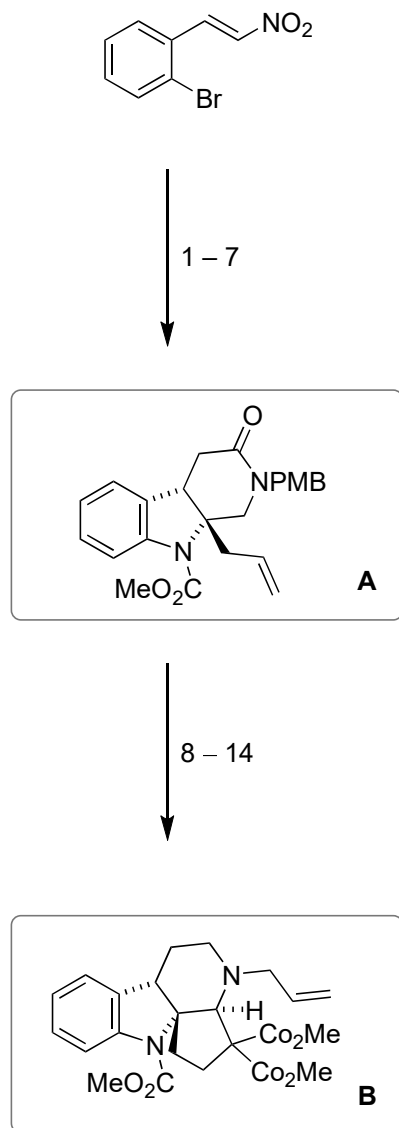
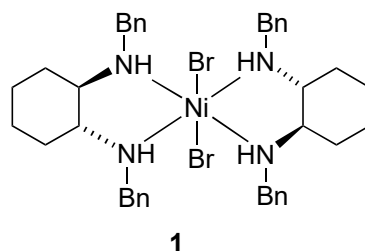


Total Synthesis of (+)-Vallesamidine and (+)-14,15-Dehydrostrepeliopine

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



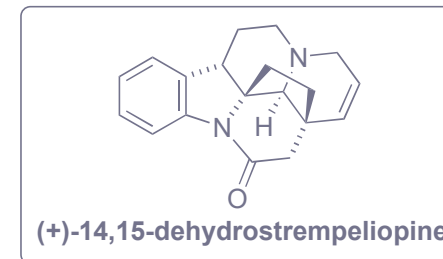
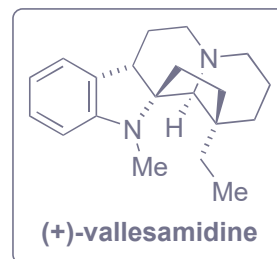
- 1) diethyl malonate, **1**
- 2) PMBNH₂, (HCHO)_n
- 3) NaCl
- 4) Pd(PPh₃)₄, DBU, allyl acetate
- 5) Zn dust, HCl
- 6) CuI, *L*-proline, K₃PO₄
- 7) ClCO₂Me



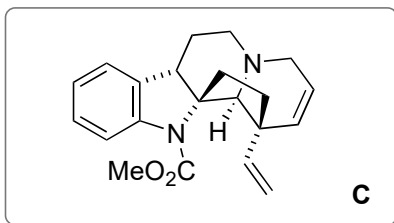
- 8) OsO₄, NMO, 2,6-lutidine, then PhI(OAc)₂
- 9) (TMSOCH₂)₂, TMSOTf
- 10) Mo(CO)₆, PhSiH₃
- 11) allyl chloroformate, NaHCO₃, then AcOH
- 12) Pd(PPh₃)₄
- 13) dimethyl malonate, *L*-proline
- 14) Yb(OTf)₃

- 3) Name of the reaction? Krapcho decarboxylation
- 4) Name of the reaction? Tsuji-Trost allylation

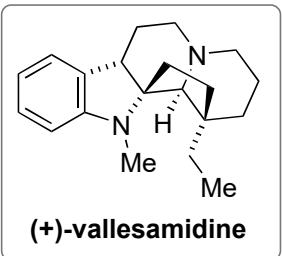
- 13) Name of the reaction? Knoevenagel condensation
- 14) Mechanism? see below



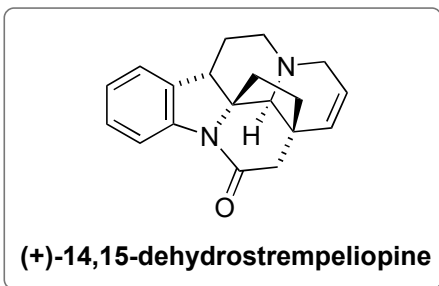
15 – 20



21 – 22



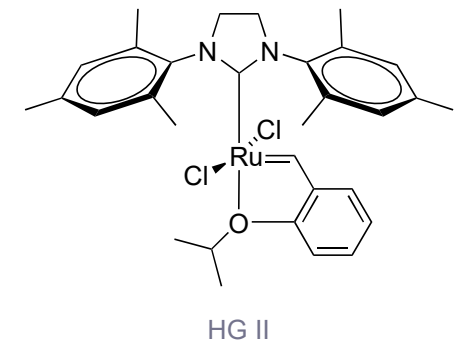
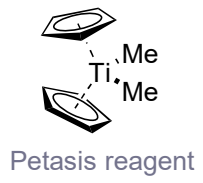
23 – 25



- 15) LAH
- 16) TBDPSCI, NEt_3 , DMAP
- 17) IBX, *then* SiO_2
- 18) Petasis reagent
- 19) $(\text{COCl})_2$, DMSO, NEt_3 , *then* $\text{Ph}_3\text{PCH}_2\text{Br}$, NaHMDS
- 20) HG II

- 21) LAH
- 22) Pd/C, H_2
- 23) *c*-Hex₂BH, *then* $\text{NaBO}_3 \cdot \text{H}_2\text{O}$
- 24) KOH, MeOH
- 25) TPAP, NMO

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



14)

