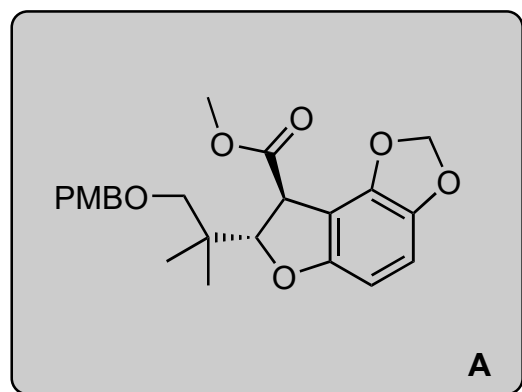
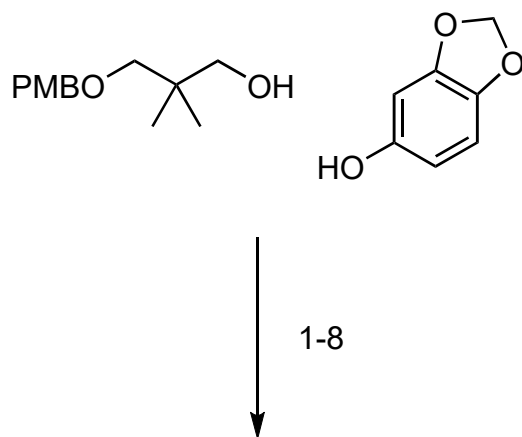


Enantioselective Synthesis of (-)-Maoecrystal V by Enantiodetermining C-H Functionalization

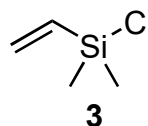
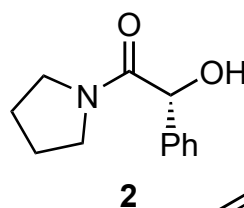
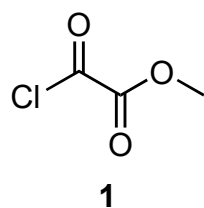
Lu, P.; Mailyan, A.; Gu, Z.; Guptill, D.M.; Wang, H.; Davies, H.M.L.; Zakarian, A.

J. Am. Chem. Soc. **2014**, *136*, 17738–17749.



9-14

- 1) PPh₃, DIAD
- 2) *n*-BuLi, THF; then CuI; then **1**
hint: ortho-ortho
- 3) NaOH, MeOH
- 4) BzCl, NEt₃, PhMe;
then DMAP, **2**
- 5) TsNHNH₂, PhH, azeotropic reflux
- 6) NEt₃
- 7) Rh₂(OAc)₄
hint: note the name of the paper;
- 8) MeOH, NaOMe



- 9) LDA, THF; then Et₂Zn;
then BnOCH₂Cl, DMPU
- 10) LiAlH₄
hint: alcohol
- 11) MeMgBr (excess), PhH, reflux
- 12) PIFA, NaHCO₃, EtOH
- 13) **3**, imidazole
- 14) PhMe, 110 °C

1) What is the name of this reaction?

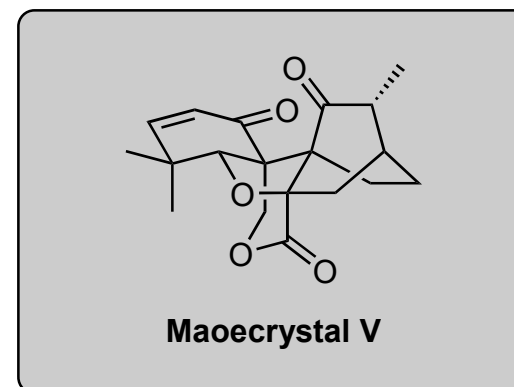
Mitsunobu esterification

4) What is the name of the carboxylic acid that compound **2** is the pyrrolidine amide of?

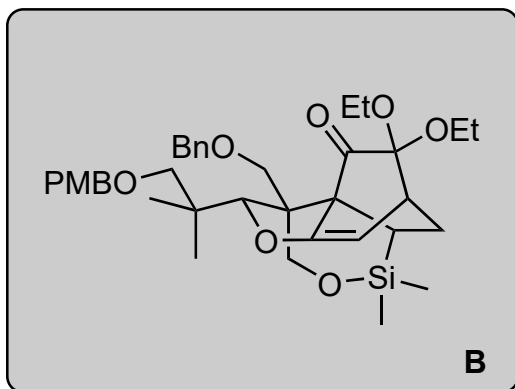
mandelic acid [(*R*)-(-)-D]

11) Rationalize the regiochemical outcome of this reaction.

