A General Strategy to Elisabethane Diterpoenes: Stereocontrolled Synthesis of Elisapterosin B via Oxidative Cyclization of an Elizabethin Precursor

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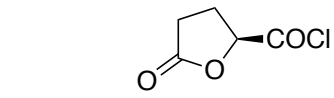


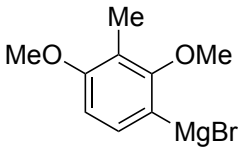
1 – 5

A

6 – 9

B

1) **1** , $ZnCl_2$, $PdCl_2(PPh_3)_2$ cat., THF
2) TsOH cat., $HC(OMe)_3$, THF
3) NaHMDS, NeI, THF
4) DIBAL-H, toluene
5) $(MeO)_2P(O)CHN_2$, *t*-BuOK, THF



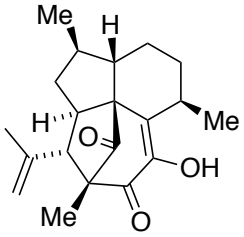
1

6) MsCl, 2,6-lutidine, 50 °C
7) $CaCO_3$, wet MeOH, 50 °C
8) $AgNO_3$ cat., NBS (1 eq.) , acetone, r.t.
9) H_2NNHTs (6 eq.), AcONa (7 eq.), MeOH, reflux

2) Which side product do you expect to occur? Hint: it can be converted back towards the desired product with MeOH, *t*-BuOK.

5) Please name the reaction in step 5 and discribe the Mechanism

8) what is the function of $AgNO_3$?



Elisapterosin B

10 – 15

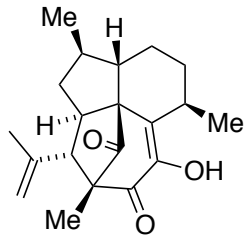
10) *E*-1-bromopropene (1.2 eq.), *t*-BuLi (2.4 eq.), –78 °C
then $ZnCl_2$ (1.2 eq.), $PdCl_2$(dppf) cat., THF, r.t.
11) DIBAL-H, –95 °C
12) *n*-BuLi, $Ph_3PCH(CH_3)_2$, r.t.
13) NaSEt (10 eq.), DMF, 90 °C
14) O_2, Salcomine, DMF, r.t.
15) toluene, 80 °C

13) Please exlain the selectivity of the reaction
Which other methods for this general transformation do you know?
14) Salcomine: Co-Salen complex
15) Please provide the possible transition states of the transformation and discuss which would lead to the desired product. Why is it favoured?

C

16 – 18

16) $Rh(PPh_3)_3Cl$, H_2, PhH, r.t.
17) LiI (2 eq.), 2,6-lutidine, 80 °C
18) CAN, MeCN, 0 °C, 10 min
then pyridine, Et_3N, 50 °C



Elisapterosin B