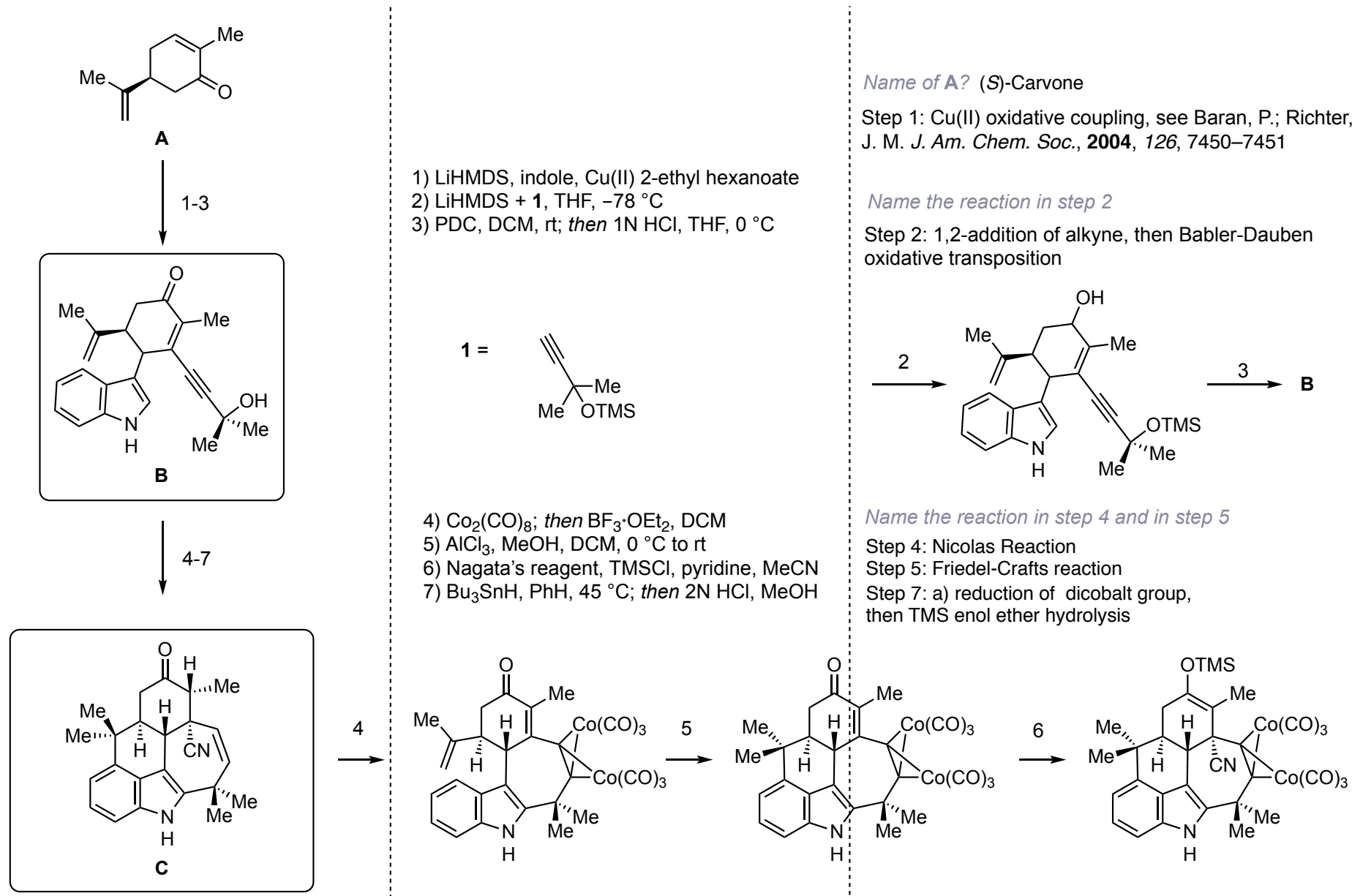
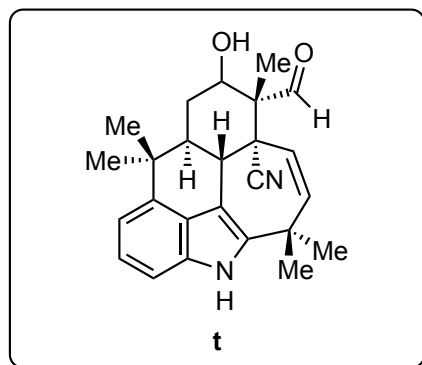


## Total Synthesis of (–)-Ambiguine P Using Sequential Indole Functionalizations

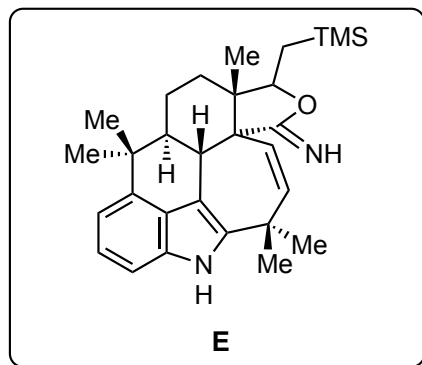
Johnson, R. E.; Ree, H.; Hartmann, M.; Lang, L.; Sawano, S; Sarpong, R *J. Am. Chem. Soc.* **2019**, *141*, 2233–2237.



