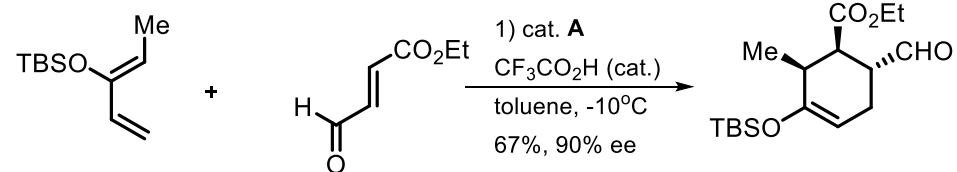


Total synthesis of (+)-Heilonine

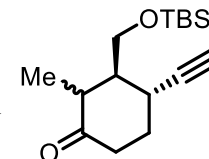
Synthesis of BB1



2) named reagent **B**
(Bestmann-Ohira reagent)
KOEt, THF, -78°C, 84%

3) DIBAL-H, THF
then *n*-Bu₄NF

4) TBSCl, imidazole,
4-DMAP, CH₂Cl₂
90% over 3 and 4



5) TMSI, HMDS

6) **C**, BF₃·OEt₂

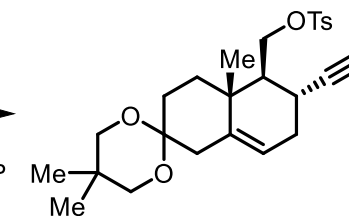
7) NaOMe, MeOH
35% over 6-7

8) neopentyl glycol
PPTS, benzene, 100°C

9) *n*-Bu₄NF, THF

10) *p*-TsCl, Et₃N, 4-DMAP
CHCl₃
79% over 8-10

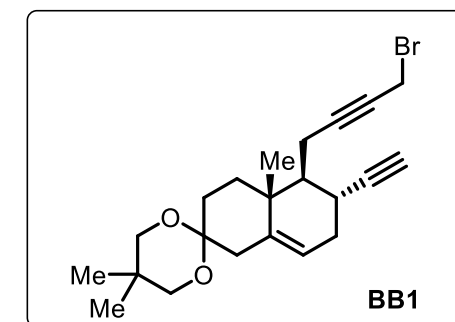
6-7 Robinson annulation



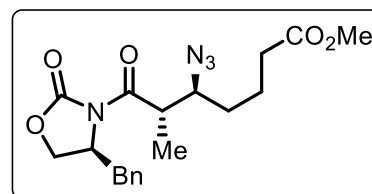
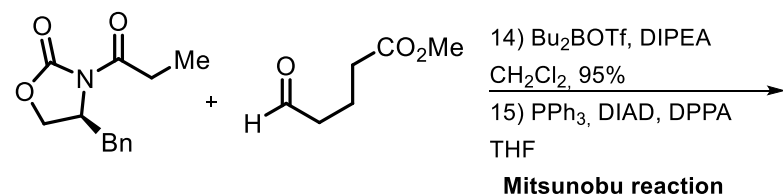
11) **D**, THF, -78°C

12) Bi(OTf)₃, (cat)
CH₃CN, -10°C

13) CBr₄, PPh₃
DIPEA, CH₂Cl₂
58% over 11-13



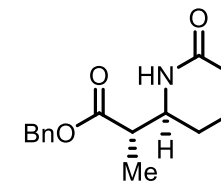
Synthesis of BB2



16) LiOBn, THF
66% over 14 and 15

17) PPh₃, H₂O
THF, 60°C, 89%

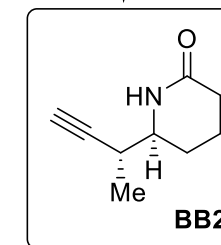
Staudinger reduction



18) LiBH₄, MeOH, THF

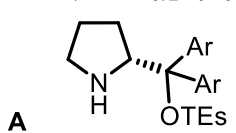
19) DMP, CH₂Cl₂
84% over 17 and 18

20) **B**, KOEt, THF, -78°C
90%

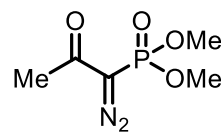


Jorgensen-Hayashi

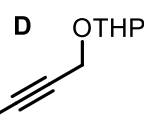
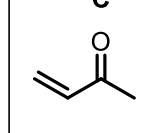
Ar = (3,5-CF₃)₂C₆H₃



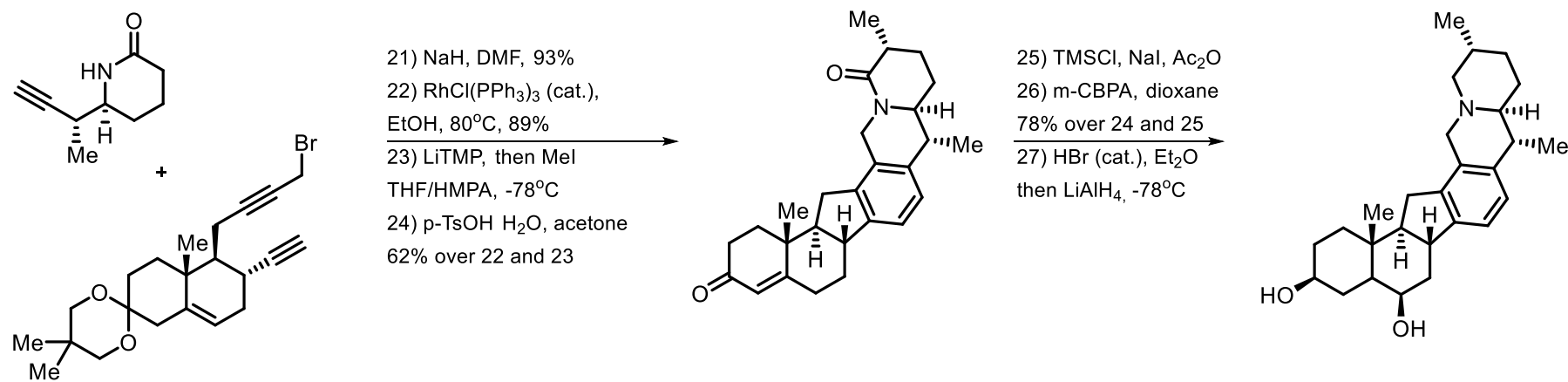
B



C



Total synthesis of (+)-Heilonine



Phototruncation of cyanine dyes (Bonus)

Suggest mechanism of the following light-promoted transformation of cyanine dyes to blue-shifted emissive products

