Synthetic Studies on Selective, Proapoptotic Isomalabaricane Triterpenoids Aided by Computational Techniques

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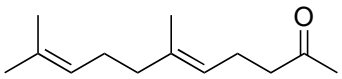


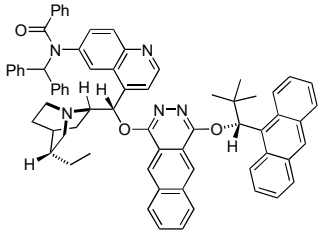
1 – 6

A

7 – 12

B

1) **1**, $K_2OsO_4 \cdot 2H_2O$, K_2CO_3, $K_3[Fe(CN)_6]$, $CH_3SO_2NH_2$
2) MsCl, py, *then* K_2CO_3, MeOH
3) TosMIC, *t*-BuOK, EtOH
4) Cp_2TiCl_2, Zn
5) TBSOTf, 2,6-lutidine
6) LDA, THF/CH_2Cl_2, −100 °C → 60 °C, *then* $LiClO_4$, $CaCO_3$, DMPU, 140 °C

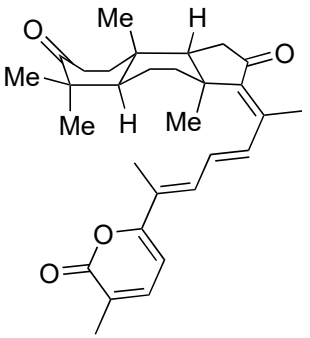


1

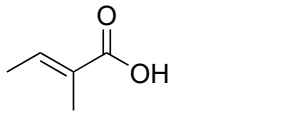
7) C_2H_2, *n*-BuLi, *then* PivCl
8) $Au(PPh_3)Cl$, AgOTf, selectfluor, *then* NH_2NHTs
9) NEt_3, $CHCl_3$/MeOH, *then* catecholborane, AcOH, *then* NaOAc, Δ
10) Cp_2ZrCl_2 (1.3 equiv), *n*-BuLi (2.4 equiv), *then* CuOAc, AcCl
11) $BH_3 \cdot SMe_2$, *then* HF, *then* H_2O_2, NaOH
12) IBX (10 equiv)

1) Name of the starting material?
3) Structure of TosMIC? Name of the reaction? What happens with aldehydes under the same conditions? What change in the experimental procedure needs to be made to get the same product as with ketones?
6) Propose a mechanism. Name of the reaction?

8) Propose a mechanism. Name of the first reaction? Structure of selectfluor?
9) Hint: No fluorine is left in the molecule after NEt_3, $CHCl_3$/MeOH. Who developed this reduction? Classify the reaction.
10) Propose a mechanism.



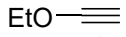
stelletin A



13 – 16

13) $(COCl)_2$, DMF, *then* NEt_3
14) OsO_4, NMO, *then* $PhI(OAc)_2$
15) $BH_3{\bullet}SMe_2$, **2**, Et_2Zn, *then* substrate, *then* aq. HCl
16) LiTMP, $CH_2(Bpin)_2$

13) Hint: Dimerization
14) Name of the reaction?
16) Name of the reaction?



2

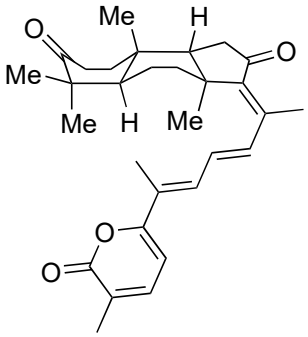
C

B

17 – 18

17) $(COBr)_2$, DMF
18) $Pd(OAc)_2$, PPh_3, TMSOK, **C**

18) Name of the reaction?



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