A Concise Synthesis of (−)-Aplyviolene Facilitated by a Strategic Tertiary Radical Conjugate Addition

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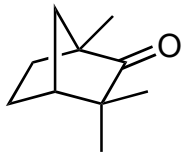
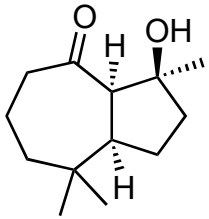
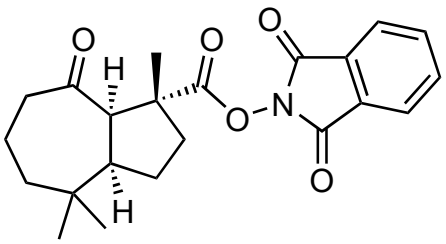


1-8



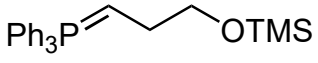
A

9-14

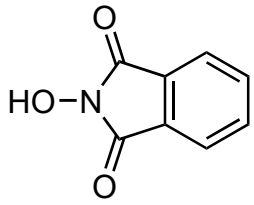


B

1) NH_2OH
2) H_2SO_4, Δ
3) DIBALH
4) **1**; *then* HCl
5) I_2, PPh_3
6) $AgNO_2$
7) PhNCO, Et_3N, Δ
8) Pd/C, Ra-Ni, $B(OH)_3$, H_2



1



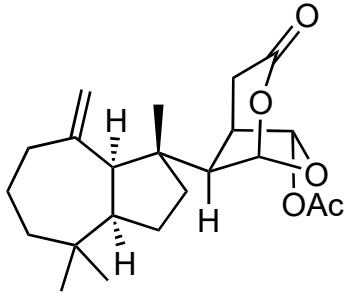
2

9) TsOH, Δ
10) Vinyl-MgBr, CuCN, HMPA
11) $TMSCH_2Li$
12) O_3, *then* PPh_3, HF
13) $NaClO_2$
14) **2**, DCC

2) Beckmann fragmentation

7) PhNCO is a dehydrating agent [3+2] cycloaddition

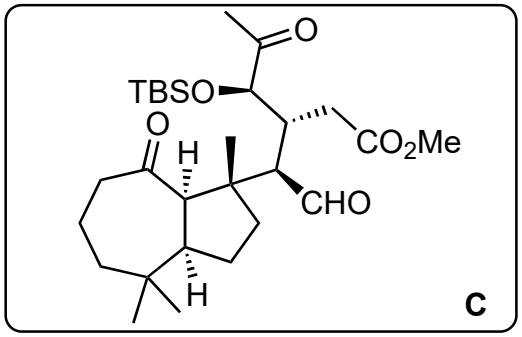
8) Two catalysts do two independent reductions



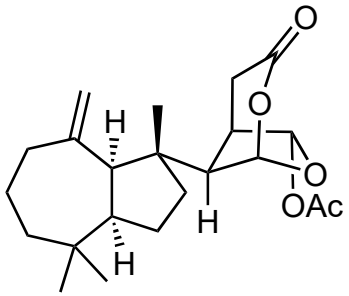
(–)-Aplyviolene

B

15-20

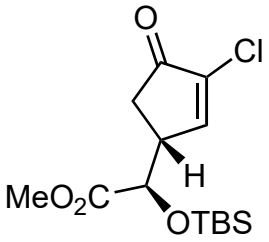


21-25

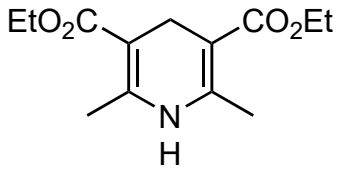


(–)-Aplyviolene

15) **3**, **4**, $[Ru(bpy)_3](BF_4)_2$, DIPEA, blue LEDs
16) $Me_2CuCNLi_2$, TBSCl, HMPA
17) $TiCl_4$, Zn, CH_2Br_2
18) $(CO_2H)_2$
19) OsO_4, NMO
20) $Pb(OAc)_4$



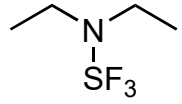
3



4

21) TBAF
22) DAST
23) NaOH
24) $SnCl_2$
25) *m*-CPBA

16) Chloro-ketone to silyl enol ether
17) Similar to Tebbe ester olefination (Takai-Lombardo olefination)



DAST

22) Hemiacetal to anomeric fluoride
24) Lactonization