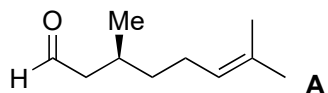


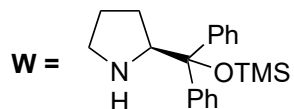
Asymmetric Total Synthesis of Cerorubenic Acid-III
 Liu, X.; Liu, J.; Wu, J.; Huang, G.; Liang, R.; Chung, L. W.; Li, C.-C.
J. Am. Chem. Soc. **2019**, *141*, 2872–2877



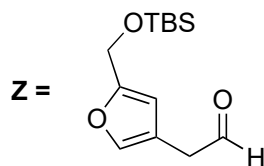
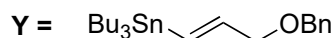
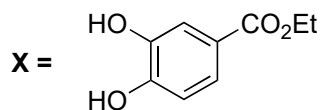
1–4



5–7



- 1) MVK, **W** cat. **X** cat.
- 2) LiOH·H₂O cat. *i*-PrOH
- 3) **Y**, *n*-BuLi then CuCN, MeLi; add substrate then TMSCl, Et₃N
- 4) *n*-BuLi then ZnBr₂, **Z** then DIBAL-H



- 5) PTSA, acetone then TBAF
- 6) VO(acac)₂ cat. *t*-BuOOH then Ac₂O, DMAP, Et₃N
- 7) TMP, MeCN, 170 °C

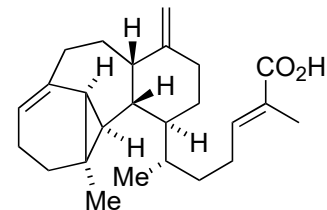
Name of the starting material?

Please provide the mechanism of the reaction in **Step 1 and 2**.

Please provide the mechanism of the reaction in **Step 3 and 4**.

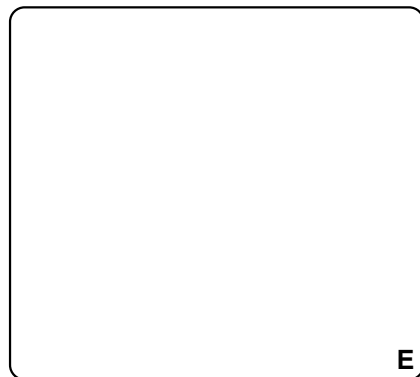
Please provide the name and mechanism of the reaction in **Step 6**.

Key step: Please classify the reaction in **Step 7** and provide a mechanism.

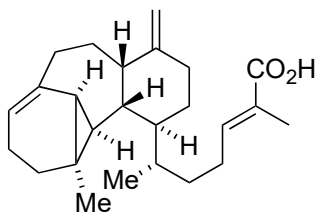


Cerorubenic Acid-III

8–13



14–19



Cerorubenic Acid-III

- 8) DIBAL-H
- 9) KHMDS, THF, 0 °C *then* 1-tosylimidazole *then* LiBr
- 10) sodium naphthalenide, H₂O, THF
- 11) TBSOTf, Et₃N *then* KHMDS
1-tosylimidazole *then* TBAF
- 12) DMP
- 13) *t*-BuOK, *t*-BuOH

- 14) N₂H₄•H₂O, KOH, (CH₂OMe)₂, 190 °C
then AcOH:H₂O:THF (4:2:1), RT
- 15) Ac₂O, DMAP, Et₃N *then* DMP
- 16) KHMDS
- 17) NiCl₂•6H₂O, NaBH₄, MeOH
- 18) CH₃PPh₃Br, *n*-BuLi
- 19) methacrylaldehyde, Grubbs II *then* AgNO₃, NaOH

Hint: sodium naphthalenide cleaves in total 2 C–O bonds and reduces a double bond. Under anhydrous conditions a diene can be isolated. Provide its structure.

Please provide the name of the reaction in **Step 14**.