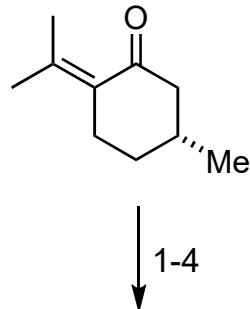
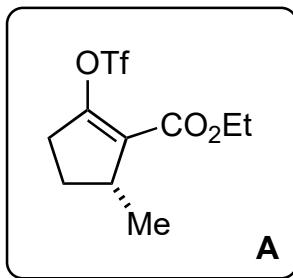


A Short Synthesis of Delavatine A Unveils New Insights into Site-Selective Cross-Coupling of 3,5-Dibromo-2-pyrone

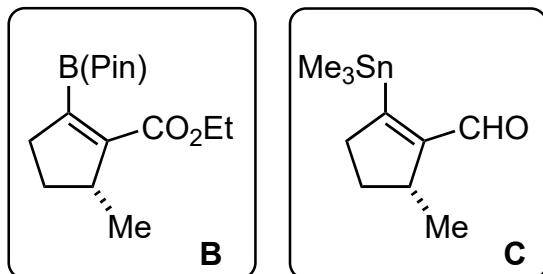
Palani, V.; Hugelshofer, C. L.; Kevlishvili, L.; Liu, P.; Sarpong, R.
J. Am. Chem. Soc. **2019**, *141*, 2652–2660.



- 1) Br_2
- 2) EtONa
- 3) O_3
- 4) $\text{LDA}, \text{Tf}_2\text{O}$



- 5 6-8

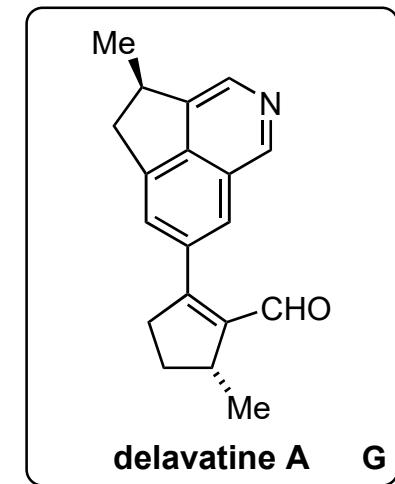


- 5) $\text{Pd}(\text{dppf})\text{Cl}_2, \text{B}_2\text{pin}_2$
- 6) $(\text{Me}_3\text{Sn})_2\text{CuLi}$
- 7) Dibal-H
- 8) TPAP, NMO

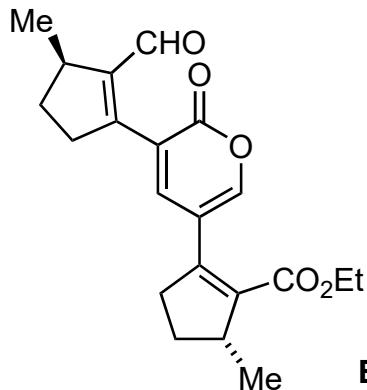
- 2) Show the mechanism of step 2.
hint: A cyclopentane is formed

- 5) Which by-product must be avoided ?
 Suzuki-coupling between vinyl triflate and vinyl-boronate

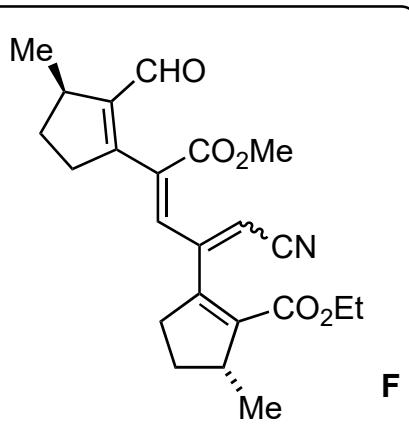
- 6) Propose two mechanisms
 Michael-retro-Michael or
 1,4-addition followed by an E1cB or
 Oxidative addition-Reductive Elimination



D
↓
9,10



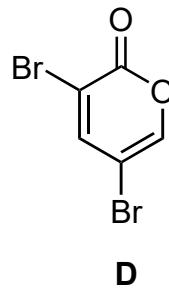
↓
11



↓
12-15

G

- 9) $\text{Pd}(\text{PPh}_3)_4$, CuI , B
10) $\text{Pd}(\text{PPh}_3)_4$, CuTC, C

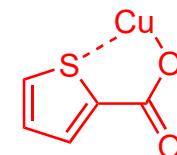


- 11) NaCN , then K_2CO_3 , MeI

- 12) TBSOTf , Et_3N ,
then DBU , PhMe , Δ
13) LiAlH_4
14) $(\text{COCl})_2$, DMSO , Et_3N
15) NH_4OAc ,

- 9) Give the name of steps 9 and 10
Suzuki-Cross-Coupling

- 10) Show the structure of CuTC



- 11) Show the mechanism of step 11
1,6-addition followed by a
vinylogous retro-oxa-Michael

- 12) Show the mechanism of step 12

