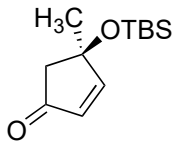
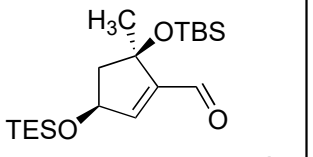
# Asymetric Total Synthesis of Havellocate

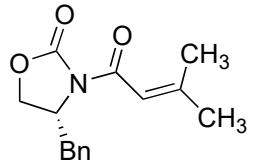
Nicholas J. Hafeman, Melinda Chan, Tyler J. Fulton, Eric J. Alexy, Steven A. Loskot, Scott. C. Virgil, and Brian M. Stoltz, *J. Am. Chem. Soc*. **2022**, *144*, 20232−20236.



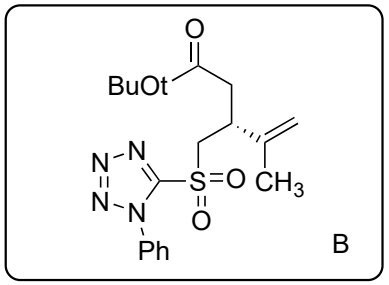

**1–5**




A



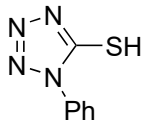

**6-9**




B

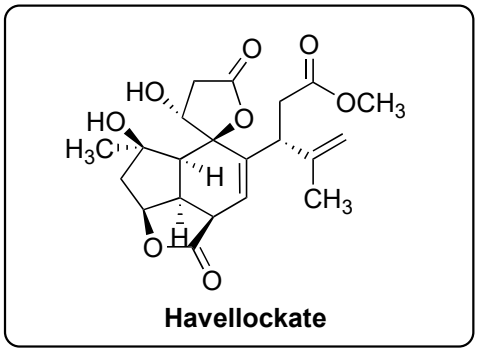
1) $Br_2$, $CH_2Cl_2$ *then* $Et_3N$
2) NaCN, TBAI, $CH_2Cl_2/H_2O$
3) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, MeOH
4) TESCl, imidazole
5) DIBAL

6) NaHMDS, *t*-Bu bromoacetate
7) $LiBH_4$
8) **1**, DIAD, $PPh_3$
9) $H_2O_2$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$




**1**

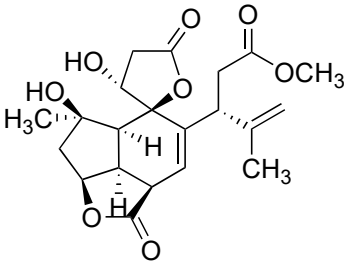
3. Name of the reaction? Luche reduction




**Havellockate**

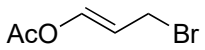
**A+B**

**10-20**



**Havellockate**

10) KHMDS
11) TBAF
12) propiolic acid, DIC, DMAP *then* 110 °C
13) $VO(acac)_2$, TBHP
14) $Cp_2TiCl_2$, $Mn^0$, collidine · HCl, 1,4 cyclohexadiene
15) IBX
16) HCOOH *then* $CH_2N_2$
17) **2**, $Zn^0$, THF
18) NaOMe, MeOH
19) $[Ir(cod)Cl]_2$, $(EtO)_3SiH$ *then* $H_2O_2$, KF, $KHCO_3$
20) $[Cu(MeCN)_4]OTf$, TEMPO, bpy, *N*-methylimidazole, $O_2$



**2**

10. Name of the reaction? Julia-Kociensky reaction

12. Name of the reaction? Steglich esterification

17. Name of the reaction? Barbier allylation

19. Name of the reaction? Tamao-Fleming oxidation

20. Name of the reaction? Stahl oxidation