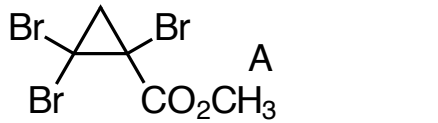
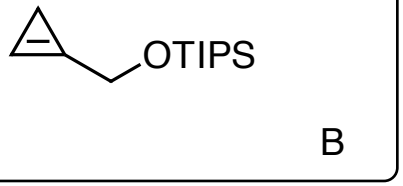
Synthesis Challenge # 36

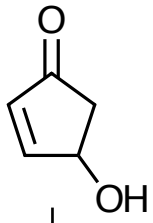
"Total Synthesis, Relay Synthesis, and Structural Confirmation of the C18-Norditerpenoid Alkaloid Neofinaconitine",
Y. Shi, J. T. Wilmot, L. U. Nordstrøm, D. S. Tan, D. Y. Gin, *J. Am. Chem. Soc.* **2013**, *135*, 14313–14320
11.06.2015



1-3

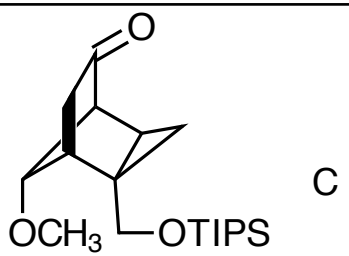
1) Dibal
2) TIPSCl
3) CH_3Li





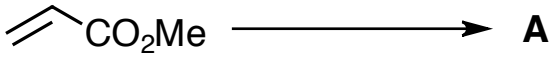
4) CH_3I/Ag_2O
5) TBSOTf/Et_3N/**B**
6) NaOH

