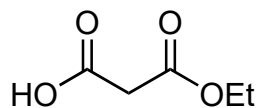


Total Synthesis of Bipolamine I

Qiu, X.; Pierce, J. G.*

J. Am. Chem. Soc. **2022**, *144* (28), 12638–12641

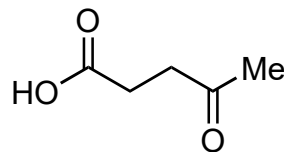


1-5

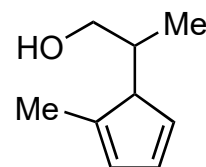


6-10

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



1



2

- 6) *t*-BuOK, *t*-BuOH
- 7) **2**, 10 mol% $\text{HClRu}(\text{CO})(\text{PPh}_3)_3$, 10 mol% dipfp, 1M dioxane, 115 °C
- 8) Grubbs II, 80 °C
- 9) TBAF
- 10) MnO_2

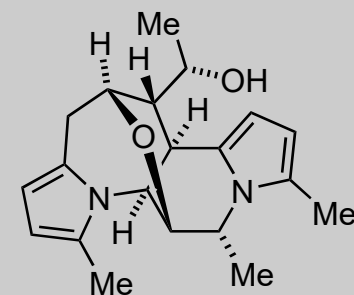
2) Please name the reaction

6) What about reaction that makes terminal alkyne from internal alkyne? What reagents could be used?

7) Hint: alkyne-to-allene isomerization and enantioselective allene-alcohol coupling

J. Am. Chem. Soc. **2015**, *137* (9), 3161–3164

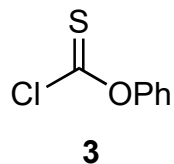
10) Hint: ether bridge formed, allylic alcohol oxidized and pyrrole addition



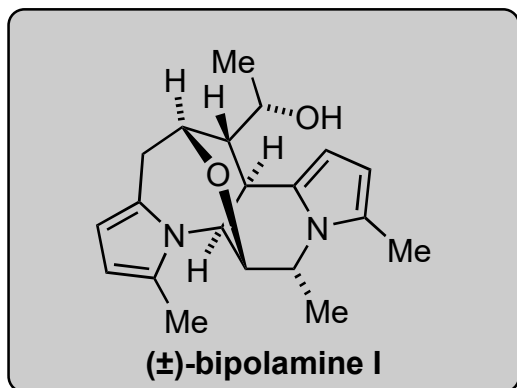
(±)-bipolamine I



- 11) LiHMDS, acetaldehyde
- 12) imidazole, DMAP, TBSCl
- 13) SmI_2
- 14) KHMDS, DMAP, **3**
- 15) BEt_3 , $n\text{-Bu}_3\text{SnH}$, then TBAF



11-15



13) Hint: ether bridge cleaved and shifted