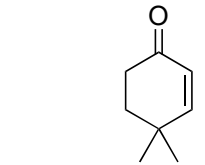
Enantioselective Total Synthesis of Macfarlandin C

Allred, T. K.; Dieskau, A. P.; Zhao, P.; Lackner, G. L.; Overman, L. E. *Angew. Chem., Int. Ed.* **2020**, *59*, 6268-6272.



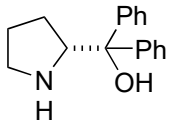
1 - 5

A

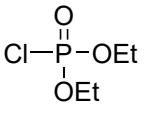
6 - 9

B

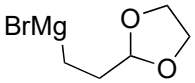
1) I_2, K_2CO_3, DMAP
2) **1**, $B(OMe)_3$, $BH_3 \bullet Et_2NPh$
3) **2**, *N*-methylimidazole
4) **3**, CuCN, LiCl
5) vinylMgBr, $ZnCl_2$, cat. $Pd(Ph_3)_4$



1



2



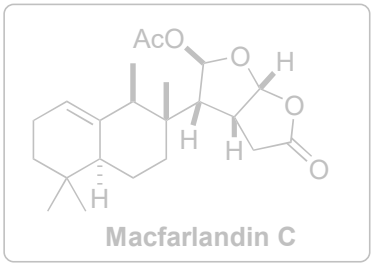
3

6) cat. (η-6-nap)$Cr(CO)_3$, H_2
7) cat. PPTS, H_2O/aceton
8) DMP
9) $MeAl(BHT)_2$, MeMgBr

2) Name of the reaction? Stereochemistry?

4) Mechanism type?

6) *Hint* - migration of double bond.
7) Name of the reaction?
Hint: Two reactions.
9) Name of the Al reagent?

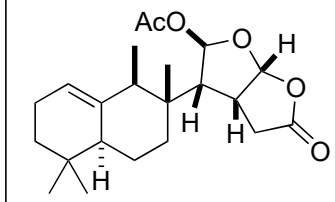


Macfarlandin C

10 - 15

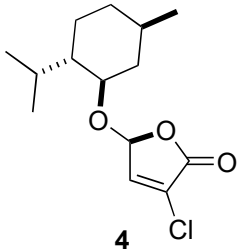
C

16-20



Macfarlandin C

10) $ClOCO_2Me$, cat. DMAP, Et_3N
11) CsOH, THF/H_2O
12) $Ir[dF(CF_3)ppy]_2$, blue LED, **4**
13) $CHOCO_2Et$, LiHMDS
14) cat. DMAP, TFAA, pyridine *then* DBU
15) cat. $Mn(dpm)_3$, $Ph(O\textit{i}\text{-}Pr)SiH_2$, O_2



4

16) LAH
17) PCC
18) HCl, H_2O
19) DMAP, Ac_2O, Et_3N
20) cat. NHC-CuCl, cat. NaO*t*Bu, polymethylhydrosiloxane(PMHS)

14) Mixture of isomers formed
15) Name of the reaction?