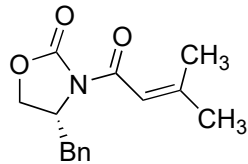
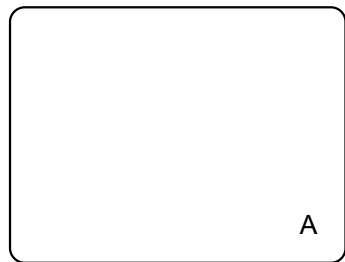
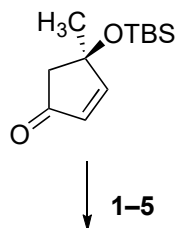


## Asymmetric Total Synthesis of Havellockate

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.



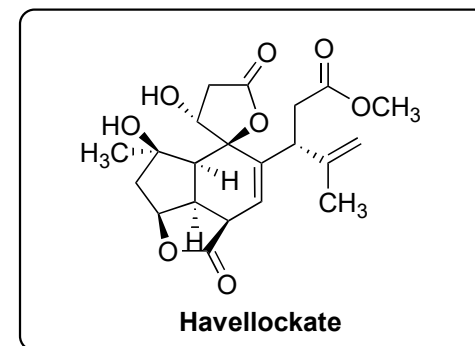
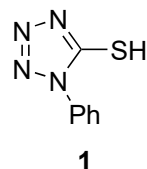
6-9



- 1) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> then Et<sub>3</sub>N
- 2) NaCN, TBAI, CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O
- 3) NaBH<sub>4</sub>, CeCl<sub>3</sub> · 7H<sub>2</sub>O, MeOH
- 4) TESCl, imidazole
- 5) DIBAL

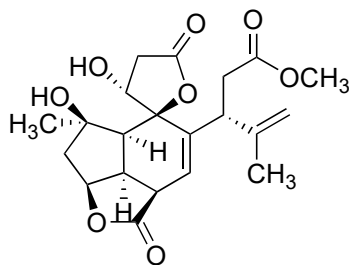
3. Name of the reaction?

- 6) NaHMDS, *t*-Bu bromoacetate
- 7) LiBH<sub>4</sub>
- 8) **1**, DIAD, PPh<sub>3</sub>
- 9) H<sub>2</sub>O<sub>2</sub>, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O



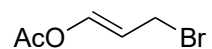
A+B

10-20



Havellockate

- 10) KHMDS
- 11) TBAF
- 12) propionic acid, DIC, DMAP *then* 110 °C
- 13) VO(acac)<sub>2</sub>, TBHP
- 14) Cp<sub>2</sub>TiCl<sub>2</sub>, Mn<sup>0</sup>, collidine · HCl, 1,4 cyclohexadiene
- 15) IBX
- 16) HCOOH *then* CH<sub>2</sub>N<sub>2</sub>
- 17) **2**, Zn<sup>0</sup>, THF
- 18) NaOMe, MeOH
- 19) [Ir(cod)Cl]<sub>2</sub>, (EtO)<sub>3</sub>SiH *then* H<sub>2</sub>O<sub>2</sub>, KF, KHCO<sub>3</sub>
- 20) [Cu(MeCN)<sub>4</sub>]OTf, TEMPO, bpy, *N*-methylimidazole, O<sub>2</sub>



**2**

10. Name of the reaction?

12. Name of the reaction?

17. Name of the reaction?

19. Name of the reaction?

20. Name of the reaction?