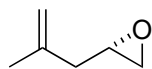
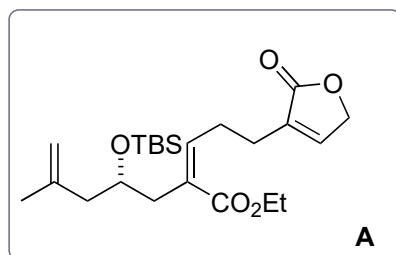


# Asymmetric Total Synthesis of Hispidanin A

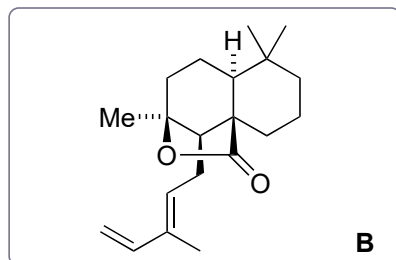
H. Deng, W. Cao, R. Liu, Y. Zhang, B. Liu, *Angew. Chem. Int. Ed.* **2017**, *56*, 5849.



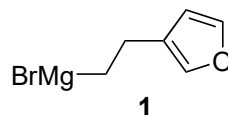
1 – 8



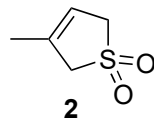
9 – 19



- 1) *n*-BuLi, HCCOEt, BF<sub>3</sub>•OEt<sub>2</sub>
- 2) TBSCl, imH, DMAP
- 3) Au(PPh<sub>3</sub>)Cl, EtOH/THF
- 4) LDA, HCO<sub>2</sub>Et
- 5) LiOH, NMI, TsCl
- 6) FeCl<sub>3</sub>, **1**
- 7) HBr<sub>3</sub>, py, MeOH/CH<sub>2</sub>Cl<sub>2</sub>
- 8) ClCH<sub>2</sub>COOH

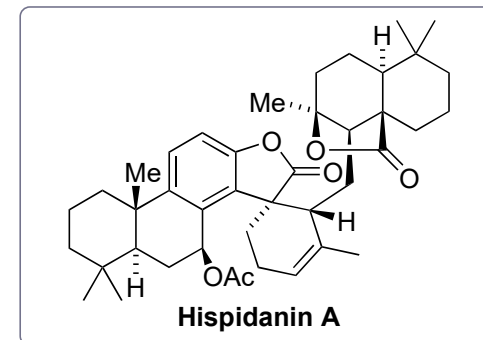
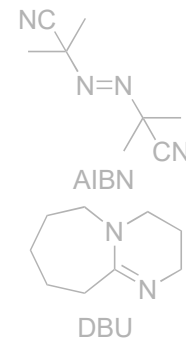


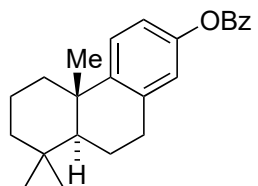
- 9) Fe(acac)<sub>3</sub>, PhSiH<sub>3</sub>
- 10) Py•HF
- 11) PhOC(S)Cl, py, DMAP
- 12) AIBN, *n*-Bu<sub>3</sub>SnH, 110 °C
- 13) DIBAL (1.2 equiv)
- 14) MsCl, NEt<sub>3</sub>
- 15) K<sub>2</sub>OsO<sub>4</sub>•2H<sub>2</sub>O, NMO, NaIO<sub>4</sub>
- 16) DBU
- 17) **2**, LiHMDS, CuI
- 18) py, 110 °C
- 19) MeLi



4) Name of the reaction? Claisen condensation

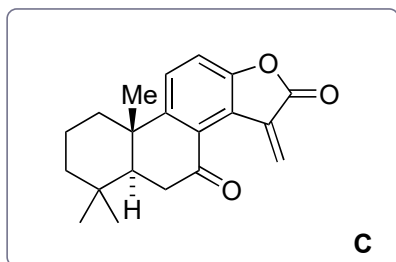
- 9) How does the existing point chirality control the absolute configuration of the product? Draw the transition state. see below
- 12) Name of the reaction? Barton–McCombie deoxygenation
- 12) Structure of AIBN? see below
- 16) Structure of DBU? see below
- 18) Classify the reaction. Cheletropic reaction



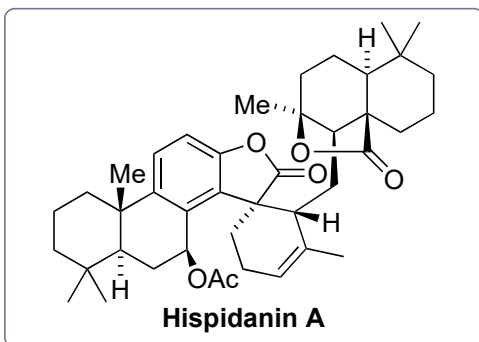


[6 steps from *m*-cresol]

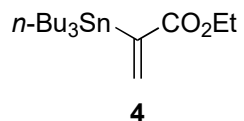
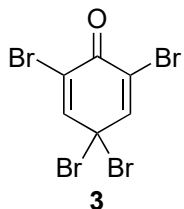
20 – 26



27 – 29



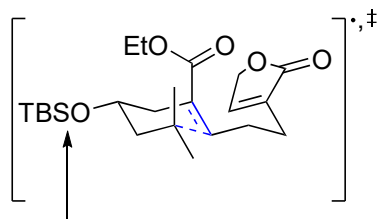
- 20) CrO<sub>3</sub>, HOAc
- 21) LiOH
- 22) **3**
- 23) MOMCl, DIPEA
- 24) PdCl<sub>2</sub>(PhCN)<sub>2</sub>, CuI, Ph<sub>3</sub>As, **4**
- 25) Amberlyst-15, THF/MeOH
- 26) K<sub>2</sub>CO<sub>3</sub>, MeOH



- 27) **B**, 22 °C
- 28) NaBH<sub>4</sub>
- 29) Ac<sub>2</sub>O, MgClO<sub>4</sub>

24) Name of the reaction? Stille coupling

9)



The transition state for formation of the first six-membered ring features a chair conformation. The bulky OTBS group prefers an equatorial position thus dictating the configuration of the newly formed stereocenters (substrate-control).