Total Synthesis of Astellatol

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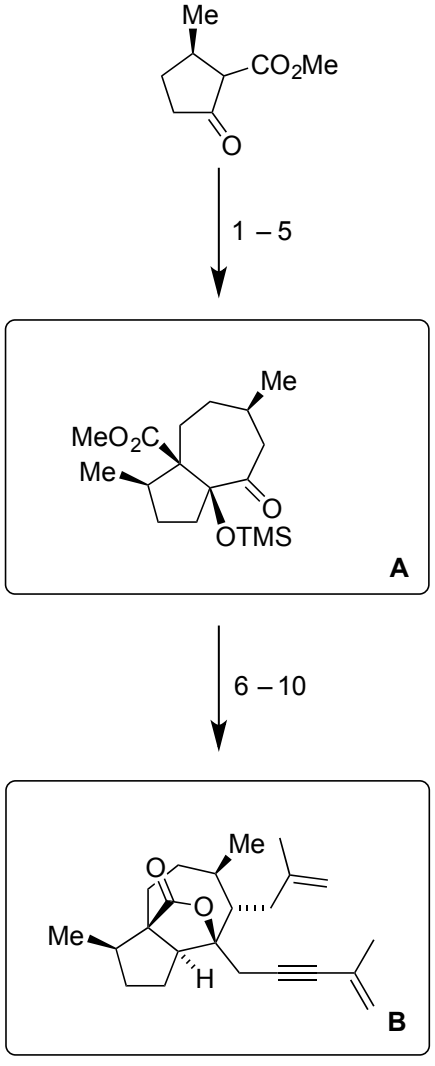
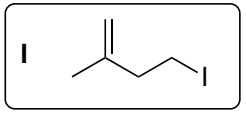
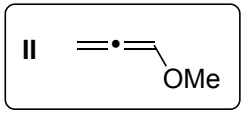


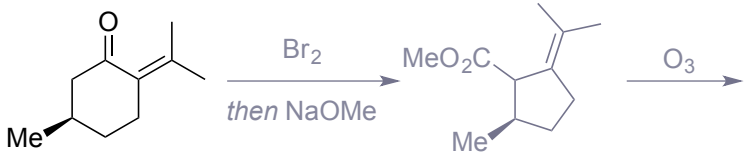
1) **I**, Cs_2CO_3, HMPA
2) **II**, *n*-BuLi
3) TMSOTf, NEt_3, *then* 1M HCl
4) Grubbs II
5) Pd/C, H_2





6) 10% HCl
7) SmI_2
8) LDA, 2-methyl allylbromide
9) Mg, $HgCl_2$ (cat.), propargyl bromide
10) $PdCl_2(PPh_3)_2$, CuI, NEt_3, 2-bromopropene

How could you prepare the starting material from *(R)*-pulegone in 2 steps?

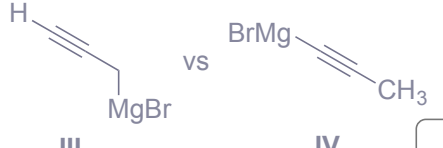


(R)-Pulegone

[Favorskii rearrangement]

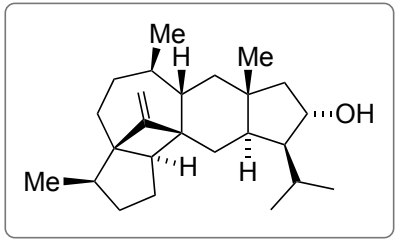
Step 9: Why is $HgCl_2$ added to the reaction?

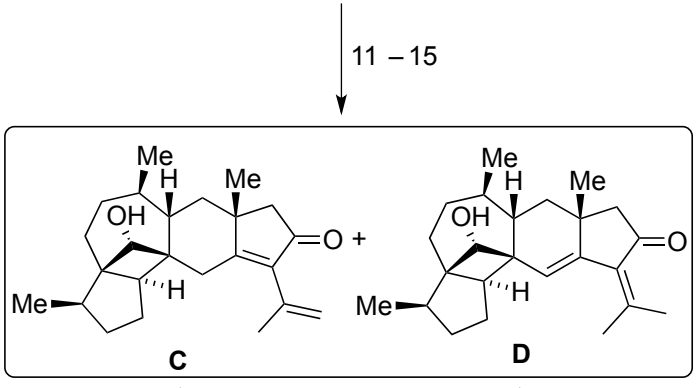
Hg(II)-catalyst speeds up the formation of **III** over the unwanted abstraction of the acetylenic H and therefore formation of **IV**



III **IV**

Org. Lett. **2007**, *9*, 3535.





11) $Co_2(CO)_8$
12) DBU, HMPA,
then Et_3OBF_4, DIPEA
13) DIBAL-H
14) TPAP, NMO
15) SmI_2, MeOH, HMPA

16) Crabtree's catalyst, H_2
17) Pd/C, H_2

18) TPAP, NMO
19) NaHMDS
then Davis oxaziridine
20) $NaBH_4$, $CeCl_3 \bullet 7\ H_2O$
21) Crabtree's catalyst, H_2
22) $(Im)_2C{=}S$
23) $P(OMe)_3$
24) MeLi
25) $SOCl_2$, pyridine
26) $BH_3{\bullet}SMe_2$
then H_2O_2, NaOH

In step 15 two products (**C** and **D**) are formed, which can both be converted into **E** by employing different hydrogenation conditions.

Step 22 + 23: Please name the reaction [Corey-Winter olefination]