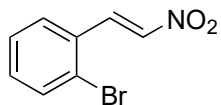
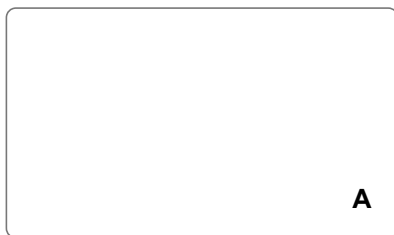


Total Synthesis of (+)-Vallesamidine and (+)-14,15-Dehydrostrempepiopine

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



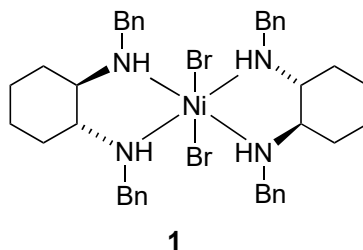
1 – 7



8 – 14



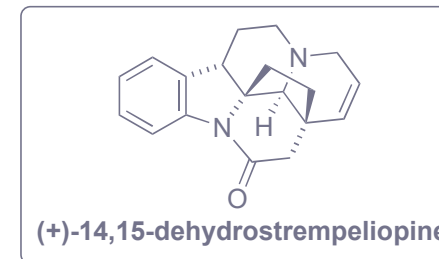
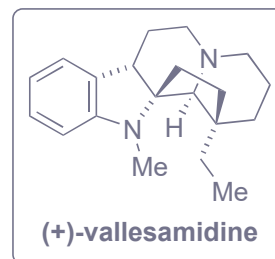
- 1) diethyl malonate, **1**
- 2) PMBNH₂, (HCHO)_n
- 3) NaCl
- 4) Pd(PPh₃)₄, DBU, allyl acetate
- 5) Zn dust, HCl
- 6) CuI, *L*-proline, K₃PO₄
- 7) ClCO₂Me



- 8) OsO₄, NMO, 2,6-lutidine, *then* PhI(OAc)₂
- 9) (TMSOCH₂)₂, TMSOTf
- 10) Mo(CO)₆, PhSiH₃
- 11) allyl chloroformate, NaHCO₃, *then* AcOH
- 12) Pd(PPh₃)₄
- 13) dimethyl malonate, *L*-proline
- 14) Yb(OTf)₃

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

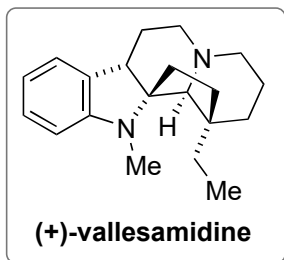
- 13) Name of the reaction?
- 14) Mechanism?



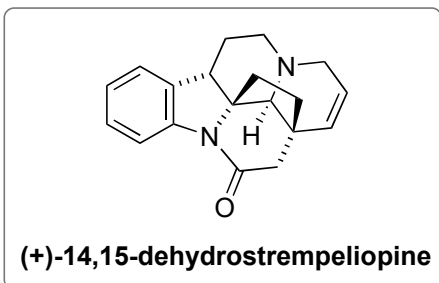
15 – 20



21 – 22



23 – 25



- 15) LAH
- 16) TBDPSCI (1 equiv),
NEt₃, DMAP
- 17) IBX, *then* SiO₂
- 18) Petasis reagent, *then* TBAF
- 19) (COCl)₂, DMSO, NEt₃,
then Ph₃PCH₃Br, NaHMDS
- 20) HG II

- 18) Structure of Petasis reagent?
- 20) Structure of HG II?

- 21) LAH
- 22) Pd/C, H₂
- 23) *c*-Hex₂BH, *then* NaBO₃•H₂O
- 24) KOH, MeOH
- 25) TPAP, NMO