A Short Synthesis of Delavatine A Unveils New Insights into Site-Selective Cross-Coupling of 3,5-Dibromo-2-pyrone

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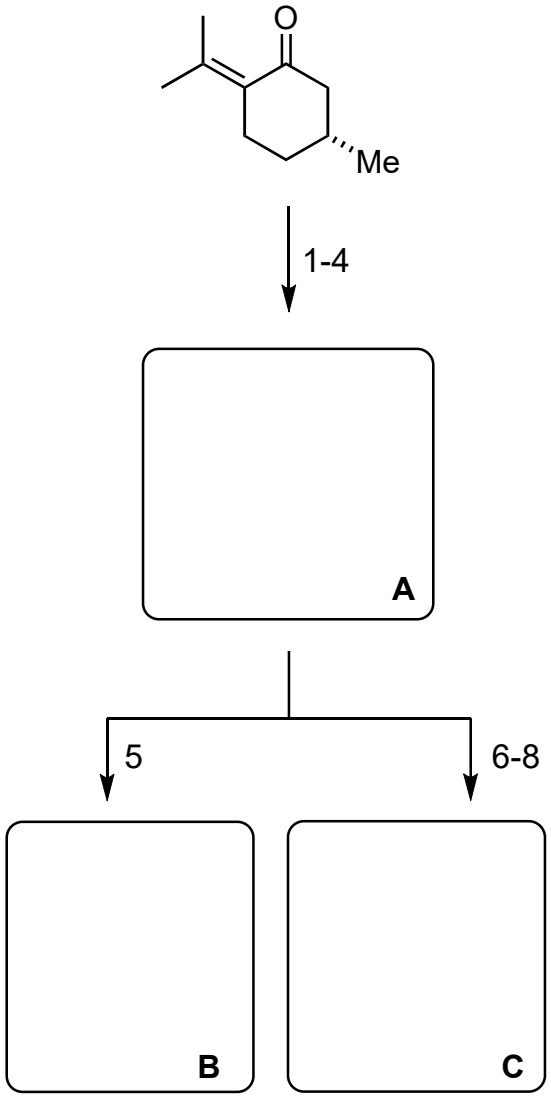


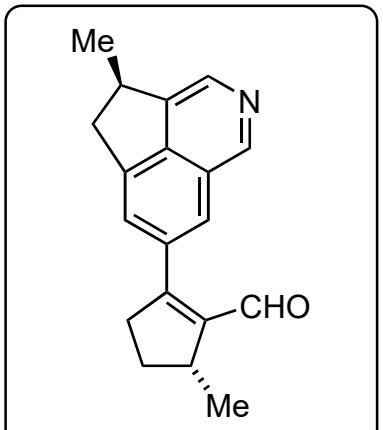
1) Br_2
2) EtONa
3) O_3
4) LDA, Tf_2O

5) $Pd(dppf)Cl_2$, B_2pin_2
6) $(Me_3Sn)_2CuLi$
7) Dibal-H
8) TPAP, NMO

2) Show the mechanism of step 2.
hint: A cyclopentane is formed

5) Which by-product must be avoided ?

6) Propose two mechanisms ?



delavatine A **G**

D

9,10

E

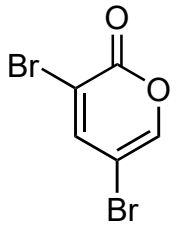
11

F

12-15

G

9) $Pd(PPh_3)_4$, CuI, **B**
10) $Pd(PPh_3)_4$, CuTC, **C**



D

11) NaCN, *then* K_2CO_3, MeI

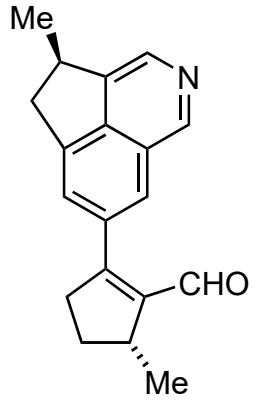
12) TBSOTf, Et_3N,
then DBU, PhMe, Δ
13) $LiAlH_4$
14) $(COCl)_2$, DMSO, Et_3N
15) NH_4OAc,

9) Give the name of steps 9 and 10

10) Show the structure of CuTC

11) Show the mechanism of step 11

12) Show the mechanism of step 12



delavatine A **G**