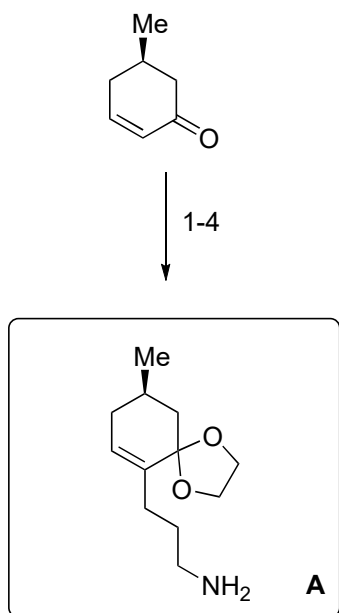


# Total Synthesis of (+)-Complanadine A Using an Iridium-Catalyzed Pyridine C-H Functionalization

Daniel F. Fischer and Richmond Sarpong

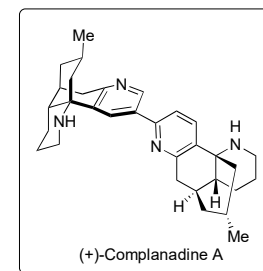
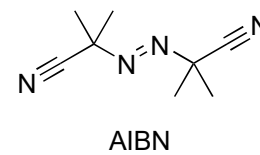
*J. Am. Chem. Soc.*, 2010, 132 (17), pp 5926–5927

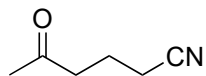


- 1)  $I_2$ , pyridine, DCM
- 2) acrylonitrile, AIBN,  $HSnBu_3$ , PhH
- 3)  $HOCH_2CH_2OH$ ,  $HC(OEt)_3$ , TsOH, reflux
- 4)  $LiAlH_4$ ,  $Et_2O$ ,  $0\text{ }^\circ\text{C}$

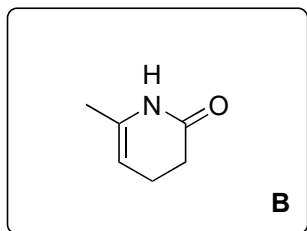
How would you make the starting material from (R)-pulgenone?

What is the structure of AIBN? Provide a mechanism.

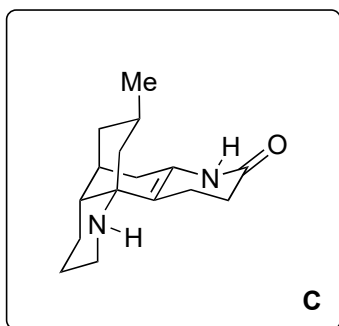




↓ 5



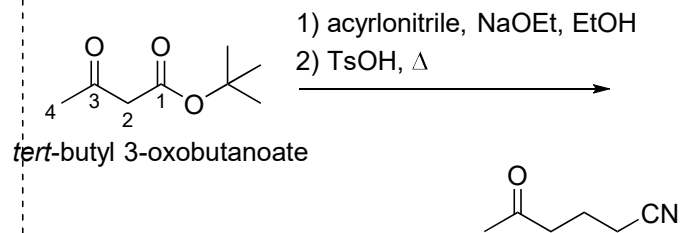
↓ 6



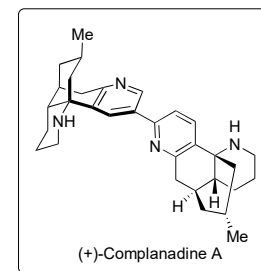
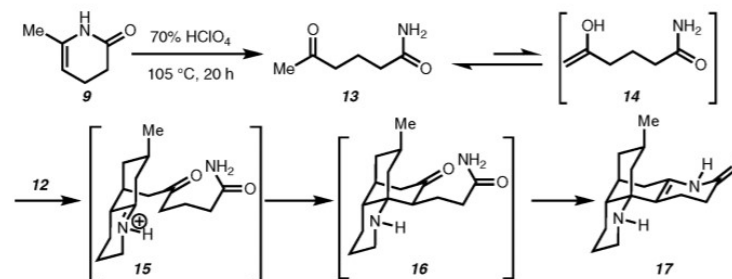
5)  $\text{Zn}(\text{NO}_3)_2$ , acetone oxime,  $\text{H}_2\text{O}$  90 °C  
then 120 °C, vacuum.

6) **A**,  $\text{HClO}_4$ , dioxane  $\Delta$

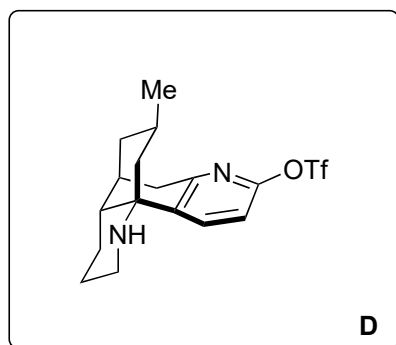
How would you prepare this starting material?



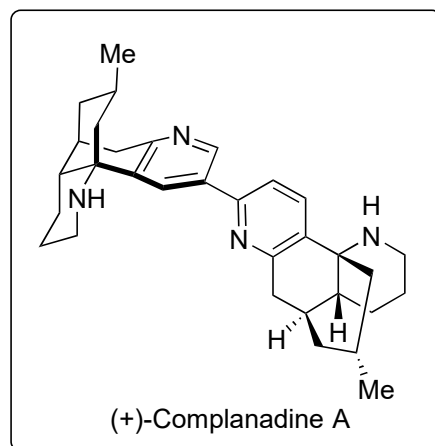
Provide a mechanism and rationalize the stereoselectivity for step 6.



7-9

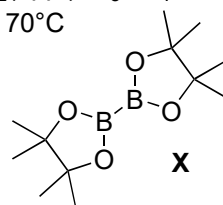


10-13



- 7)  $\text{Boc}_2\text{O}$ ,  $\text{NEt}_3$ , THF 60 °C
- 8)  $\text{Pb}(\text{OAc})_4$ ,  $\text{CHCl}_3$ , RT then  $\text{K}_2\text{CO}_3$
- 9)  $\text{Tf}_2\text{O}$ , pyridine, -78 °C  $\rightarrow$  RT

- 10)  $\text{Pd}(\text{OAc})_2$  dppf,  $\text{NH}_4\text{O}_2\text{CH}$ ,  $\text{NEt}_3$ , DMF
- 11) **X**,  $[\text{Ir}(\text{COD})(\text{OMe})_2]_2$ , dtbu-bipy, THF, 80 °C
- 12) **D**,  $\text{PdCl}_2(\text{dppf})$ ,  $\text{K}_3\text{PO}_4$ , DMF
- 13) 6N HCl, 70°C



Provide a rationale for the regioselectivity in step 11  
(a) *J. Am. Chem. Soc.* 2002, 124, 390. (b) *Science* 2002, 295, 305.

What is the name of the reaction in step 12.