Total Synthesis of (-)-Bipolarolide D

Chesnokov, G. A.; Friedli, J.; Carta, F. J.; Gademann, K.

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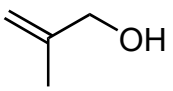


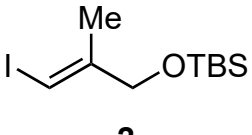
1-6

A

7-10

1) $CH_3C(OEt)_3$, propionic acid (cat.), Δ
then *i*-PrMgCl, $CH_3NH(OMe)HCl$
2) TMS-acetylene, *n*-BuLi
then (*S*,*S*)-Noyori cat., KOH, *i*-PrOH
3) K_2CO_3, MeOH
then NaH, TBAI, MBnCl
4) $Co(CO)_8$
5) **1**, *t*-BuLi, CuI *then* Comin's reagent
6) propargyl alcohol, $Pd(PPh_3)_2Cl_2$, CuI
then Ac_2O, NEt_3

1



2

7) $Au(PPh_3)Cl$, $AgNTf_2$
then AcCl, MeOH, K_2CO_3
8) SO_3Py, NEt_3, $DMSO/CH_2Cl_2$
then Ohira-Bestmann reagent, K_2CO_3
9) $HSnBu_3$, AIBN, Δ *then* CSA
10) LiHMDS, TMSCl
then O_2, $Pd(OAc)_2$

1) Name of the reaction?

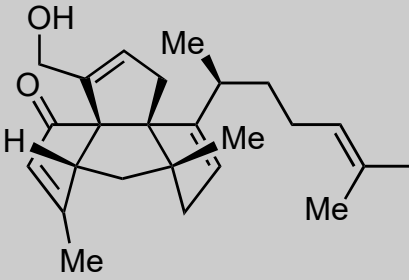
2) *hint: newest stereocenter is (S)-configured*

4) Name of the reaction?

7) Name of the reaction?
hint: higher subsituted olefin formed

8) Name of the reactions?

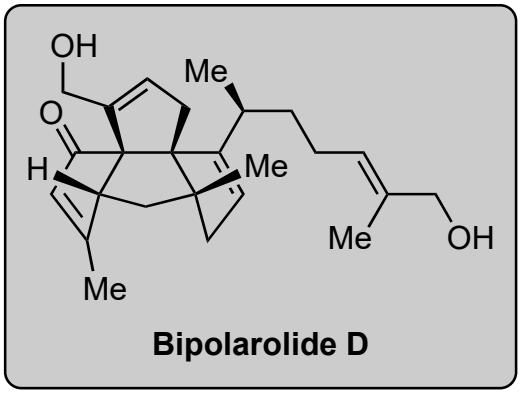
10) Name of the reaction?



Bipolarolide D

B

11-18



Bipolarolide D

11) *m*-CPBA th*en* MeLi
12) LiTMP, Et_2AlCl
13) Imidazole, TBSCl (1.05 eq.)
then Na, NH_3 (l.)
14) PCC, NaOAc
15) crotyl Grignard
16) **2**, 9-BBN then NaOH, $Pd(PPh_3)_4$
17) $SOCl_2$, 2,6-lutidine
18) TBAF

14) Name of the reaction?

15) *hint: compare with NP*