Total Synthesis of the Tetracyclic Pyridinium Alkaloid *epi*-Tetradehydrohalicyclamine B

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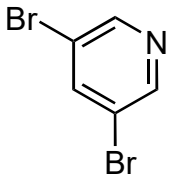
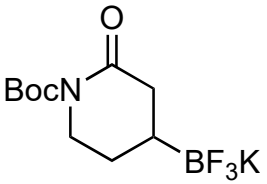


1-7

A

8-11

1) *i*-PrMgCl•LiCl
2) allyl bromide, CuCN•2 LiCl (1 mol %)
3) BF_3•Et_2O *then* 9-BBN
4) TMEDA, H_2O_2, NaOH
5) DMP
6) Bestmann-Ohira reagent, K_2CO_3, MeOH
7) LiHMDS *then* MeI



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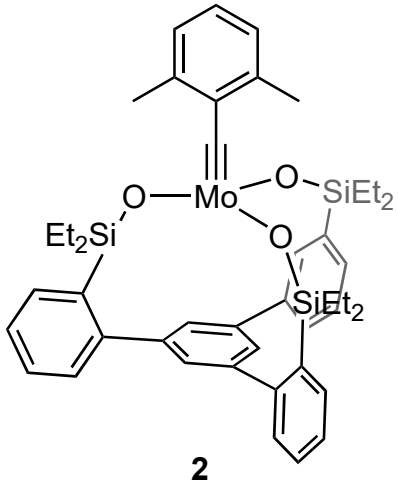
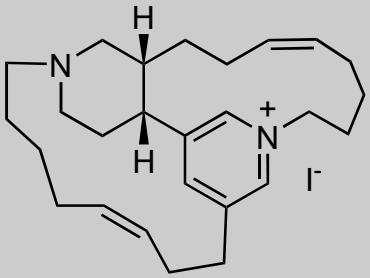


2

8) **1**, $NiCl_2$•DME/dtbbpy (3 mol %), Cs_2CO_3, $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1 mol %)
9) TFA
10) NaH, 7-iodo-2-heptyne
11) **2** (30 mol %)

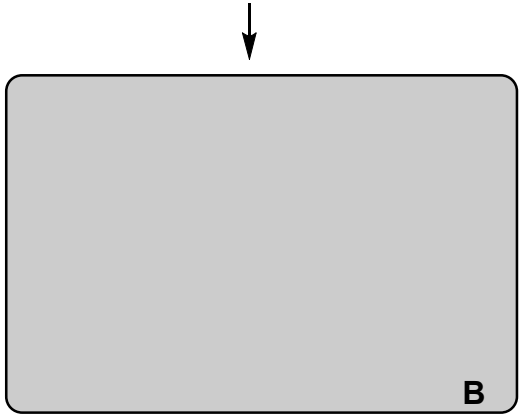
1) Name the starting material

3) HINT - temporary protecting group
3) Draw 9-BBN

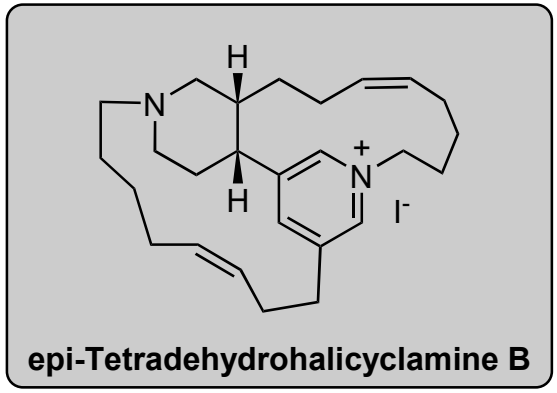


epi-Tetradehydrohalicyclamine B

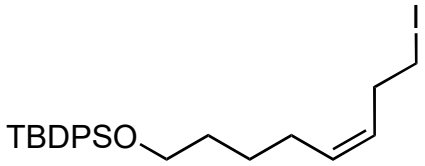
8) Propose a reaction mechanism (using words is fine)



12-18



epi-Tetradehydrohalicyclamine B



3

12) LDA *then* **3**
13) $Ni(OAc)_2 \cdot H_2O$, $NaBH_4$, H_2, $C_2H_4(NH_2)_2$
14) $[IrCl(CO)(PPh_3)_2]$ (12 mol %), tetramethyldisiloxane
15) $NaCNBH_3$, HOAc
16) TBAF
17) I_2, PPh_3, imidazole
18) MeCN (reflux)

12) HINT - single *trans* product
13) HINT - ν = 1637 cm^{-1}
14) Name the catalyst;
HINT - product contains a new alkene