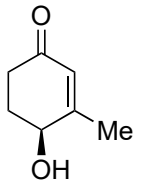
Total Synthesis of Daphenylline, Daphnipaxianine A, and Himalenine D

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



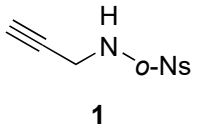
1 – 3

A

4 – 9

B

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



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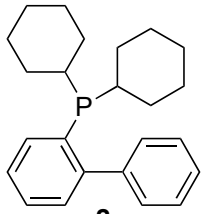
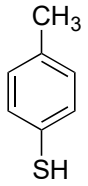


2

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



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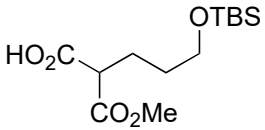

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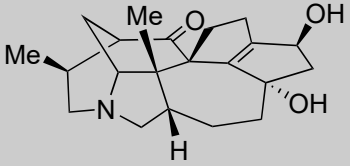
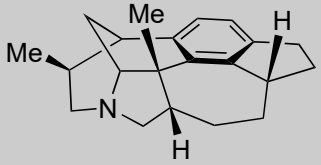
3) Name the ring closure using Baldwin's rules.

3) What is the role of 2,4,6-tri-tert-butylpyrimidine?

8) Name the reaction.



himalenine D



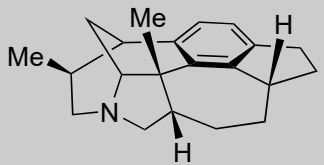
daphenylline

B

10 – 12

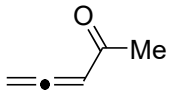
C

13 – 16



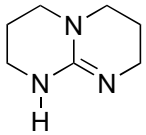
daphenylline

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.

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

C

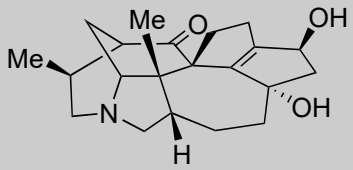
17 – 18

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