidine? It helps prevent the acid-promoted desilyation of the reactant.

8) Name the reaction. Jones oxidation



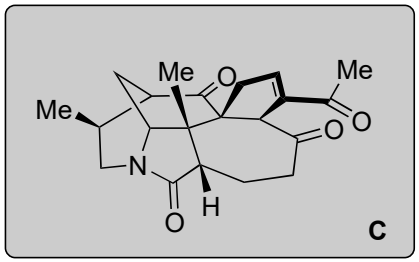

**himalenine D**




**daphenylline**

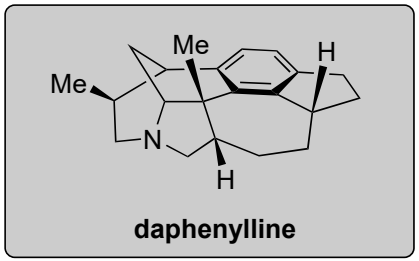
**B**

10 – 12



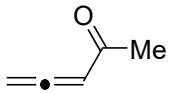

**C**

13 – 16



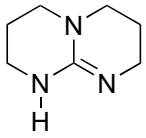

**daphenylline**

10) UV light
11) **5**, DPPF
12) LiI, MeCN/DMSO




**5**

13) **6**
14) $Et_3SiH$, TFA
15) Lawesson's reagent
16) Raney Ni

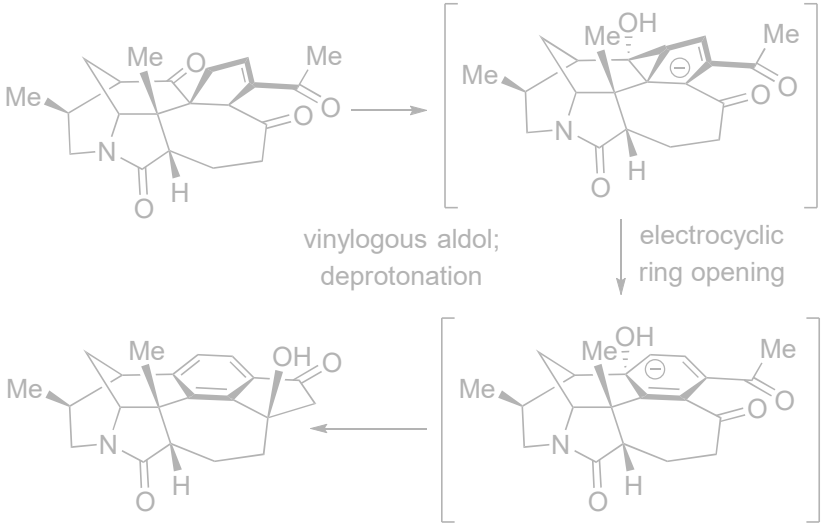



**6**

10) *Hint: generates a unsaturated diketone*
11) Classify the reaction as a cycloaddition. [3+2] cycloaddition

13) Describe a mechanism for this step. Hint: *ring-expansion*, *aromatization, and ring-closure* occur under these conditions.

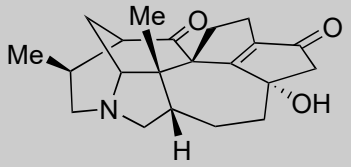
The mechanistic pathway of step 13 described by Li et al.:



**C**

17 – 18

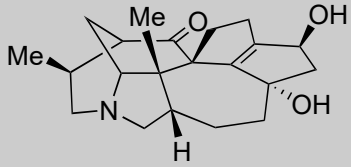
17) $IrCl(CO)(PPH_3)_2$, $(Me_2HSi)_2O$,
*then* $NaBH(OAc)_3$
18) DBU, LiCl




**daphnipaxianine A**

19

19) $NaBH_4$, $CeCl_3$




**himalenine D**