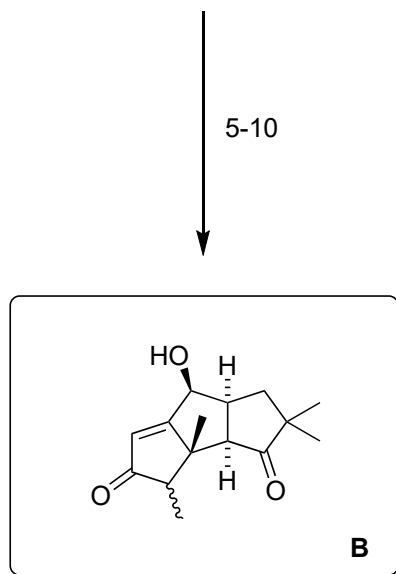
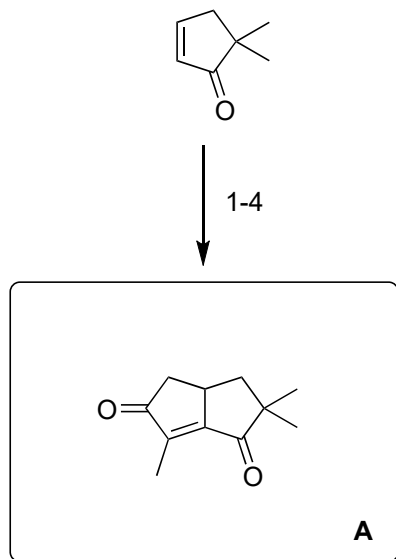
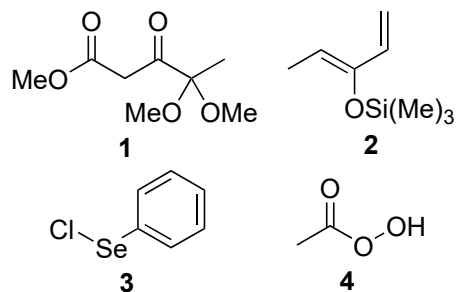


Total Synthesis of *dl*-Coriolin

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



- 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

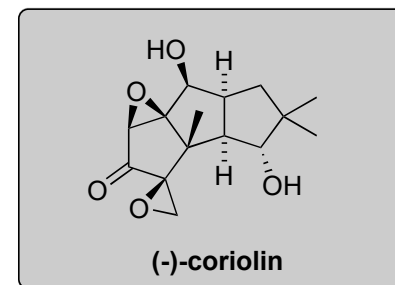
4) Classify this ene reaction. *Retro-ene*, *retro-heteroene*

5) *Hint*: *single addition to enone*.

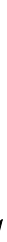
7) Name the reaction. *Jones oxidation*

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

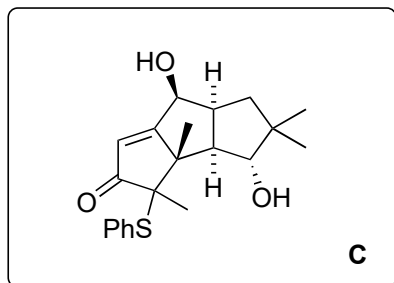
10) Name the reaction. *Aldol condensation*



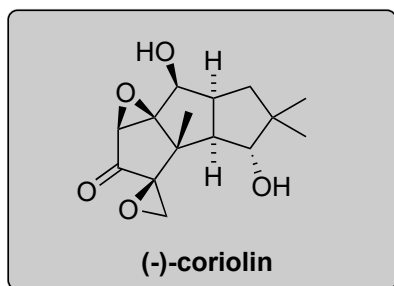
B



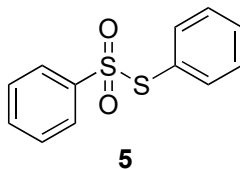
11-16



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. epoxidation of α -face would result in an energetically unacceptable trans ring fusion.

16) *Hint: first, β -elimination.*

18) Classify this ene reaction. Retro-ene, retro-heteroene