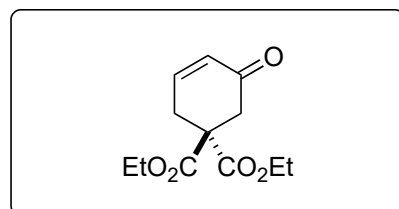


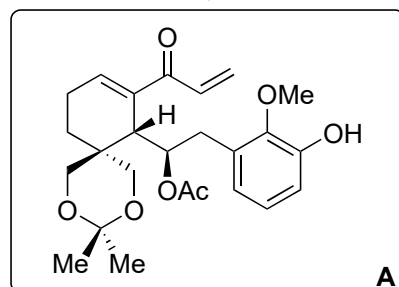
# Asymmetric Total Syntheses of (+)-Davisinol and (+)-18-Benzoyldavisinol: A HAT-Initiated Transannular Redox Radical Approach

Kuan Yu, Fengjie Yao, Qingrui Zeng, Hujun Xie, Hanfeng Ding

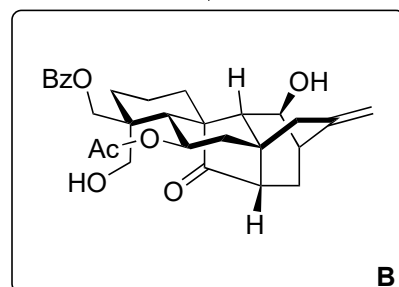
*J. Am. Chem. Soc.* **2021**, *143*, 10576–10581.



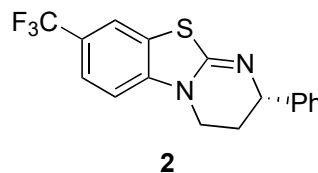
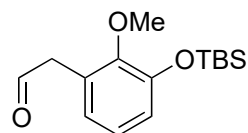
1-6



7-11



- 1) LDA, DIBAL
- 2) 2,2-DMP, PPTS, acetone
- 3) LDA, LiBr, **1**
- 4) Ac<sub>2</sub>O, DIPEA, **2**
- 5) L-Selectride, PhNTf<sub>2</sub>
- 6) [Pd(PPh)<sub>3</sub>]<sub>4</sub>, LiCl, CO, Sn(C<sub>2</sub>H<sub>3</sub>)<sub>4</sub>; TBAF

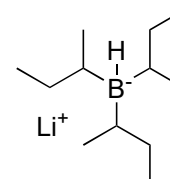


- 7) PhI(OAc)<sub>2</sub>, MeOH
- 8) Co(acac)<sub>2</sub>, TMDSO, O<sub>2</sub>, *i*-PrOH
- 9) Sml<sub>2</sub>, MeOH
- 10) MePPh<sub>3</sub>Br, *t*-BuOK; acidic work-up
- 11) BzCN, DMAP

- 4) Classify the reaction.

Kinetic resolution.

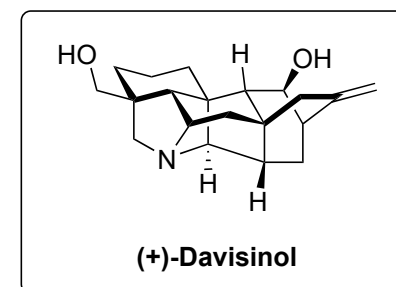
- 5) Give the structure of L-Selectride.

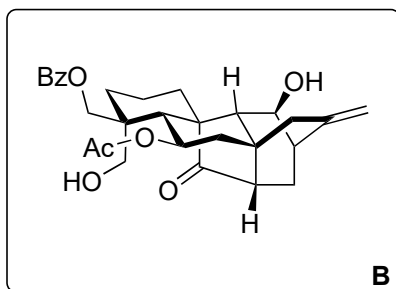


- 6) Name the reaction.

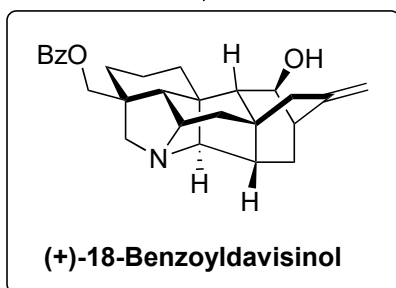
Stille carbonylative cross-coupling.

- 8) Propose a mechanism.

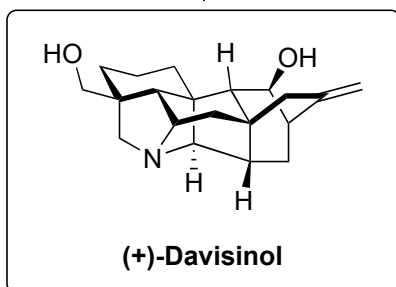




12–16



17

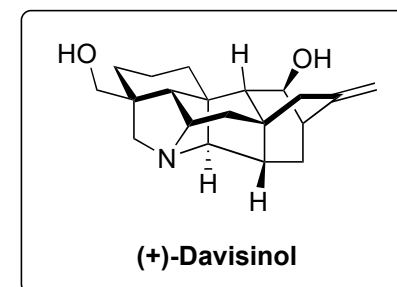


- 12) TEMPO, NCS
- 13) PMBNH<sub>2</sub>, AcOH; NaBH<sub>4</sub>, NaHCO<sub>3</sub>
- 14) TBSOTf, NEt<sub>3</sub>; DDQ
- 15) TCDI, DMAP
- 16) AIBN, *n*-Bu<sub>3</sub>SnH; TFA

- 17) K<sub>2</sub>CO<sub>3</sub>, MeOH

15) Name the newly formed functional group.

Thiocarbamate.



Mechanistic proposal for step 8:

