Protecting-Group-Free Syntheses of ent-Kaurane Diterpenoids: [3+2+1] Cycloaddition/Cycloalkenylation Approach

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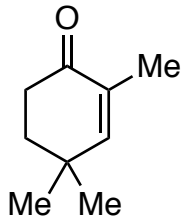
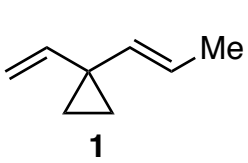


1-3

A

5-7



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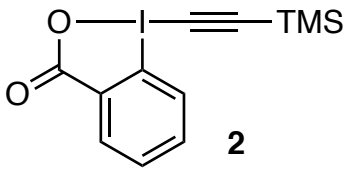
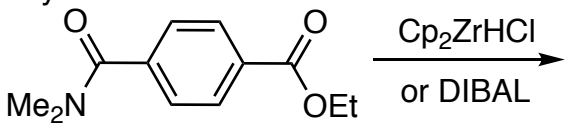


2

1) **1,** Cp_2ZrHCl, TMSCl, $CuBrMe_2S$, BF_3Et_2O
2) *t*-BuOK, TBAF, **2**
3) $[Rh(CO)_2Cl]_2$, CO
4) TIPSOTf, DBU, then $Pd(OAc)_2$

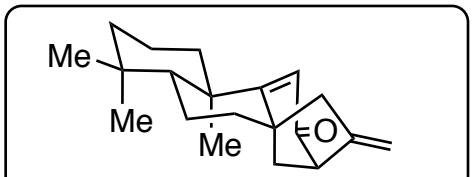
5) $Mn(dpm)_3$, $PhSiH_3$, O_2
6) $SOCl_2$, Et_3N
7) $NaBH_4$, -78°C

1) The name of the Zr reagent. What's the product of the reaction below, explain why?

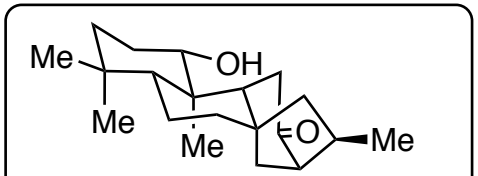


2) The mechanism?
3) The mechanism? *hint: [3+2+1] cycloaddition.* What's the name of the homologous [2+2+1] reaction that also involves CO?
5) Name and mechanism of the reaction? What reaction can achieve oppsite regioselectivity?

Hint:
5) and 6) to isomerize one double bond;
7) both are desired products



12-oxo- 9,11-dehydrokaurene



***ent*-1α-hydroxykauran-12-one**

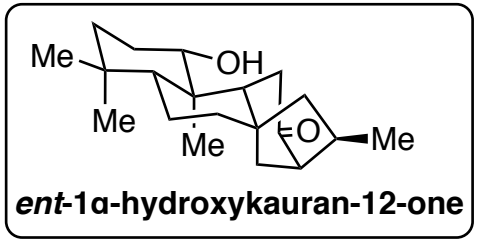
B

+

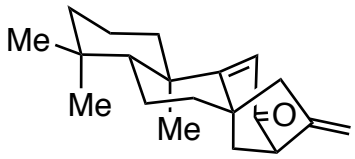
C

from B
8

from C
9-12



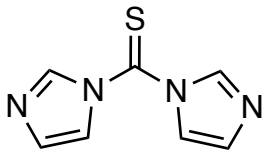
***ent*-1α-hydroxykauran-12-one**



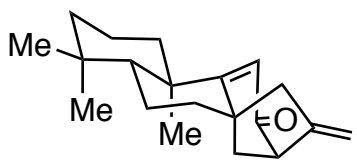
12-oxo- 9,11-dehydrokaurene

8) TCDI, DMAP, then nBu_3SnH, AIBN
9) $NaBH_4$, $CeCl_3$
10) Raney Ni, H_2
11) MnO_2 DCM
12) Li/NH_3, EtOH, -78°C

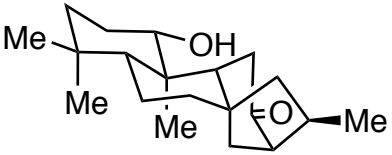
8) Name and mechanism of the reaction?
10) Rationalize the regio- and stereoselectivity



TCDI



12-oxo- 9,11-dehydrokaurene



***ent*-1α-hydroxykauran-12-one**