Site-Specific Photochemical Desaturation Enables Divergent Syntheses of *Illicium* Sesquiterpenes

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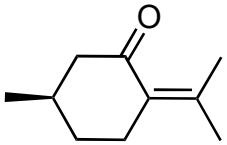


1–2

A

3

B

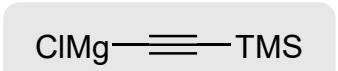
4–7

C

1) Br_2, Et_2O;
then NaOEt
2) KHMDS, HMPA, allyl iodide, THF, –78 °C

3) *m*CPBA, $NaHCO_3$, MeCN, 0 °C;
then $RuCl_3$, $NaIO_4$, r.t.

4) $SOCl_2$, Et_3N, CH_2Cl_2, –78 °C
5) KHMDS; *then* $LiAlH_4$
6) DMP
7) **1**, THF, –78 °C to 23 °C



1

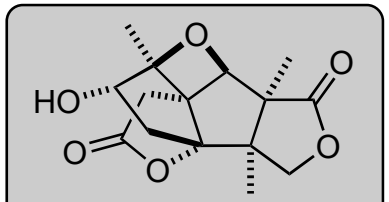
Name the starting material

1) Please name the reaction and describe the mechanism.

3) *hint*: a lactone is formed

5) *hint*: chemoselective reduction

7) Product obtained as single diastereomer; suggest which one and develop a rationale.



merrilactone A

8

D

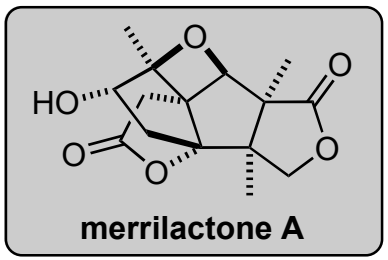
9–11

E

12

F

13



merrilactone A

8) $Pd(OAc)_2$, B_2pin_2, toluene/MeOH, 50 °C;
then H_2O_2, NaOH, THF, 0 °C

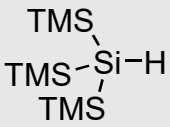
9) *p*-TsOH, MeCN, 23 °C
10) CDI, CH_2Cl_2, 23 °C;
then PhSeNa
11) TTMSS, AIBN, benzene, 80 °C

12) Ph_2CO, NBS, HFIP, violet LED

F is sometimes also referred to as *Danishefsky's intermediate*

13) *m*CPBA, EtOAc, 23 °C;
*then p*TsOH•H_2O, EtOAc/MeOH, 23 °C

8) *hint*:
(a) product chemical formular:
$C_{17}H_{28}O_4Si$
(b) a carbocycle and a quaternary center are formed



TTMSS

12) *hint*:
(a) look at the title
(b) the stereocenter that delivered the chiral information for the synthesis is planarized in this step

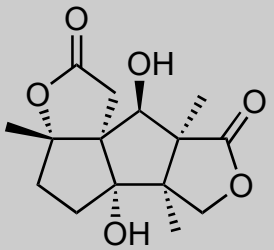
Additional:

F

14

merrilactone B

15



anislactone B

16

anislactone A

14) Ph(*i*PrO)SiH_2, $Co(acac)_2$, O_2, THF, 23 °C

15) K_2CO_3, MeOH, 23 °C;
then HCl

16) K_2CO_3, MeOH, 23 °C;
then HCl

14) Name this reaction

16) *hint*: epimerization