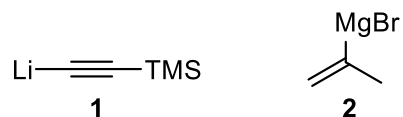
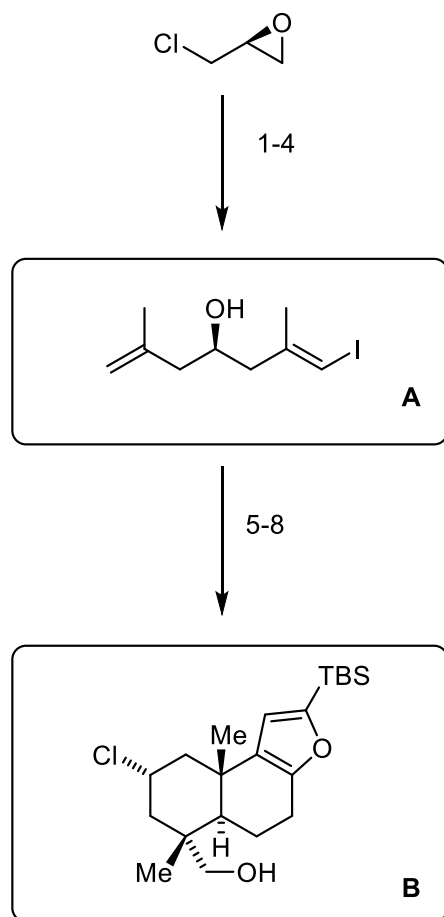
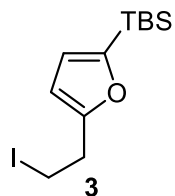


### Total Synthesis of Haterumaimide J

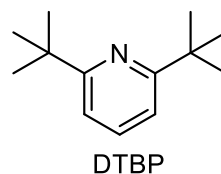
Michalak, S. E.; Nam, S.; Kwon, D. M.; Horne, D. A.; Vanderwal, C. D.  
*J. Am. Chem. Soc.* **2019**, *141*, 9202–9206.



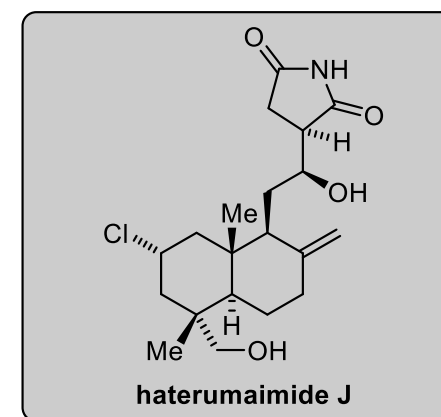
- 1) **1**,  $\text{BF}_3 \cdot \text{OEt}_2$ , THF  $-78^\circ\text{C}$  then NaOH
- 2) **2**, CuI, THF,  $-78^\circ\text{C}$  then  $\text{K}_2\text{CO}_3$ , MeOH
- 3)  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{Me}_3\text{Al}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-45^\circ\text{C}$ . then  $\text{I}_2$
- 4) triphosgene, pyridine,  $\text{CH}_2\text{Cl}_2$ ,  $45^\circ\text{C}$



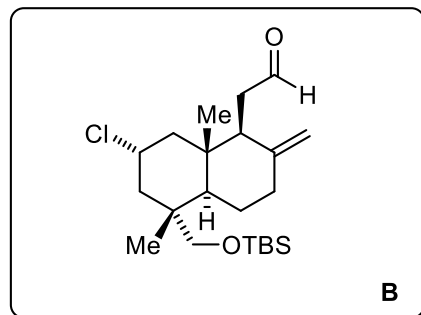
- 5)  $(\text{DHQD})_2\text{PYR}$ ,  $\text{K}_2\text{OsO}_2(\text{OH})_2$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$
- 6) TsCl, DMAP,  $\text{Et}_3\text{N}$ , then  $\text{K}_2\text{CO}_3$ , MeOH
- 7) **3**, *t*-BuLi, 9-BBN-OMe,  $\text{Et}_2\text{O}/\text{THF}$ , then  $\text{Pd}(\text{dppf})\text{Cl}_2$ ,  $\text{K}_3\text{PO}_4$ , DMF
- 8)  $\text{EtAlCl}_2$ , DTBP,  $\text{CH}_2\text{Cl}_2/\text{PhMe}$ ,  $-78^\circ\text{C}$



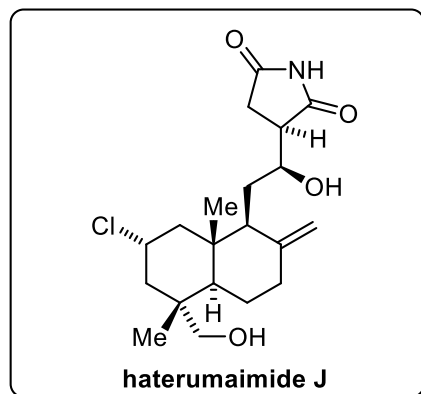
- 1) Name the starting material.  
*(S)*-epichlorohydrin
- 3) Name the reaction  
*Negishi carboalumination*
- 5) Name the reaction - 6:1 syn:anti ratio.  
*Sharpless dihydroxylation*
- 7) Name the reaction, show a mechanism  
*B-alkyl Suzuki coupling*
- 8) Draw a 3 dimensional transition state  
*see last page*



