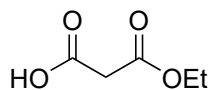
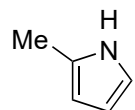
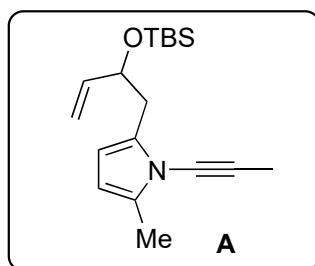


Total Synthesis of Bipolarine I

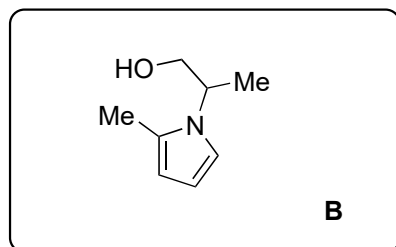
X. Qiu, J. G. Pierce, *J. Am. Chem. Soc.* **2022**, *144*, 12638–12641.



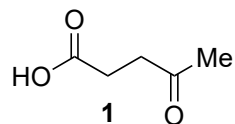
1–6



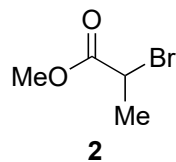
7–8



- 1) $\text{Mg}(\text{OEt})_2$, **1**, CDI
- 2) propargyl amine, AcOH
- 3) DIBAL-H
- 4) vinyl magnesium bromide
- 5) TBSCl, imidazole, DMAP
- 6) *t*-BuOK, *t*-BuOH

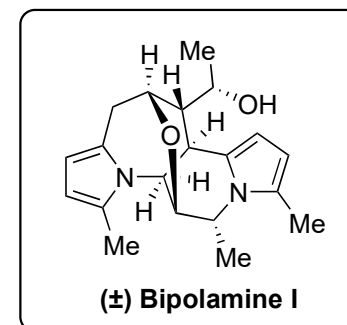


- 7) NaH, **2**, 0 °C
- 8) LiAlH_4



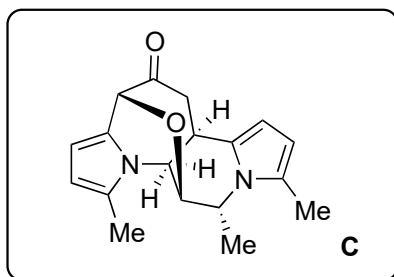
- 2) Name of the reaction?

Paal–Knorr pyrrole synthesis

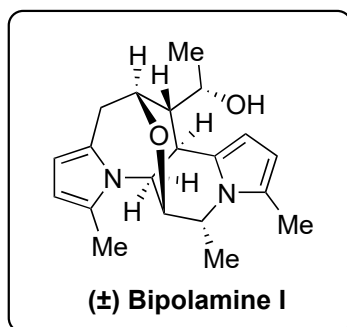


A + B

9-12



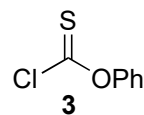
13-17



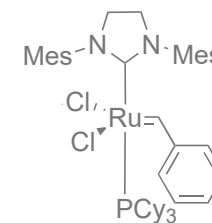
- 9) 10 mol% $\text{HClRu}(\text{CO})(\text{PPh}_3)_3$,
10 mol% dippf, 1M dioxane, 115 °C
- 10) Grubbs II, 80 °C
- 11) TBAF
- 12) MnO_2

- 13) LiHMDS, acetaldehyde
- 14) imidazole, DMAP, TBSCl
- 15) SmI_2
- 16) KHMDS, DMAP, **3**

- 17) BEt_3 , $n\text{-Bu}_3\text{SnH}$, then TBAF



10) Structure of Grubbs II catalyst?



12) Hint: ether bridge formed, allylic alcohol oxidized and pyrrole addition

15) Hint: ether bridge cleaved and shifted