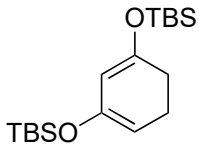
Total Synthesis of Vinigrol

T. J. Maimone, J. Shi, S. Ashida, P. S. Baran, *J. Am. Chem. Soc.* **2009**, *131*, 17066.



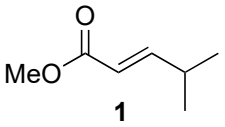
1–7

A

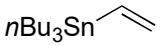
8–13

B

1) $AlCl_3$, **1**
2) LDA, Tf_2O
3) $Pd(PPh_3)_4$, LiCl, **2**
4) DIBAL (2.5 equiv)
5) DMP
6) Allyl-MgCl, *then* Δ
7) DMP

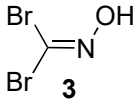


1



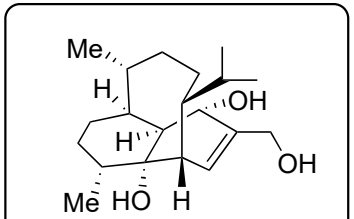
2

8) LDA, MeI
9) TBAF
10) $Me_4NBH(OAc)_3$
11) MsCl, py
12) KHMDS
13) $KHCO_3$, **3**



3

3) Name of the reaction?



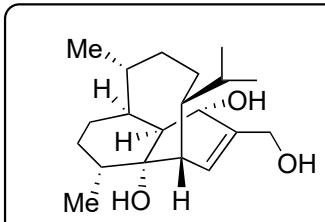
Vinigrol

B

14–21

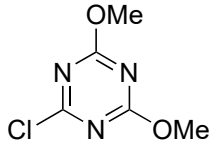
C

22–25



Vinigrol

14) DIBAL (1.2 equiv)
15) Crabtree cat., H_2, $B(O\text{-}i\text{Pr})_3$
16) NaH, CS_2, MeI
17) 180 °C
18) $LiAlH_4$ (20 equiv)
19) HCO_2H, **4**, **5**, DMAP
20) $COCl_2$, NEt_3
21) AIBN, $n\text{-}Bu_3SnH$



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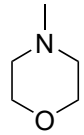

5

22) OsO_4, NMO
23) TEMPO, NaOCl
24) $TrisNHNH_2$
25) *n*-BuLi, TMEDA, *then* $(CH_2O)_n$

15) Write the structure of Crabtree catalyst

23) Hint: chemoselective oxidation of one hydroxy group

25) Name of the reaction?