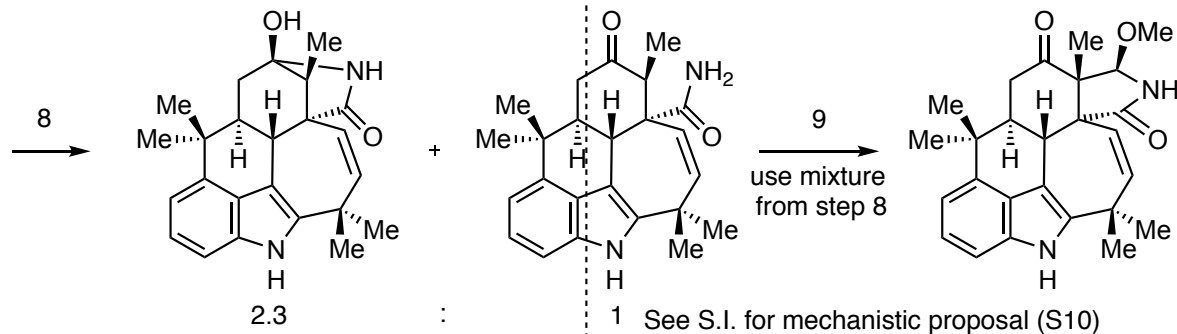
8-11



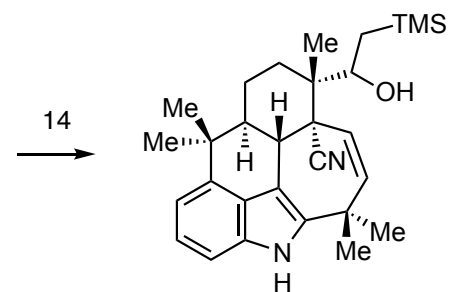
12-15



- 8) Wilkinson's catalyst, acetaldoxime,  
30 °C, PhMe  
9) NaHMDS, methyl formate, THF  
10) NaBH<sub>4</sub>, MeOH  
11) Tf<sub>2</sub>O, 2,6-di-tert-butylpyridine, DCM, -78 °C

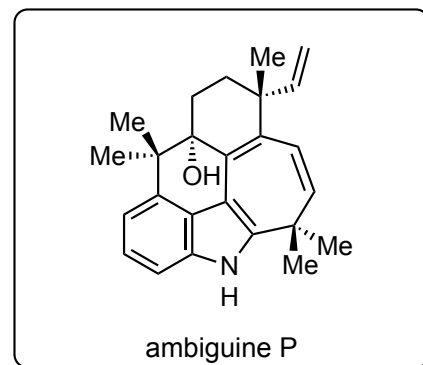


- 12) TCDI, DMAP, DCM, 45 °C  
13) Bu<sub>3</sub>SnH, AIBN, PhMe, 80 °C  
14) TMSCH<sub>2</sub>Li, THF  
15) PPTS, DCE, 120 °C,  $\mu$ wave

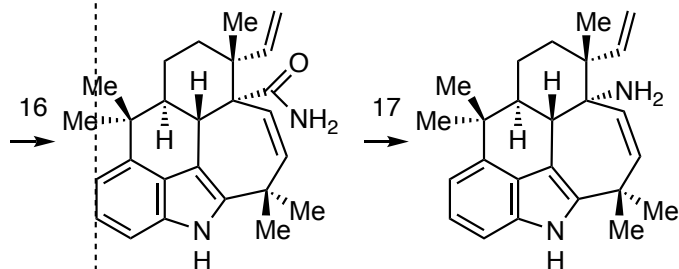
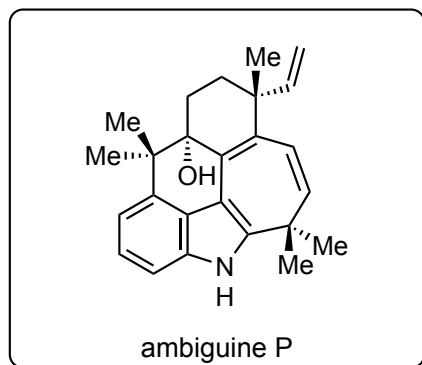


steps 14-16: Peterson-Type olefination + nitrile hydration

Step 8: Hydrolysis of nitrile



16-21



- 16) TBAF, THF, 100 °C,  $\mu$ wave
- 17) PIDA, KOH, H<sub>2</sub>O, dioxane
- 18) Ac<sub>2</sub>O, HCO<sub>2</sub>H, DCM
- 19) COCl<sub>2</sub>, NEt<sub>3</sub>, DCM, 0 °C\
- 20) KOtBu, DMSO,  $\mu$ wave, 150 °C
- 21) SeO<sub>2</sub>, dioxane

- Step 17: Hofmann rearrangement  
Step 18: formylation and dehydration (step 19)  
yields isonitrile  
Step 20: elimination of isonitrile  
Step 21: d.r. 1.5:1 in favor of ambiguline