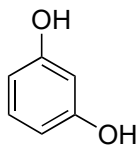


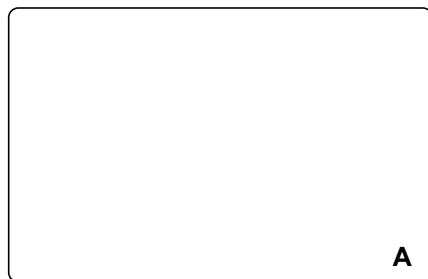
Total Synthesis of Cycloinumakiol

Tao Xu and Guangbin Dong

ACIE **2014**, *53*, 10733–10736.



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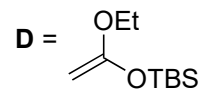


7–8

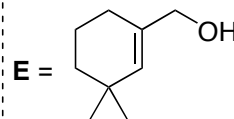


- 1) I_2
- 2) Tf_2O , DIPEA
- 3) Cs_2CO_3
- 4) TBSCl, ImH, DMAP
- 5) *n*-BuLi, **D**
- 6) HF (40%)

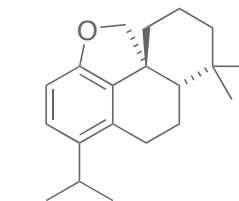
- 7) DIAD, PPh_3 , **E**
- 8) $[Rh(CO)_2Cl]_2$, $P(C_6F_5)_3$, THF, 140 °C, 24 h, 64%



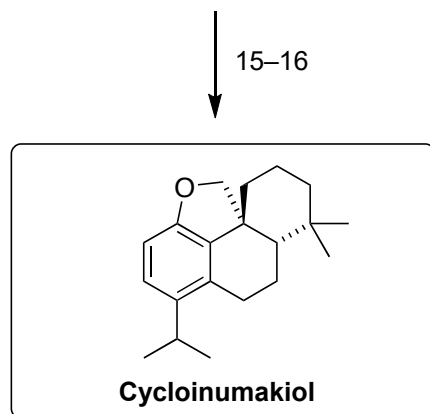
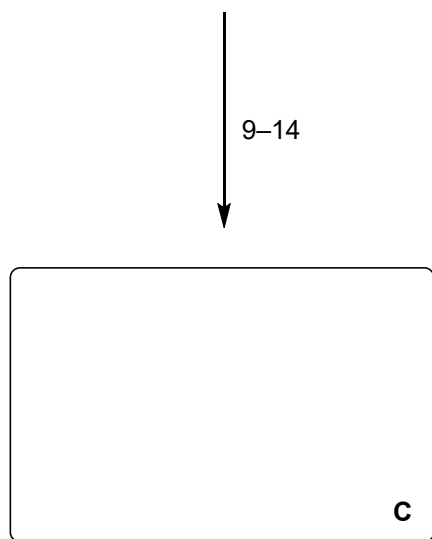
Step 5: Explain the selectivity! Draw the orbitals!



Step 8: Think of a mechanism!



Cycloinumakiol



- 9) NBS, NH_4OAc (10%), Et_2O
- 10) $\text{Pd}(\text{PPh}_3)_4$, **F**
- 11) Pd/C , H_2
- 12) LAH, *then* Martin's sulfurane
- 13) O_3 , PPh_3
- 14) DBU, 130 °C, 18 h

- 15) Zn , TiCl_4 , pyr, THF, 90 °C
- 16) H_2 , Pd/C

Step 9: What is the role of NH_4OAc ?

