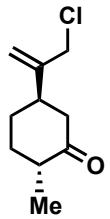
Asymmetric Total Synthesis of (-)-Vinigrol



1) LiHMDS, 2-chloroacetyl chloride, THF, then NH_3 aq.
2) DIBAL, DCM, -78 °C

A

3) Mg, **N**, CuI, THF

B

4) *n*-BuLi, HCHO (gas)
5) $VO(acac)_2$, TBHP, DCM

C

6) Boc_2O, DMAP, DCM then $AgSbF_6$, trifluoroethanol

D

7) hydroquinidine (0.2 eq.), PhCN, 170 °C

E

8) Wilkinson, H_2 (1000 psi), PhMe then BH_3•THF, 0 °C to 80 °C then NaOH, H_2O_2

F

9) IBX (5 eq.), DMSO, 80 °C then $NaHCO_3$, $Na_2S_2O_3$•$5H_2O$

mechanism for this transformation?

G + **H**

$NaHCO_3$, DMSO, r.t.

10) SmI_2 (2.2 eq.), THF/H_2O

I

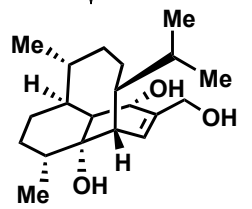
11) LiHMDS, Mander's reagent
12) PhSeBr, pyr

J

13) DIBAL (6 eq.), LDA (1.2 eq.), THF

K (5%) + **L** (63%)

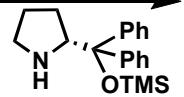
14) $^1O_2$, *hv*, $NaHCO_3$ then PMe_3



(-)-Vinigrol

isovaleraldehyde

CH_2O (aq)



(5 mol%)

M

a) Ph_3PCH_3Br, *n*-BuLi
b) PPh_3, CBr_4

N