Total Synthesis of Vilmoraconitine

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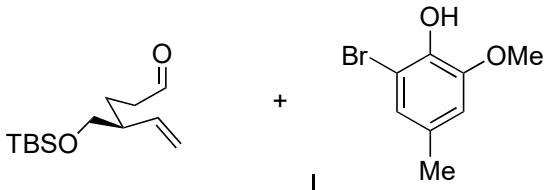


1-5

1) *n*-BuLi
2) $PhI(OAc)_2$, MeOH
3) 180 °C
4) NaH, MeI
5) TBAF *then* IBX

3) Name of the reaction?

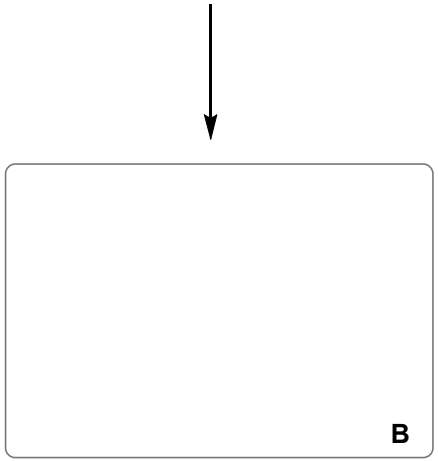
5) Structure of IBX?

A

6-11

6) MeI, *t*-BuOK
7) $EtNH_2$•HCl, $NaBH_3CN$
then NaOH, $(Boc)_2O$
8) $LiAlH_4$
9) *p*-TsOH
10) SmI_2
11) O_3, $FeSO_4$•$7H_2O$, MeOH,
4-methoxybenzenethiol

11) Who developed this protocol?



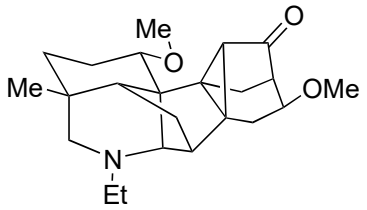
12-18

12) TFA
13) LDA, Mander´s reagent
14) Cs_2CO_3, MVK
15) KHMDS
16) $TiCl_4$, MeOH
17) $LiAlH_4$
18) AZADO, CuCl, bpy, DMAP, air

12) Name of the reaction?
hint Two new rings are formed

18) Name of the reaction?

19-27



vilmoraconitine

19) $(EtO)_2P(O)CH_2CN$, LDA
20) TMSOTf
21) I_2, $NaHCO_3$, THF/H_2O
22) TMP, TBSOTf
then 150 °C *then* *p*-TsOH
23) $NaBH_4$
24) MeI, *t*-BuOK
25) LDA, O_2 *then* $SnCl_2$, aq. Na_2CO_3
26) $LiAlH_4$
27) AZADO, CuCl, bpy, DMAP