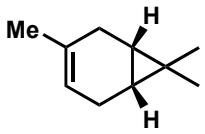
Bioinspired Total Synthesis of (+)-Euphorikanin A

Yanxing Jia et al, ACIE 2022 (accepted manuscript)



(+)-3-Carene

1) *m*CPBA
2) TMP, nBuLi, Et_2AlCl
3) I_2, PPh_3, imidazole
4) $P(OEt)_3$, PhMe, reflux

A

5) O_3, DCM/MeOH, then Me_2S
6) DBU, DCM

B

7) MeLi, CuI
8) NaHMDS, **1**, THF

C

9) $TiCl_4$, Et_3N, **2**

D

10) MOMBr, TBAI, DIPEA
11) 2 M HCl
12) DMP
13) $NaClO_2$, NaH_2PO_4

E

14) 4-PPY, TsCl, Et_3N
15) $LiAlH_4$
16) TBAF, THF

F

hint: F is a tricycle

17) TMSOTf, Ac_2O, -30°C
18) PTSA, MeOH

G

hint: conditions in 17 also affect the MOM protecting group

19) DIBAL
20) IBX

H

step 19: DIBAL reduces only the most accessible acetates

21) $TiCl_4$, Zn, py
22) DIBAL
23) Bobbitt´s salt

I

24) NCS, Me_2S

J

25) Ac_2O, DMAP
26) SeO_2, TBHP

K

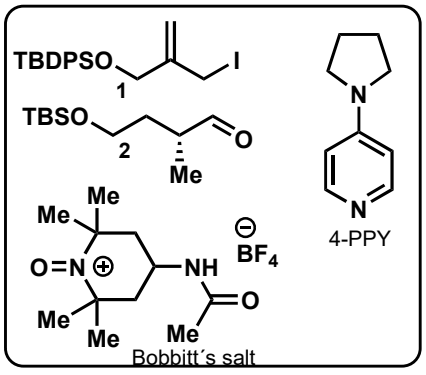
27) Tf_2O, py, then $NaHCO_3$
28) Ac_2O, DMAP, py

L

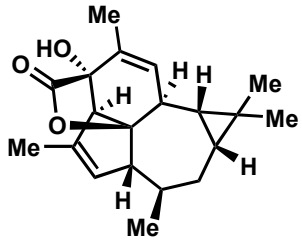
29) $Pd(PtBu_3)_2$, NMO, Et_3SiH, 70°C

M

30) KOH, MeOH



Bobbitt´s salt



(+)-Euphorikanin A