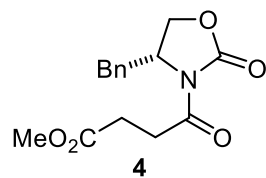
9-13



14-16



- 9) TBSCl, imidazole
- 10) O<sub>2</sub>, rose bengal, hv, CH<sub>2</sub>Cl<sub>2</sub>,  
then TBAF, MeI
- 11) H<sub>2</sub>, Pd/C
- 12) Ph<sub>3</sub>P=CH<sub>2</sub>
- 13) DIBAL-H

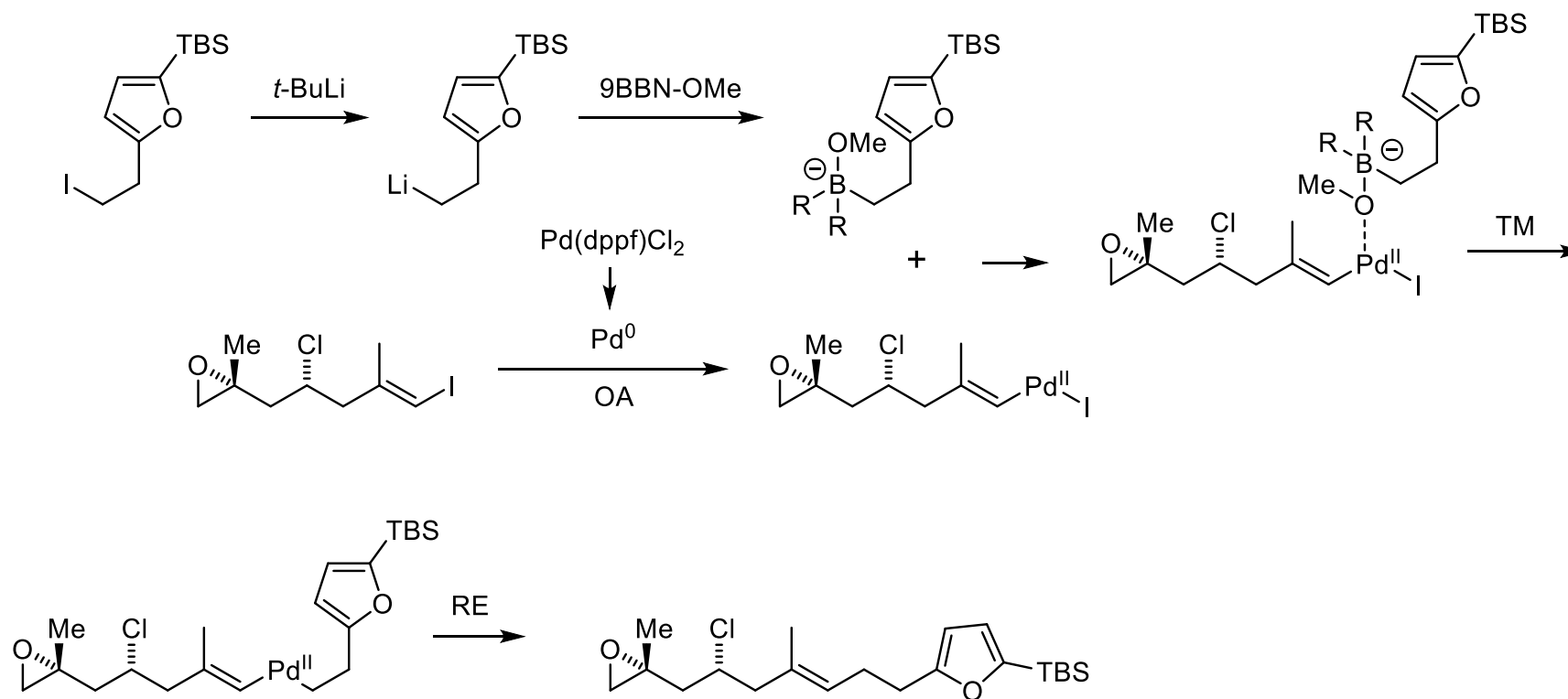


- 14) **4**, Cy<sub>2</sub>BOTf, NEt<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>
- 15) NH<sub>3</sub>/MeOH, then NaH, THF
- 16) HF•pyr

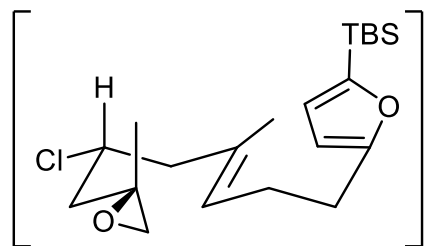
10) What is the role of rose bengal?

*To generate singlet oxygen from triplet oxygen - it's a photosensitizer*

**Mechanism for Step 7:**



**Transition state 8:**



>20:1 dr dictated by the chlorine atom being in the more preferable equatorial position.