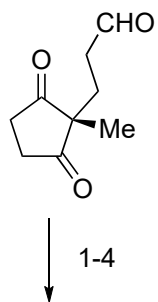
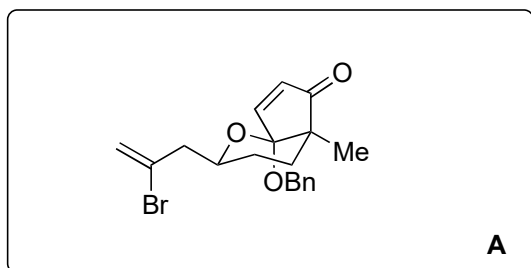


Total Synthesis of Aplysiasecosterol A

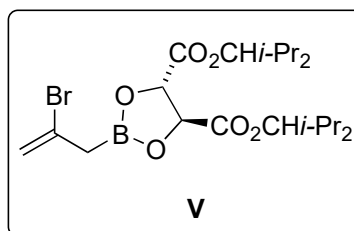
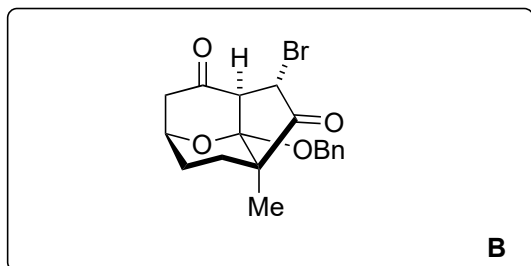
Zhaohong Lu, Xiang Zhang, Zhicong Guo, Yu Chen, Tong Mu, and Ang Li
J. Am. Chem. Soc. **2018**, *140*, 9211-9218.



1-4



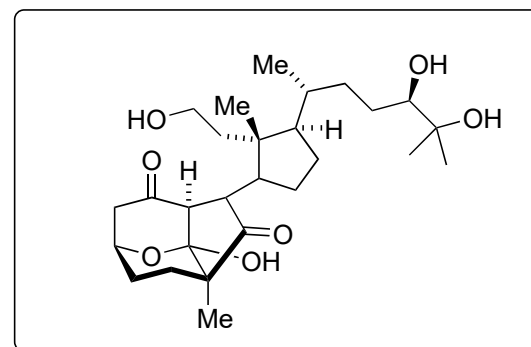
5-8

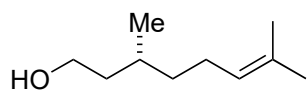


- 1) **V**
- 2) BnOH, MsOH
- 3) TMSOTf, NEt₃
- 4) IBX, MPO

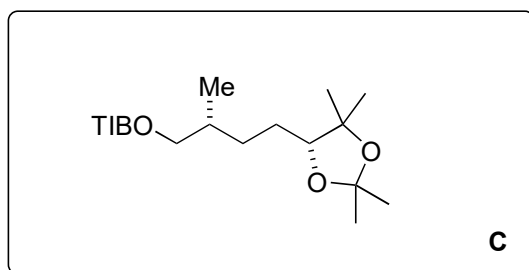
- 5) (TMS)₃SiH, 1,1'-azobis(cyanocyclohexane)
- 6) KHMDS, TMSCl
- 7) NBS
- 8) O₃, SMe₂

hint: more than one transformation takes place in step 1

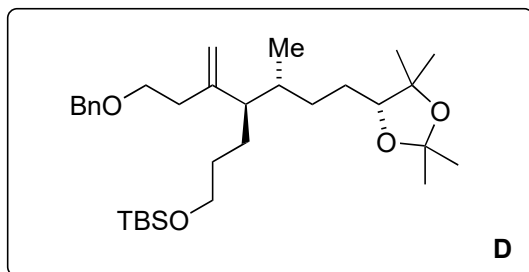




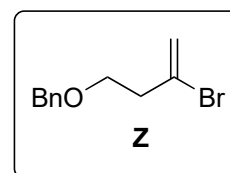
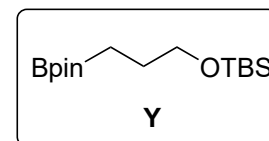
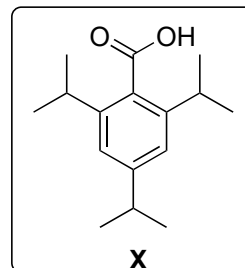
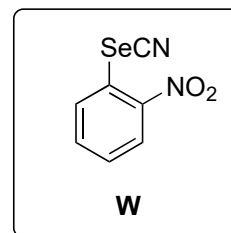
9-13



14-17



- 9) AD-mix- β , MsNH₂
 10) acetone, TsOH
 11) **W**, Bu₃P, *m*-CPBA
 12) O₃, NaBH₄
 13) **X**, PPh₃, DIAD



- 14) (+)-sparteine, *s*-BuLi, **Y**
 15) **Z**, *t*-BuLi, NaOMe, I₂
 16) TBAF, AcOH
 17) DMP

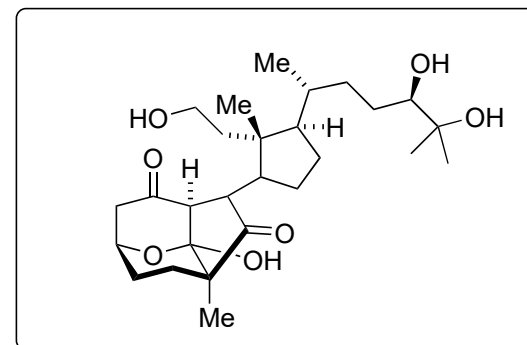
step 13: Name of the reaction?

