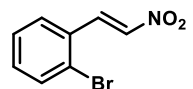


Total synthesis of (+)-Vallesamidine and (+)-14,15-Dehydrostrepeliopine



1) diethyl malonate,
1 (1 mol%), PhMe, r.t.

A

2) PMBNH₂, (HCHO)_n,
EtOH, 80 °C
3) NaCl, DMSO, 160 °C

B

4) Pd(PPh₃)₄ (1 mol%), DBU,
allyl acetate, DCM, 0 °C

C

5) Zn dust, 6 M HCl aq.,
EtOH/EtOAc, 0 °C
6) CuI (10 mol%), L-proline (20 mol%),
K₃PO₄, DMSO, 80 °C
7) ClCO₂Me, 65 °C

D

8) OsO₄ (2 mol%), NMO, 2,6-lutidine,
acetone/H₂O; then PhI(OAc)₂
9) (TMSOCH₂)₂, TMSOTf (10 mol%),
DCM, -78 °C → r.t.
10) Mo(CO)₆ (10 mol%), PhSiH₃,
THF, 65 °C

E

11) allyl chloroformate, NaHCO₃,
DCE, 80 °C; then AcOH, THF/H₂O, 90 °C
12) Pd(PPh₃)₄ (2.5 mol%), DCM, r.t.

F

13) dimethyl malonate, L-proline, DMSO, r.t.

G

14) Yb(OTf)₃ (10 mol%), PhMe, reflux

H

15) LAH, THF, 0 °C → 22 °C
16) TBDPSCI, NEt₃, DMAP, DCM
17) IBX, EtOAc, reflux; then SiO₂, DCM

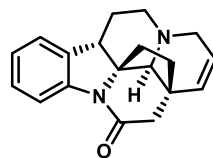
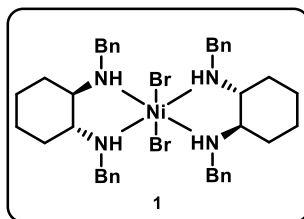
I

18) Cp₂TiMe₂, PhMe, 80 °C;
then TBAF, THF, 70 °C
19) (COCl)₂, DMSO, NEt₃, DCM, -78 °C → 0 °C;
then Ph₃PCH₃Br, NaHMDS, THF, -78 °C → r.t.

J

20) HG 2 (10 mol%), PhMe, 80 °C

K

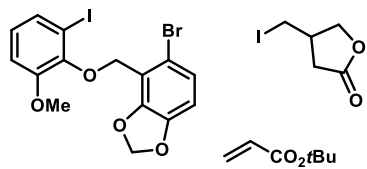


(+)-14,15-dehydrostrepeliopine

23) *c*-Hex₂BH, then NaBO₃ · H₂O, THF
24) 6 M KOH aq., MeOH, 100 °C
25) TPAP (10 mol%), NMO, DCM

21) LAH, THF, 0 °C → 65 °C
22) Pd/C, H₂, MeOH, r.t.

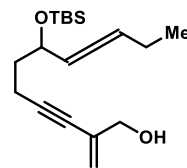
(+)-vallesamidine



$\text{Pd}(\text{OAc})_2$ (10 mol%), PPh_3 (22 mol%),
 norbornene, Cs_2CO_3 , DMF, 90 °C

product & mechanism?

mechanism?



JohnphosAuNTf_2 ,
 4A MS, DCE, 0 °C → r.t.

