Two-Stage Syntheses of Clionastatins A and B

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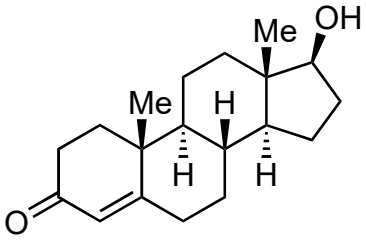


1-6

1) H_2O_2, NaOH *then* AcO_2
2) IBX, NMO
3) $NaBH_4$ *then* PivCl
4) Et_4NCl, oxone
5) 40% HBr
6) $Pb(OAc)_4$, I_2, hv

What is the name of the starting material?

Step 4: What is the name of the in situ prepared reagent for this tranformation

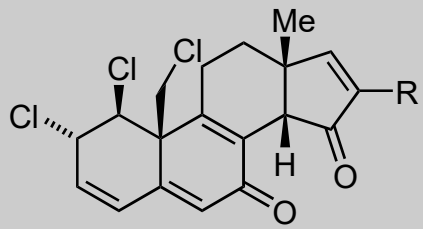
Step 6: *hint - photochemical C-H activation*

Step 9: *hint - key diene formation*

A

7-10

7) Zn, AcOH
8) TBAI, PPh_3, DCE, 120°C
9) NBS, Ph_2CO, MeCN, hv *then* Zn, AcOH
10) AcCl, MeOH *then* DMP



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

B

11-14

C

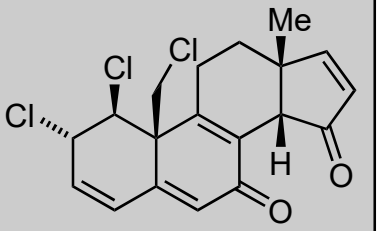
15-16

17-18

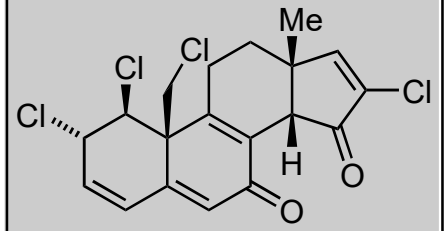
11) TMSOTf, Et_3N *then* $Pd(OAc)_2$
12) TBHP, DBU
13) H_2NNH_2*HCl, Et_3N, MeOH
14) Acr^+ - Mes BF_4^-, $Co(dmgH)_2PyCl$, $MeCN/H_2O$, blue LED (456 nm)

15) DMP, Amberlyst 15
16) SeO_2, $NaHCO_3$

17) *m*-CPBA *then* DMP
18) LiCl, Amberlyst 15 *then* SeO_2



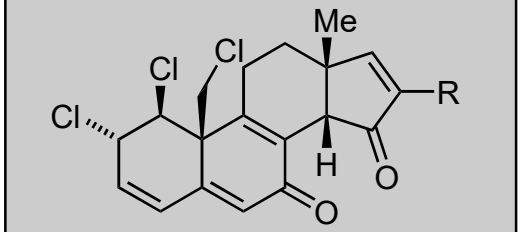
Clionastatin A



Clionastatin B

Step 11: Name of reaction?

Step 14: *hint - double bond oxidation*



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