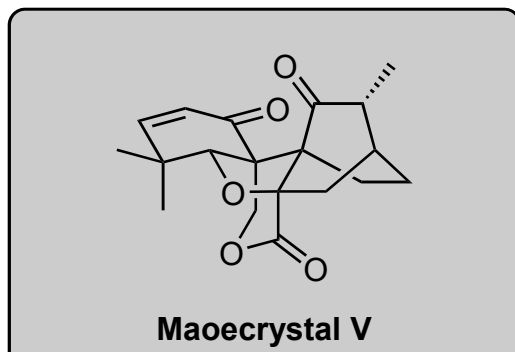
See mechanism below.



14) FRIEDEL-CRAFTS



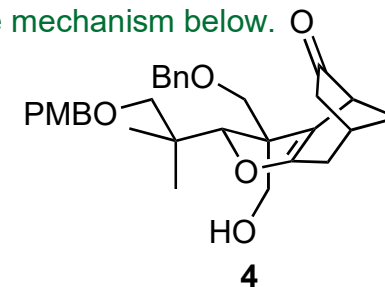
15-28



- 15) SmI_2 (≥ 4 eq.), THF/MeOH
- 16) NBu_4F
hint: two bonds are broken
- 17) CDI
- 18) $(\text{PhSe})_2$, NaBH_4
- 19) $(\text{Me}_3\text{Si})_3\text{SiH}$, AIBN
- 20) DDQ (1 eq.), rt
- 21) DMP
- 22) $\text{CH}_3\text{PPh}_3\text{Br}$, $n\text{-BuLi}$
- 23) LiHMDS , CH_3I
- 24) DDQ (10 eq.), 50°C
- 25) DMP
- 26) vinylmagnesium bromide
- 27) Hoveyda-Grubbs catalyst II
- 28) DMP

- 16) The intended product is formed in 40% yield. The major product, compound **4**, is formed in 45% yield. Propose a mechanism that accounts for this and for the unusual cleavage of a Si-C bond (leading to either products).

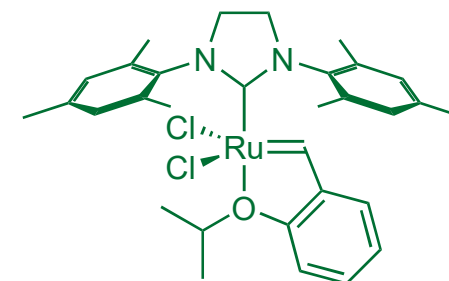
See mechanism below.



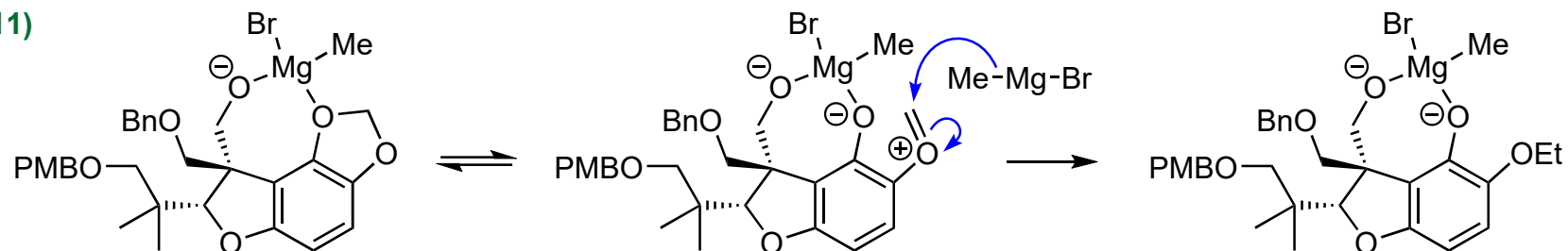
- 19) What type of reaction is this in Baldwin's classification system?

6-exo-trig

- 27) Draw the structure of this catalyst.



11)



Evidence for mechanism from reaction kinetics:

Westera, G.; Blomberg, C.; Bickelhaupt, F. J. *Organomet. Chem.* **1974**, *82*, 291-299.

16)

