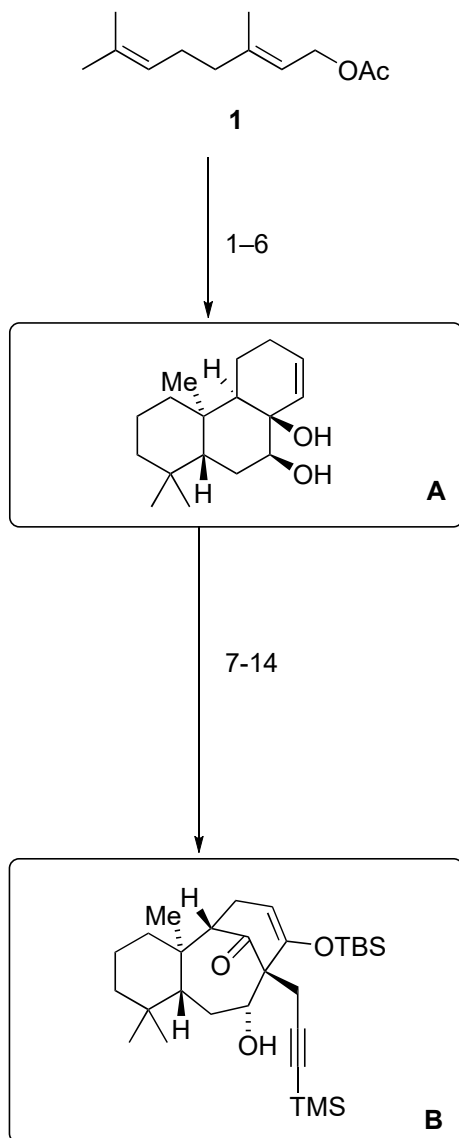
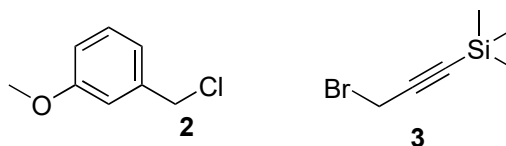


Total Synthesis of Crokonoid A

Martini, T.; Saab, N.; Muschietti, J.; Carreira, E. M., J. Am. Chem. Soc., **2025**, 147, 30606–30612.



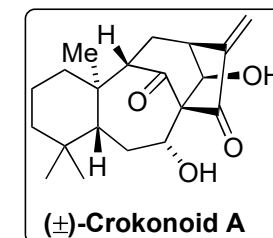
- 1) Mg, **2** (1.9 eq.) *then* to **1**/Li₂CuCl₄, 0 °C
- 2) TiCl₄ (2.0 eq.), 23 °C
- 3) Li, NH₃ *then* PPTS
- 4) Aq. Oxone, aq. NaHCO₃
- 5) H₂O₂, NaOH
- 6) N₂H₄, AcOH



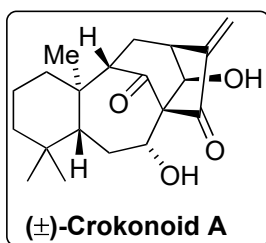
- 7) Pb(OAc)₄
- 8) H₂NOH • H₂O, Pyridine
- 9) PIDA, 1.50 eq. MeOH,
- 10) PhMe, 105 °C
- 11) LiTMP, **3**
- 12) Mo(CO)₃(NCMe)₃ *then* SiO₂
- 13) DMP
- 14) KHMDS, TBSCl *then* NaBH₄

- 2) Hint: A tricyclic compound is formed
- 4) Hint: Two reactions occur
- 5) Name of the reaction? **Scheffer-Weitz Epoxidation**
- 6) Name of the reaction? Mechanism? **Wharton Transposition**

- 7) Name of the reaction? **Criegee Oxidation**
- 9) Hint: Product is directly subjected to 10)
Name of the reactive species? **Nitrile-oxide**
- 10) Name of the reaction? **[5+2]-Dipolar CA**
- 11) pK_a of LiTMP? **~37**
- 13) 3 ¹³C peaks at ~200 ppm



15-23



- 15) DIPEA, TBAI, MOMBr
- 16) TBAF
- 17) $\text{RuCp}(\text{MeCN})_3 \cdot \text{PF}_6$, Bu_3SnH
- 18) I_2 , 2,6-lutidine
- 19) $\text{Pd}_2(\text{dba})_3$, Xantphos, Cs_2CO_3 , 85 °C
- 20) SmI_2 , HMPA, THF-TFE
- 21) SeO_2 , TBHP
- 22) DMP
- 23) aq. HCl

21) Name of the reaction? Mechanism

Riley-Oxidation

