Asymmetric Total Synthesis of Clionastatins A and B

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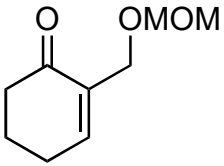


1-5

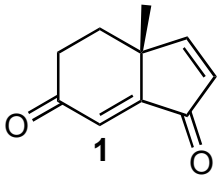
6-8

1) (*R*)-Me-CBS, BH_3•Me_2S
then Ac_2O, DMAP, Et_3N

2) KHMDS, −78 °C
then TMSCl, 23 °C
then 80 °C

3) NMM, *i*-BuOCOCl
then (Ph_2Te_2, DIBAL-H)

4) **1**, Et_3B, air
then MeOH



1

5) Et_3N, Tf_2O

6) $NaBH_4$, $CeCl_3$•$7H_2O$

7) $Pd(OAc)_2$, dppp, PMP
then DMP

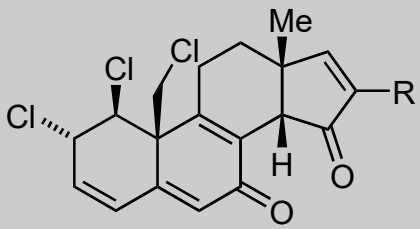
8) 6M HCl, MeOH

1) Name of the reaction

2) Name of the reaction

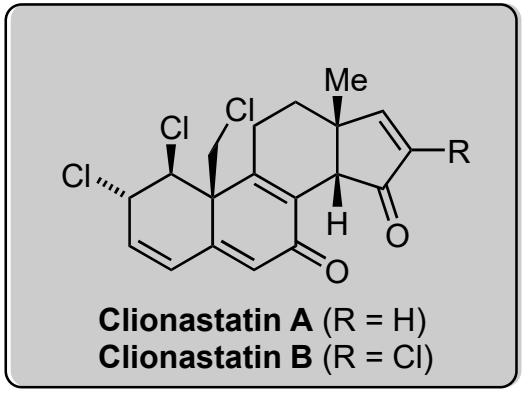
6) Hint: mixture of diols

7) Name of the reaction



Clionastatin A (R = H)
Clionastatin B (R = Cl)

9-17



Clionastatin A (R = H)
Clionastatin B (R = Cl)

9) $SOCl_2$, DMF

10) SeO_2, dioxane

11) Et_4NCl_3 (3.0 eq)

12) Ac_2O, DMAP, Et_3N

13) $TiCl_4$, LiCl

14) PPh_3, CCl_4

15) IBX, Ph_2Se_2
then LiOH

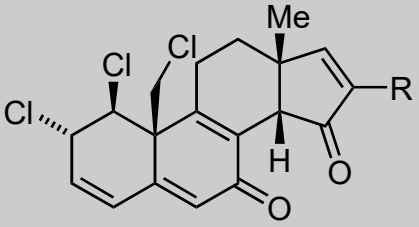
16) Martin sulfurane

17) Et_4NCl_3

9) Hint: Deoxychlorination does not occur; instead, a sultine is formed.
Sultine: cyclic ester of a sulfinic acid.

11) Name of the reagent

16) Structure of Martin sulfurane



Clionastatin A (R = H)
Clionastatin B (R = Cl)