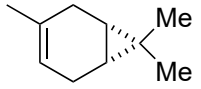
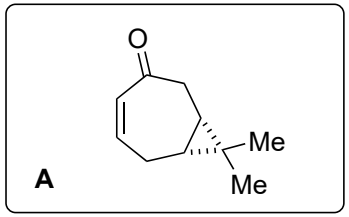
Enantioselective Total Synthesis of (+)-Euphorikanin A

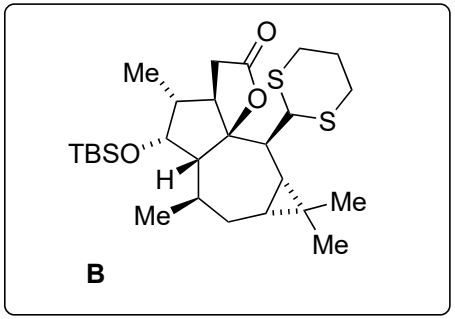
M. J. Classen; M. N. A. Böcker; R. Roth; W. M. Amberg; E. M. Carreira,
J. Am. Chem. Soc. **2021**, *143*, 22, 8261-8265



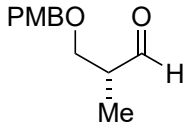
1-4



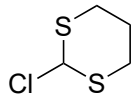
5-11



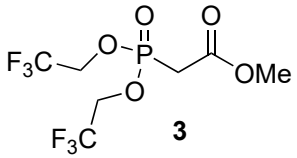
1) O_3 *then* Me_2S *then* $(MeO)_3CH$, $CeCl_3 * 7H_2O$
2) TMSCl, LDA, -78 °C to r.t.
3) $SnCl_4$ (1 eq.)
4) AcOH, 120 °C



1



2



3

5) Me_2CuLi *then* **1**
6) *t*-$BuMe_2SiOTf$, 2,6-lutidine
7) LiHMDS *then* **2**
8) DDQ
9) $SO_3 * py$, Et_3N, CH_2Cl_2, DMSO
10) **3**, KHMDS *then* **previous product**
11) SmI_2

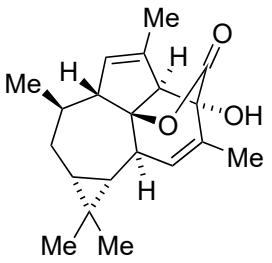
1) Name of the starting material
(+)-3-carene

9) Name reaction? **Parikh-Doering oxidation**

10a) Name reaction? **Still-Gennari**

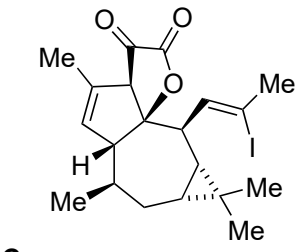
10b) In step 10 the authors first tried a HWE olefination but ended up using the olefination named above. Can you imagine why?

HWE affords E-enoate whereas Still-Gennari affords Z-enoate and the enoate geometry had an effect on the outcome of the cyclization



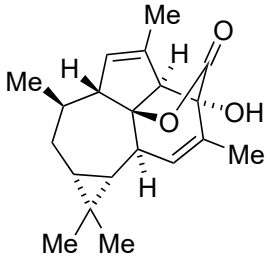
Euphorikanin A

12-18



C

19

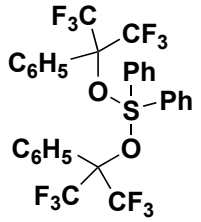


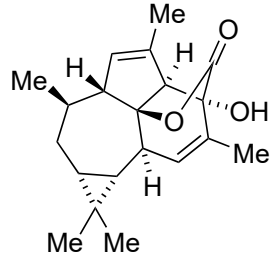
Euphorikanin A

12) PIFA
13) CBr_4, PPh_3
14) TBAF
15) Martin's sulfurane
16) Me_2CuLi *then* I_2
17) $KN(SiMe_3)_2$, Davis oxaziridine
18) DMP

19) *t*-BuLi

15) Structure of Martin's sulfurane and mechanism?





Euphorikanin A