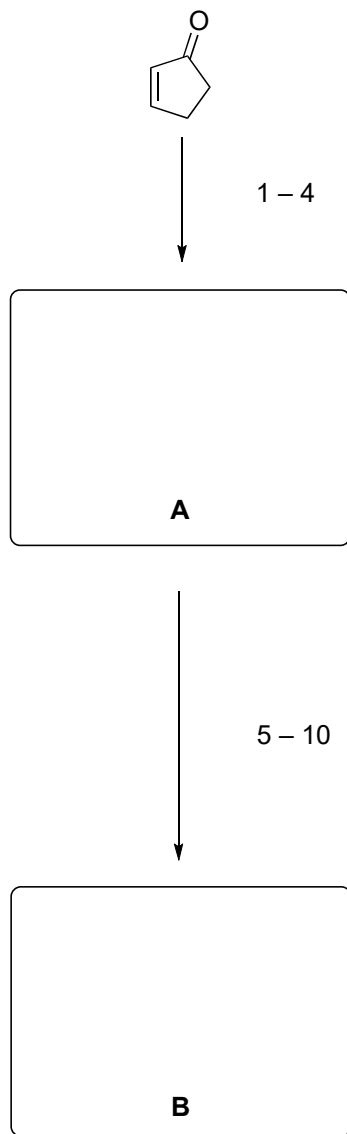


**Enantioselective Total Synthesis of (-)-Hunterine A Enabled by a  
Desymmetrization/Rearrangement Strategy**  
E. F. Hicks, K. Inoue, B. M. Stoltz, *J. Am. Chem. Soc.* **2024**, *146*, 4340–4345.



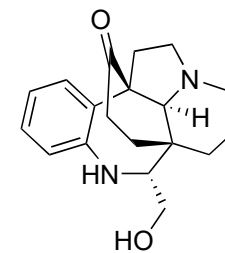
- 1)  $\text{PPh}_3$ , TBSOTf, then *n*-BuLi, then ethyl acrylate, TMSOTf then TBAF
- 2)  $\text{CuBr}\cdot\text{Me}_2\text{S}$ , vinylmagnesium bromide, TMSCl, HMPA
- 3) KO $t$ -Bu
- 4)  $[\text{RuCl}(\text{mesitylene})(R,R\text{-TsDPEN})]$ , HCOOH,  $\text{Et}_3\text{N}$

- 5) TBSCl, imidazole, DMAP
- 6)  $\text{NH}_2\text{OH}\cdot\text{HCl}$ ,  $\text{NaHCO}_3$
- 7)  $\text{SOCl}_2$
- 8)  $\text{LiAlH}_4$
- 9)  $\text{BrCH}_2\text{CN}$ ,  $\text{K}_2\text{CO}_3$
- 10)  $(\text{COCl})_2$ , DMSO,  $\text{Et}_3\text{N}$

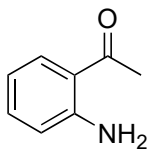
4) Hint: Only one functional group reacts

7) Name of the reaction?

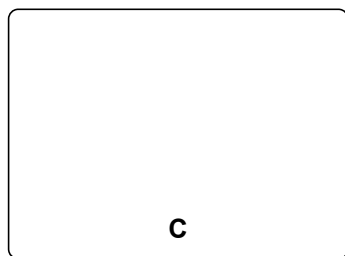
10) Name of the reaction?



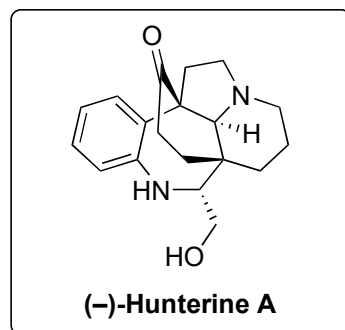
**(-)-Hunterine A**



11 – 14



15 – 21



- 11)  $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$
- 12)  $\text{I}_2, \text{Et}_3\text{N}$
- 13) Phosphomolybdic acid (PMA),  $\text{Ac}_2\text{O}$
- 14)  $\text{Boc}_2\text{O}$ , DMAP, then  $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$

- 15)  $\text{PhMgBr}$ , then  $i\text{-PrMgCl} \cdot \text{LiCl}$ , then  $\text{LaCl}_3 \cdot 2\text{LiCl}$ , then **B**
- 16)  $\text{TMSCl}$ ,  $\text{MeOH}$
- 17)  $\text{HCl}$ ,  $\text{NaNO}_2$ , then  $\text{NaN}_3$
- 18)  $\text{AgNO}_3$  (Hint: 2 Reactions)
- 19) heptane
- 20)  $h\nu$  (350 nm), then  $\text{AcOH}$
- 21)  $\text{K}_2\text{CO}_3$

12) Name of the reaction?

18) Mechanism?

19) Type of reaction?

20) Mechanism?

