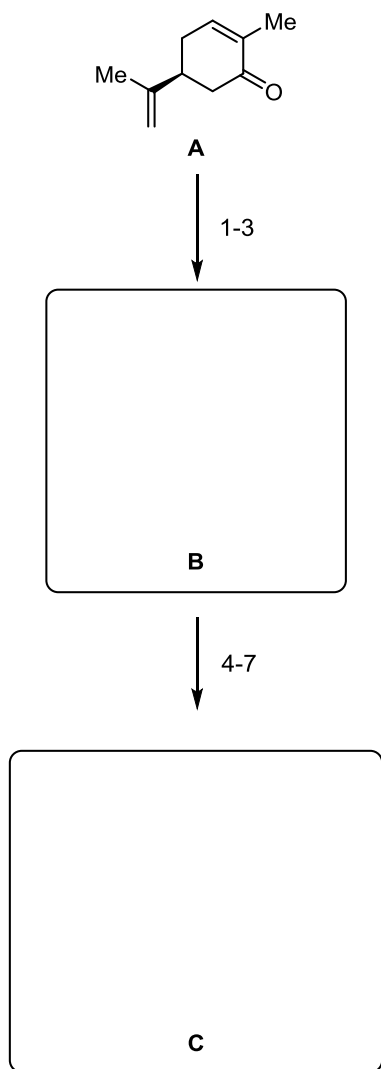
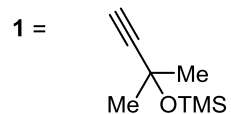


Total Synthesis of (-)-Ambiguine P Using Sequential Indole Functionalizations

Johnson, R. E.; Ree, H.; Hartmann, M.; Lang, L.; Sawano, S; Sarpong, R *J. Am. Chem. Soc.* **2019**, *141*, 2233–2237.



- 1) LiHMDS, indole, Cu(II) 2-ethyl hexanoate
- 2) LiHMDS + **1**, THF, -78 °C
- 3) PDC, DCM, rt; *then* 1N HCl, THF, 0 °C



- 4) $\text{Co}_2(\text{CO})_8$; *then* $\text{BF}_3 \cdot \text{OEt}_2$, DCM
- 5) AlCl_3 , MeOH, DCM, 0 °C to rt
- 6) Nagata's reagent, TMSCl, pyridine, MeCN
- 7) Bu_3SnH , PhH, 45 °C; *then* 2N HCl, MeOH

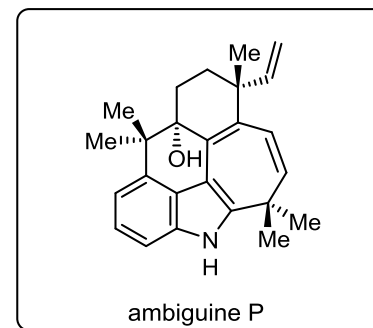
Name of **A**?

Name the reaction in step 2

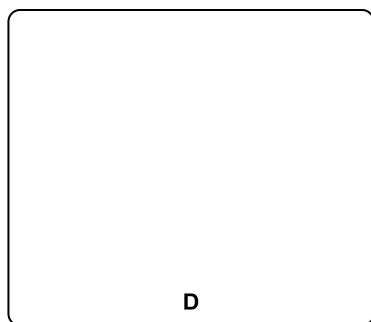
Name the reaction in step 4 (hint: a new cycle forms)

Name the reaction in step 5 (hint: a new cycle forms)

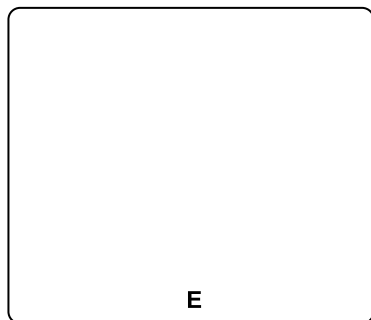
Step 7: two deprotections occur



8-11



12-15



- 8) Wilkinson's catalyst, acetaldoxime, 30 °C, PhMe
- 9) NaHMDS, methyl formate, THF
- 10) NaBH₄, MeOH
- 11) Tf₂O, 2,6-di-tert-butylpyridine, DCM, -78 °C

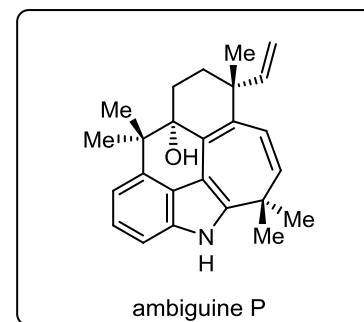
Hint: acetaldoxime is a water source (anhydrous conditions)

Hint step 11: the functional group from step 6 is reinstalled

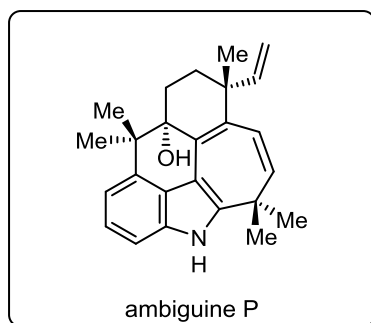
- 12) TCDI, DMAP, DCM, 45 °C
- 13) Bu₃SnH, AIBN, PhMe, 80 °C
- 14) TMSCH₂Li, THF
- 15) PPTS, DCE, 120 °C, μ wave

Name the reaction sequence in step 12-13

TCDI: Thiocarbonyldiimidazole



16-21



- 16) TBAF, THF, 100 °C, μ wave
- 17) PIDA, KOH, H₂O, dioxane
- 18) Ac₂O, HCO₂H, DCM
- 19) COCl₂, NEt₃, DCM, 0 °C
- 20) KO^tBu, DMSO, μ wave, 150 °C
- 21) SeO₂, dioxane

Name the reaction in step 17