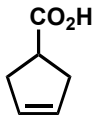
Stereoselective Total Synthesis of Eburnane-Type Alkaloids

06.03.19



1. LDA (2.2 equiv), $Cl(CH_2)_3I$
2. $(COCl)_2$, DMF then tryptamine, NEt_3

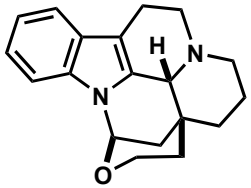
A → 3. LiHMDS → **B** → 4. $POCl_3$, MeCN, 100°C → **C** (*pentacycle*)

5. **1** (5 mol%), $NaCO_2H$, $AgSbF_6$, CTAB, H_2O, 40°C
6. Bz_2O_2, $CHCl_3$, r.t.

→ **D** → 7. OsO_4, NMO → **E** → 8. 1 M NaOMe in MeOH, reflux → [**IM1**] → **F**

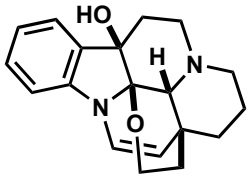
9. $Pb(OAc)_4$ → [**IM2**] → **G** → 10. $NaBH_4$, EtOH, 0°C → **H** (*hexacycle*)

11. $LiBH_4$, THF, 0°C
12. 5% HCl_{aq}, 80°C then r.t.

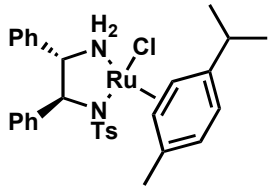


(±)-larutensine

13. $BF_3 \cdot Et_2O$ (10 equiv), DCE, reflux



(±)-terengganensine B



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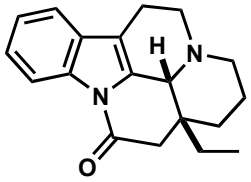
F → 14. DMSO (5 equiv), TFAA (5 equiv), NEt_3
15. $Pb(OAc)_4$, MeOH → **I** → 16. 1 M $NaOH_{aq}$ then EtSH, EDCI, DMAP
17. Pd/C, $EtSiH_3$, acetone, r.t. → **J** → 18. $HS(CH_2)_2SH$, $BF_3 \cdot Et_2O$
19. Raney-Ni, H_2, EtOH, reflux → **(±)-melokhanine E** → 20. $LiBH_4$, THF, 0°C then TFA/DCE, reflux



(±)-eburnamonine