A Carbene Catalysis Strategy for the Synthesis Protoilludane Natural Products: Total Synthesis of Armillaridin and Isovelleral

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i-PrCHO

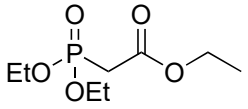
1-5

A

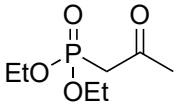
8-14

B

1) morpholine, *p*-TsOH
2) $BrCH_2CHCH_2$
3) NaH, **1**
4) O_3; DMS
5) *i*-Pr_2NEt, LiCl, **2**
6) CuO, I_2
7) $P(OEt)_3$

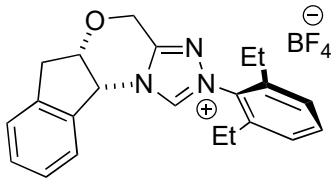


1



2

8) DIBAL-H
9) MnO_2
10) 5 mol% **3**, *i*-Pr_2NEt
11) $LiAl(Ot\text{-}Bu)_3H$
12) H_2, Pd/C
13) $(CH_2O)_n$, $Ba(OH)_2$
14) $TsNBr_2$, $MeCN/H_2O$



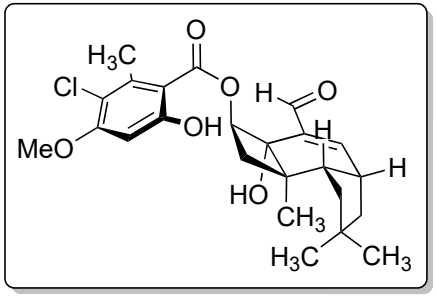
3

Which variant of the HWE reaction represents step 5? What is the role of LiCl?

Step 7: Please name the reaction

Step 10: Please come up with a mechanism

Step 11: How do you prepare the reagent? What is the difference to LAH?

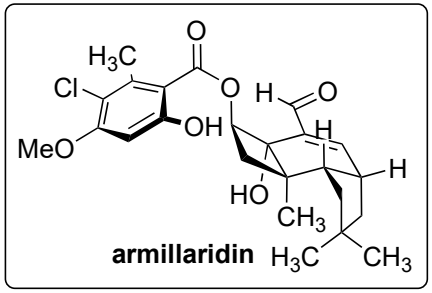


15-22

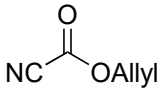
C

28-30

23-27 **isovelleral**



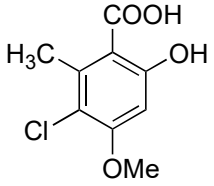
15) TBDPSCl, imH
16) Li_2CO_3, LiBr, DMF
17) LDA, **4**
18) K_2CO_3, MeI
19) $Pd_2(dba)_3$, DPPE
20) OsO_4, NMO
21) $NaIO_4$
22) VCl_3, Zn, HMPA



4

23) DMS, NCS, NEt_3
24) $NaHB(OAc)_3$
25) EDCI, DMAP, **5**
26) TBAF
27) 4-NHAc-TEMPO, *p*-TsOH

28) DIAD, PPh_3, ArCOOH
29) TBAF
30) 4-NHAc-TEMPO, *p*-TsOH

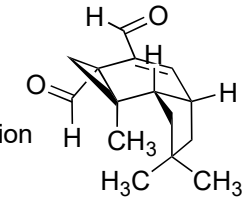


5

Step 19: Please name the reaction. What is DPPE? What could be the drawbacks of direct allylation?

Step 22: Please name the reaction. What is the active Vanadium species?

Step 23 and 28: Please name the reaction



isovelleral

Step 27 and 30: What is the active species in this reaction? What is the advantage of 4-NHAc-TEMPO over TEMPO?