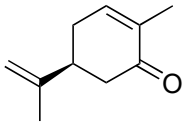
Convergent, Enantioselective Synthesis of (+)-Guanacastepene E

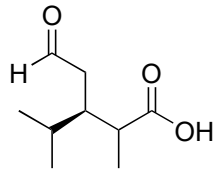
William D. Shipe and Erik J. Sorensen, *J. Am. Chem. Soc.* **2006,** *128,* 7025–7035.



A

1-3

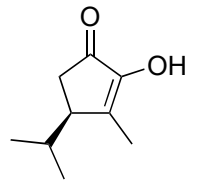
1) PtO_2, H_2, rt
2) LDA, THF, –78 °C to 0 °C; then MeI, 0 °C to rt
3) O_3, EtOAc, –78 °C; then H_2, Pd/C, rt



B

4-6

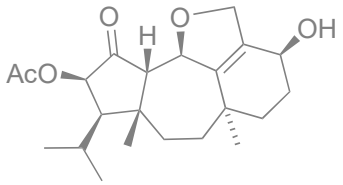
4) NaCN, *p*-TsOH, THF•H_2O, rt
5) EDCI, 0 °C to rt, CH_2Cl_2
6) LHMDS (3.0 equiv), THF, rt; then 1N HCl (aq)



C

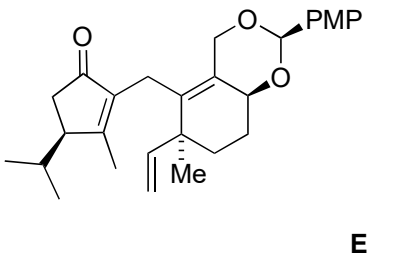
Please name compound A: (*S*)-(+)-Carvone

Please provide a mechanism for step 6.



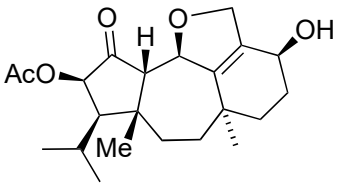
(+)-Guanacastepene E

7-9



E

10-17

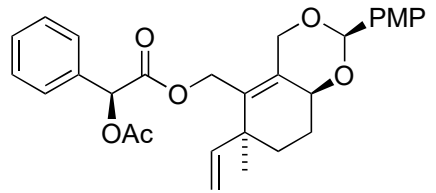


(+)-Guanacastepene E

7) Et_3N, NfF, CH_2Cl_2, rt
8) $Pd(dppf)Cl_2$, $Me_3SnSnMe_3$, NMP, 60 °C
9) **D**, LiCl, CuCl, $Pd(PPh_3)_4$, DMSO, rt to 60 °C

10) hν, *i*-Pr_2NEt (0.5 equiv), Et_2O
11) SmI_2 (2.5 equiv), HMPA, THF, rt; then, PhSeBr
12) *m*-CPBA, CH_2Cl_2, –78 °C
13) Et_3N, Et_3SiOTf, CH_2Cl_2, -78 °C,
14) m-CPBA, CH_2Cl_2, -78 °C
15) Ac_2O, DMAP, pyridine, rt
16) PPTS (0.25 equiv), MeOH, 70 °C
17) SiO_2, CH_2Cl_2, rt

D =

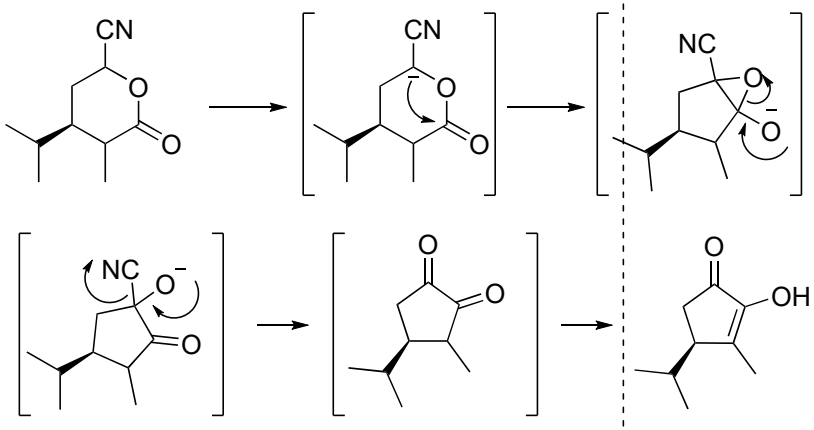


Please provide a mechanism for steps 10 and 11.

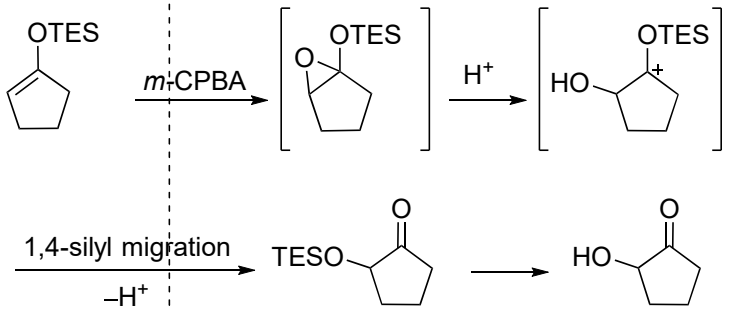
Please name the reaction of step 14 and give a mechanism for it.

Rubottom oxidation

step 6:



step 14:



step 11: