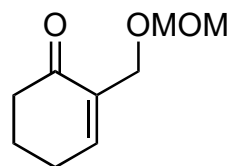


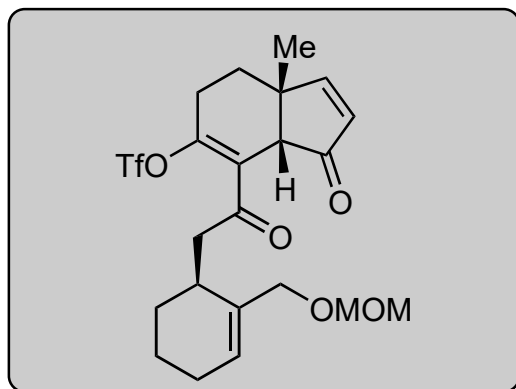
Asymmetric Total Synthesis of Clionastatins A and B

Ju, W.; Wang, X.; Tian, H.; Gui, J.

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1-5



6-8

1) (*R*)-Me-CBS, $\text{BH}_3 \cdot \text{Me}_2\text{S}$
then Ac_2O , DMAP, Et_3N

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

3) NMM, *i*-BuOCOCI
then $(\text{Ph}_2\text{Te}_2, \text{DIBAL-H})$

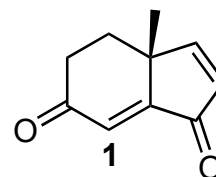
4) **1**, Et_3B , air
then MeOH

5) Et_3N , Tf_2O

6) NaBH_4 , $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$

7) $\text{Pd}(\text{OAc})_2$, dppp, PMP
then DMP

8) 6M HCl, MeOH

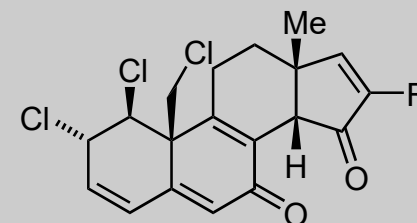


1) Name of the reaction
Corey–Bakshi–Shibata reduction

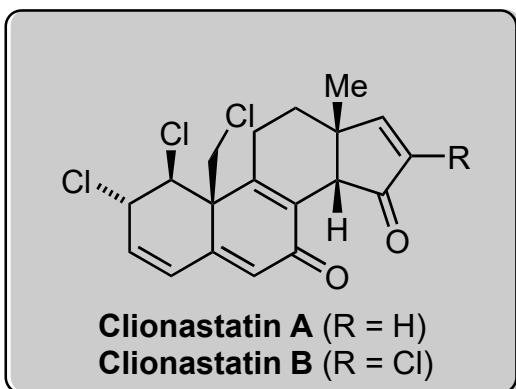
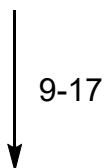
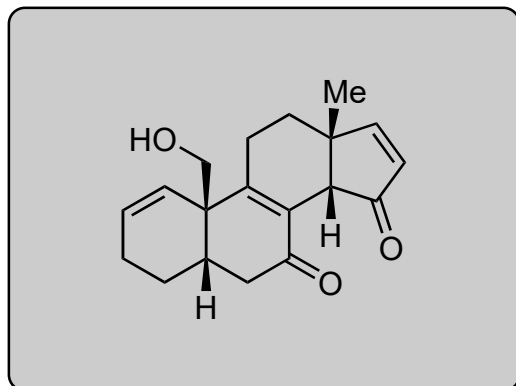
2) Name of the reaction
Ireland–Claisen rearrangement

6) Hint: mixture of diols

7) Name of the reaction
Intramolecular Heck



Clionastatin A ($\text{R} = \text{H}$)
Clionastatin B ($\text{R} = \text{Cl}$)



- 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
Mioskowski reagent

16) Structure of Martin sulfurane