4-6

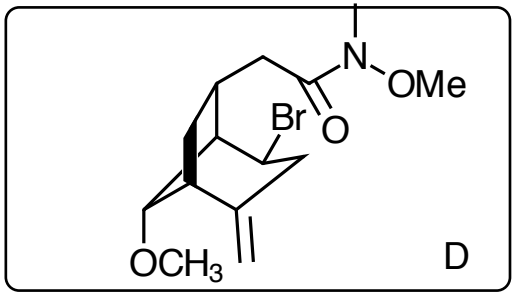


How would you prepare compund A

1) Br_2
2) NEt_3
3) $CHBr_3$, aq. NaOH, Et_3BnNCl



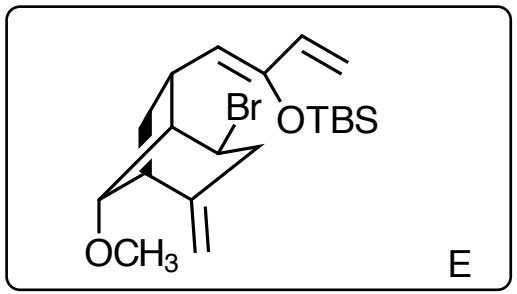
7-10

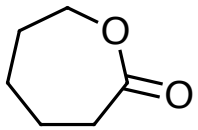


7) **I**, KHMDS
8) H_2/Pd-C
9) **II**, $AlCl_3$
10) TBAF; HBr

11-12

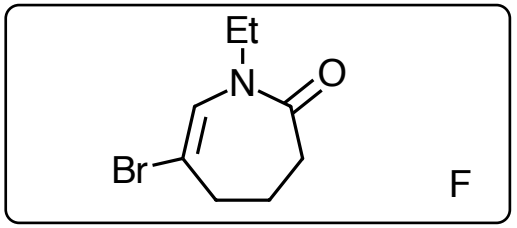
11) vinylMgBr
12) TBSOTf

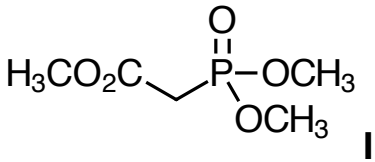




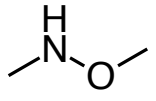
14-16

13) $EtNH_2$
14) SO_3*py, Et_3N, CH_2Cl_2/DMSO
15) *p*-TsOH
16) Br_2, Et_3N



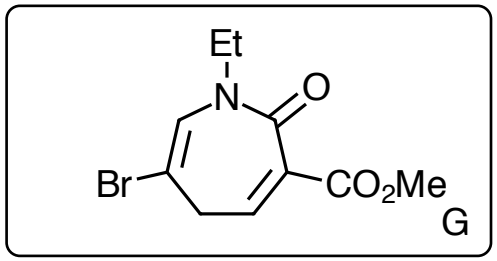


I



II

17-18

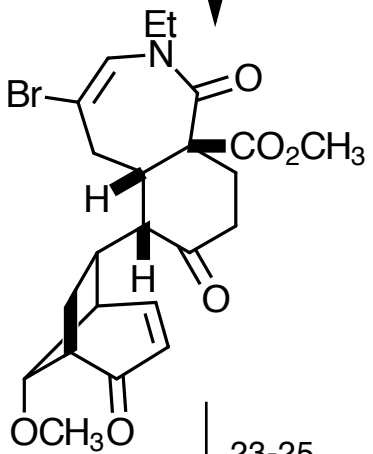


G

17) LiHMSDS, CH_3O_2CCN, PhSeCl
18) H_2O_2, CH_2Cl_2

G + **E**

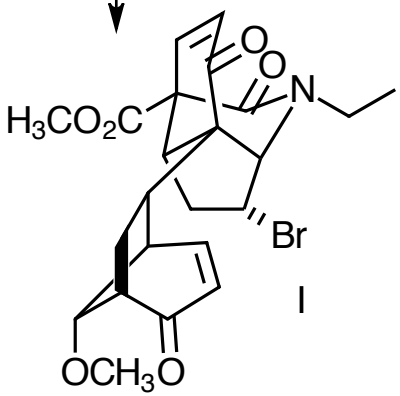
19-22



H

19) **G**, **E**, $Sc(OTf)_3$
20) OsO_4, NMO
21) $Pb(OAc)_4$
22) DBU

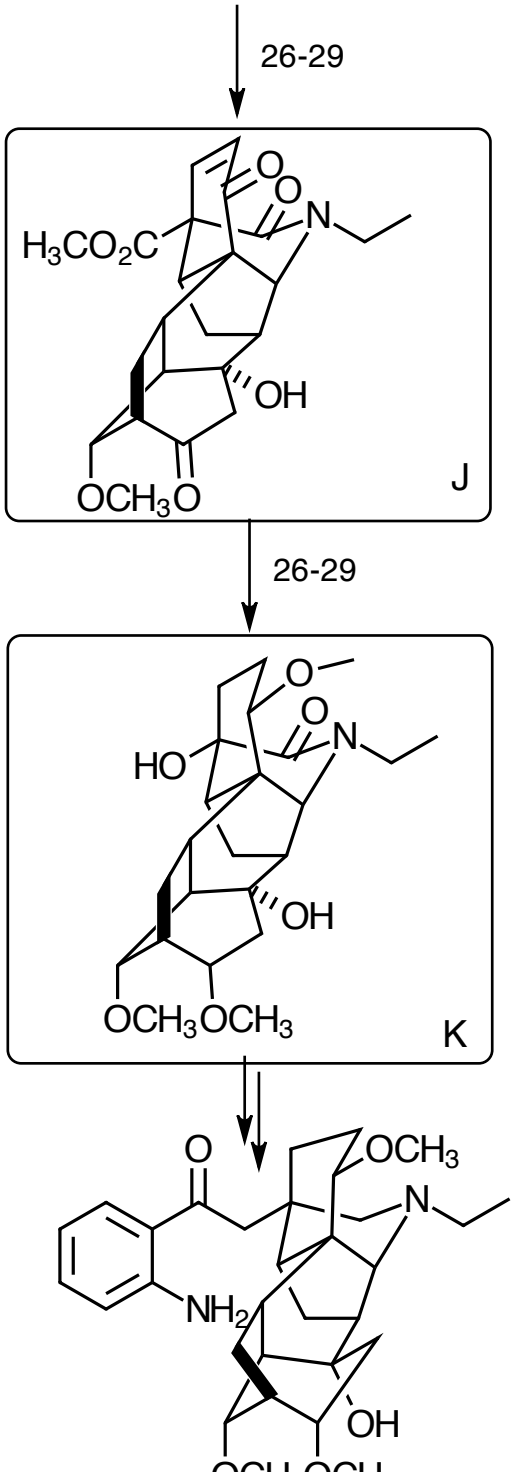
23-25



I

23) Tf_2NH
24) CAN
25) MsCl, Et_3N

Step 23: Mannich-type N-acyliminium cyclization
Step 24: allylic oxidation



26) Bu_3SnH, AIBN
27) TBSOTf, Et_3N
28) PhSeCl
29) $NaIO_4$

30) H_2/Pd-C
31) $NaBH_4$
32) CH_3I/*t*-BuOK
33) $LiBH_4$
34) CrO_3