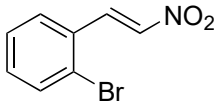
Total Synthesis of (+)-Vallesamidineand (+)-14,15-Dehydrostrempeliopine

X. Zhang, J. C. Anderson, *Angew.Chem. Int. Ed.* **2019**, *58*,18040 –18045.



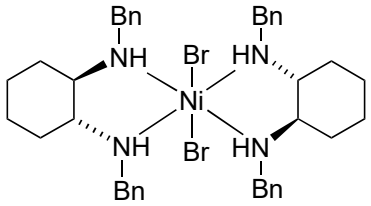
1 – 7

A

8 – 14

B

1) diethyl malonate, **1**
2) $PMBNH_2$, $(HCHO)_n$
3) NaCl
4) $Pd(PPh_3)_4$, DBU, allyl acetate
5) Zn dust, HCl
6) CuI, *L*-proline, K_3PO_4
7) $ClCO_2Me$

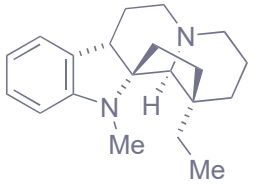


1

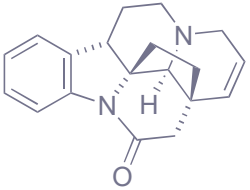
8) OsO_4, NMO, 2,6-lutidine, *then* $PhI(OAc)_2$
9) $(TMSOCH_2)_2$, TMSOTf
10) $Mo(CO)_6$, $PhSiH_3$
11) allyl chloroformate, $NaHCO_3$, *then* AcOH
12) $Pd(PPh_3)_4$
13) dimethyl malonate, *L*-proline
14) $Yb(OTf)_3$

3) Name of the reaction?
4) Name of the reaction?

13) Name of the reaction?
14) Mechanism?



(+)-vallesamidine



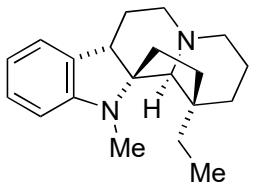
(+)-14,15-dehydrostrempeliopine

15 – 20

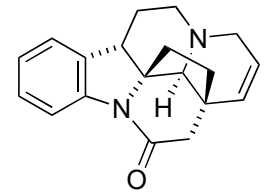
C

21 – 22

23 – 25



(+)-vallesamidine



(+)-14,15-dehydrostrempeliopine

15) LAH
16) TBDPSCl, NEt_3, DMAP
17) IBX, *then* SiO_2
18) Petasis reagent
19) $(COCl)_2$, DMSO, NEt_3, *then* Ph_3PCH_3Br, NaHMDS
20) HG II

21) LAH
22) Pd/C, H_2
23) *c*-Hex_2BH, *then* $NaBO_3 \cdot H_2O$
24) KOH, MeOH
25) TPAP, NMO

16) 1 equiv TBDPSCl
18) Structure of Petasis reagent?
20) Structure of HG II?