Mitsunobu reaction

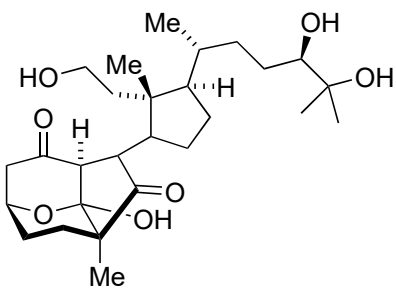
step 15: Name of the reaction?

Draw the mechanism!

Zweifel-Evans-olefination



18-22



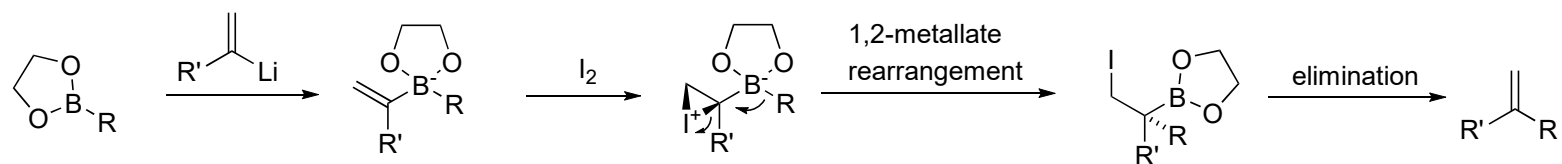
Aplysiasecosterol A

- 18) **B**, Et₃B, air, Bu₃SnH
- 19) Burgess reagent
- 20) Fe(dpm)₃, Ph(*i*-PrO)SiH₂
- 21) aq. HClO₄
- 22) Pd(OH)₂/C, H₂

step 18: draw the mechanism

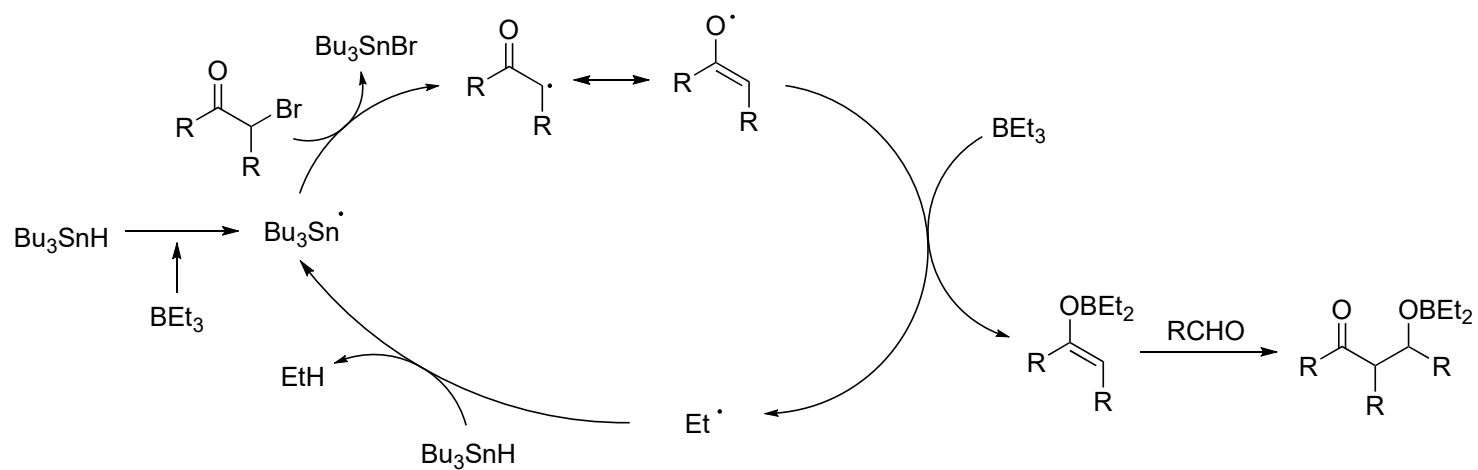
step 20: see *J. Am. Chem. Soc.*, **2014**, *136*,
1304–1307.

Zweifel-Evans-olefination



For a review see: R. J. Armstrong, V. K. Aggarwal *Synthesis*, **2017**, 49, 3323–3336.

Mechanism step 18:



Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, 29, 1041.