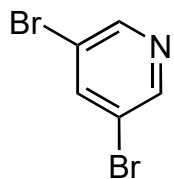
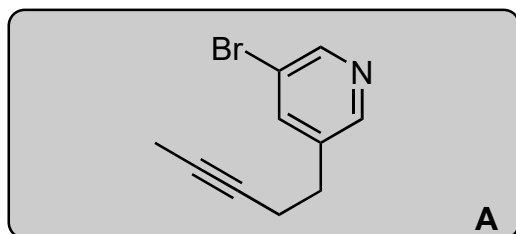


Total Synthesis of the Tetracyclic Pyridinium Alkaloid *epi*-Tetradehydrohalicyclamine B

Dalling, A. G.; Späth, G.; Fürstner, A.
Angew. Chem. Int. Ed. **2022**, *61*, e202209651.

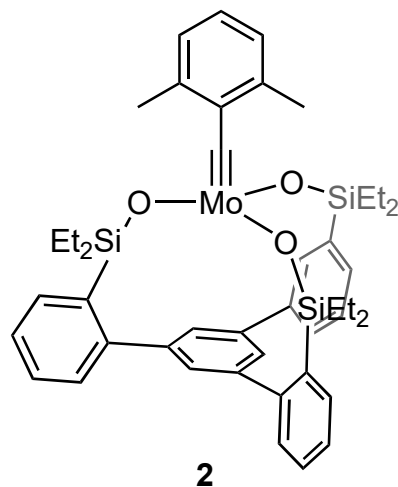
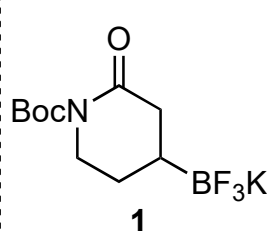


1-7



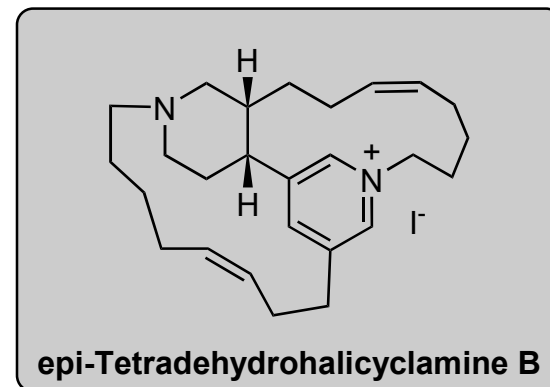
8-11

- 1) *i*-PrMgCl•LiCl
- 2) allyl bromide, CuCN•2 LiCl (1 mol %)
- 3) BF₃•Et₂O *then* 9-BBN
- 4) TMEDA, H₂O₂, NaOH
- 5) DMP
- 6) Bestmann-Ohira reagent, K₂CO₃, MeOH
- 7) LiHMDS *then* MeI

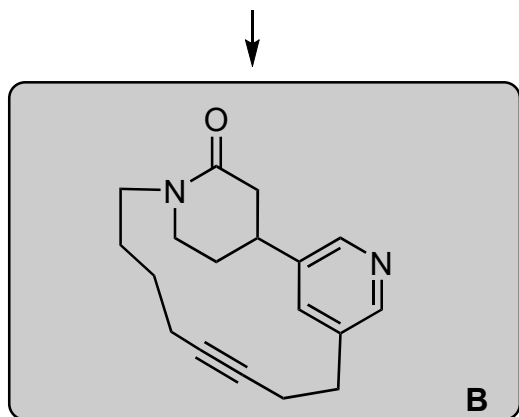


- 8) **1**, NiCl₂•DME/dtbbpy (3 mol %), Cs₂CO₃, [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (1 mol %)
- 9) TFA
- 10) NaH, 7-iodo-2-heptyne
- 11) **2** (30 mol %)

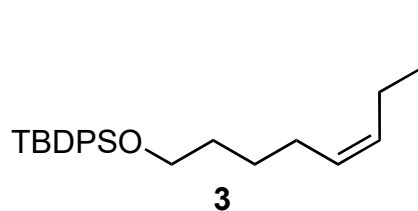
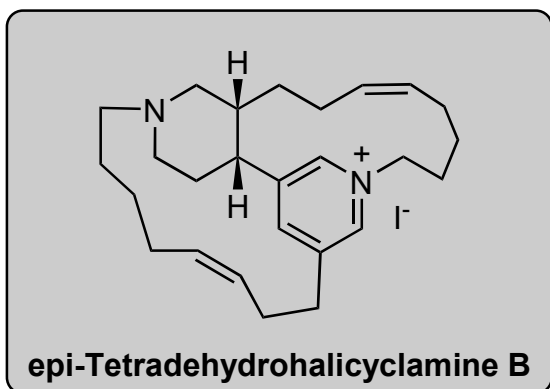
- 1) Name the starting material
- 3) HINT - temporary protecting group
- 3) Draw 9-BBN



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



↓
12-18



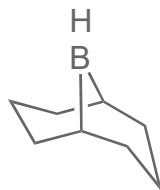
- 12) LDA then **3**
- 13) Ni(OAc)₂•H₂O, NaBH₄, H₂, C₂H₄(NH₂)₂
- 14) [IrCl(CO)(PPh₃)₂] (12 mol %),
tetramethyldisiloxane
- 15) NaCNBH₃, HOAc
- 16) TBAF
- 17) I₂, PPh₃, imidazole
- 18) MeCN (reflux)

please color the solutions grey. this makes it easier for the viewer to quickly find the solutions

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

solution to step 1: 3,5-dibromopyridine

solution to step 3:



solution to step 8: Ni OA into pyridyl bromide and Ir oxidation of BF_3K salt to form secondary radical; capture of secondary radical by Ni(II) pyridyl complex to form transient Ni(III) that undergoes RE

solution to step 14: Vaska's complex