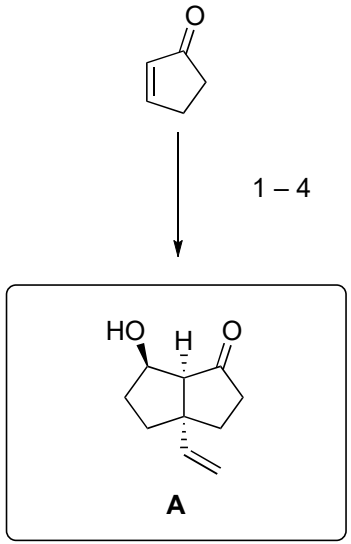
Enantioselective Total Synthesis of (−)-Hunterine A Enabled by a Desymmetrization/Rearrangement Strategy

E. F. Hicks, K. Inoue, B. M. Stoltz, *J. Am. Chem. Soc.* **2024**, *146*, 4340–4345.



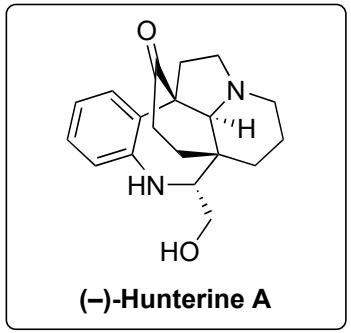
1) PPh_3, TBSOTf, *then* *n*-BuLi, *then* ethyl acrylate, TMSOTf *then* TBAF
2) $CuBr{\cdot}Me_2S$, vinylmagnesium bromide, TMSCl, HMPA
3) KO*t*-Bu
4) [RuCl(mesitylene)(*R*,*R*-TsDPEN)], HCOOH, Et_3N

4) Hint: Only one functional group reacts

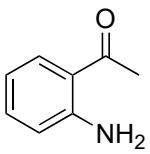
5) TBSCl, imidazole, DMAP
6) $NH_2OH{\cdot}HCl$, $NaHCO_3$
7) $SOCl_2$
8) $LiAlH_4$
9) $BrCH_2CN$, K_2CO_3
10) $(COCl)_2$, DMSO, Et_3N

7) Name of the reaction?
Beckmann rearrangement

10) Name of the reaction?
Swern oxidation



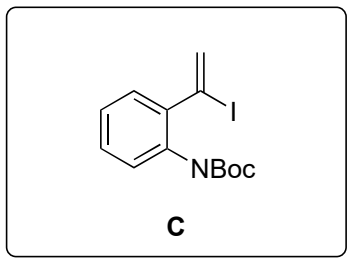
(–)-Hunterine A



11 – 14

11) $NH_2NH_2.H_2O$
12) I_2, Et_3N
13) Phosphomolybdic acid (PMA), Ac_2O
14) Boc_2O, DMAP, then $NH_2NH_2.H_2O$

12) Name of the reaction?
Barton vinyl iodide synthesis

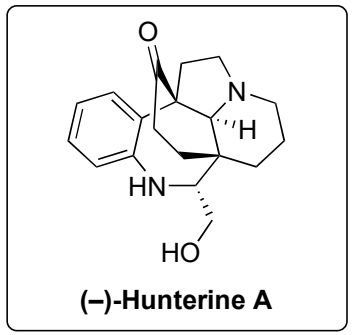


C

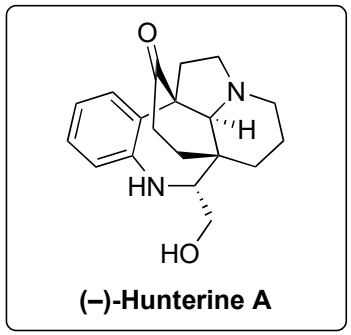
15 – 21

15) PhMgBr, *then* *i*-PrMgCl·LiCl, *then* $LaCl_3$·2LiCl, *then* **B**
16) TMSCl, MeOH
17) HCl, $NaNO_2$, *then* NaN_3
18) $AgNO_3$
19) heptane
20) *hv* (350 nm), *then* AcOH
21) K_2CO_3

18) Mechanism?
19) Type of reaction?
dipolar cycloaddition
20) Mechanism?

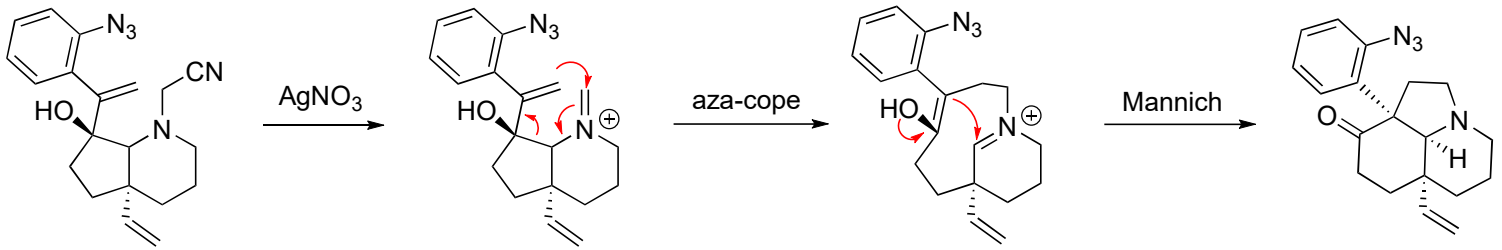


(–)-Hunterine A



(–)-Hunterine A

Mechanism Step 18)



Mechanism Step 20)