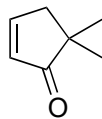


Total Synthesis of *dl*-Coriolin

S. Danishefsky, R. Zamboni, M. Kahn, S. J. Etheredge
J. Am. Chem. Soc. **1980** *102*, 6, 2097–2098.



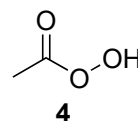
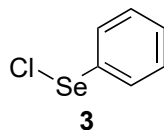
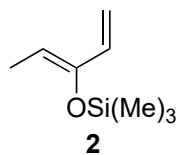
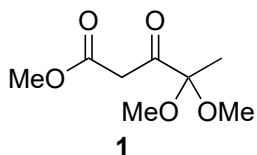
1-4



5-10



- 1) **1**, MeONa, MeOH
- 2) *p*-TsOH, reflux
- 3) **2**, 120 °C
- 4) **3** then **4**



- 5) MeLi (2.5 eq.), -78 °C
- 6) O₃
- 7) CrO₃, aq. H₂SO₄
- 8) Ba(OH₂) (aq.)
- 9) Pb(OAc)₄
- 10) *t*-BuOK, then *p*-TsOH, reflux

2) *Hint*: C₁₅H₂₄O₆ → C₁₁H₁₄O₂

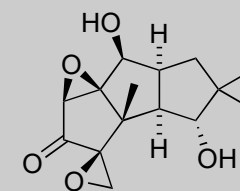
4) Classify this ene reaction.

5) *Hint*: single addition to enone.

7) Name the reaction.

8) *Hint*: decarboxylation of bridgehead β -keto acid.

10) Name the reaction.

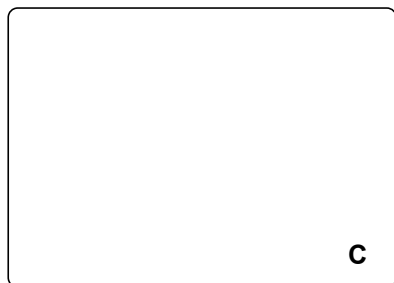


(-)-coriolin

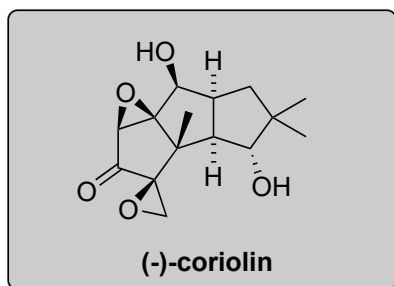
B



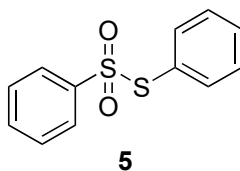
11-16



17-19



- 11) *t*-BuOK
- 12) DIBAL (3 eq.), -78 °C
- 13) Li, NH₃, MeOH
- 14) *m*-CPBA
- 15) PCC (1.5 eq.)
- 16) LDA, 0 °C then **5**, 0 °C



- 17) *m*-CPBA
- 18) reflux
- 19) H₂O₂

- 11) *Hint: deconjugation of enone*
- 12, 13) *Hint: global reduction of carbonyls*
- 14) Rationalize the direction of epoxidation.
- 16) *Hint: first, β-elimination.*

- 18) Classify this ene reaction.