Total Synthesis of (±)-Myrocin C

Chu-Moyer, M. Y., Danishefsky, S. J., Shulte, G. K.,
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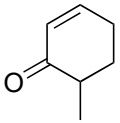


1-4

1) TBSOTf, Et_2NMe
2) *p*-benzoquinone, rt, 5 days
3) DMDO, -78 ºC to 0 ºC
4) $NaBH_4$, $CeCl_3 \bullet 7H_2O$

1: The thermodinamic product was separated and submitted to step 2

Explain the stereochemistry in step 2
Explain the mechanism in step 3
Name the reaction in step 4

A

5-9

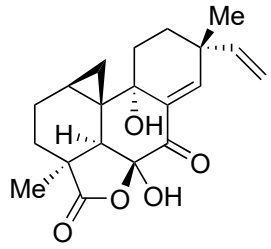
5) Ac_2O, DMAP
6) TBAF
7) $NaIO_4$
8) $NaBH_4$
9) TBSOTf, Et_3N

B

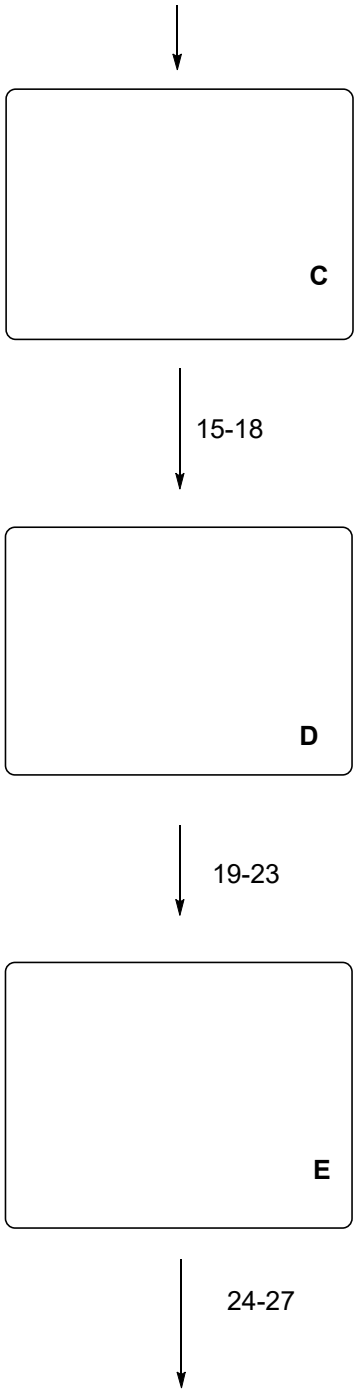
10-14

10) MeONa, MeOH, aq. workup
11) PDC
12) H_2O_2, NaOH, MeOH
13) NaHMDS, Hendrickson–McMurray reagent
14) LiCl, $Bu_3SnCHCH_2$, $Cl_2Pd(PPh_3)_2$

What is the role of LiCl in step 14?



(±)-Myrocin C



15) AcOH, TBAF
16) DMAP, Et_3N, MsCl
17) Me_3SnLi, 1.1 eq, 0 ºC, 5 min.
Then 1.1 more eq, 5 min
18) (*E*)-3-methyl-4-oxobut-2-enoic acid, DCC, DMAP

19) PhH, reflux
20) Ph_3PCH_3Br, NaHMDS
21) DIBALH
22) PDC
23) DIB, I_2, hν

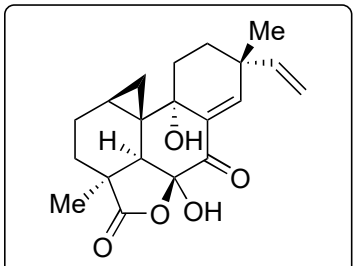
24) AIBN, aged, neat $HSnBu_3$, 80 ºC
25) DMP
26) H_2O_2, NaOH, MeOH
27) *p*-OMe-PhSH, *n*-BuLi, 0 ºC, then Me_3Al, then **25**

What is the role of AcOH in step 15?

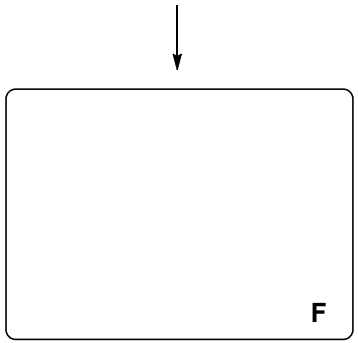
Explain the mechanism in step 17

22: Regioselective reaction

Explain the mechanism and name the reaction in step 23. Last stage of the reaction did not take place. That is one of the roles of step 24.

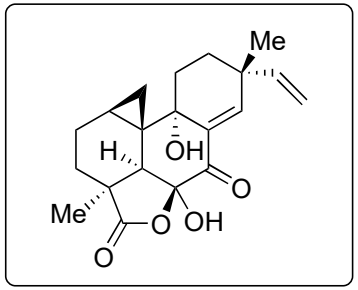


(±)-Myrocin C



28-30

28) DMDO
29) *t*-BuOK, *t*-BuOH, O_2
30) $P(OEt)_3$



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