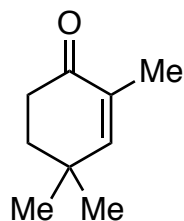


# Protecting-Group-Free Syntheses of ent-Kaurane Diterpenoids: [3+2+1] Cycloaddition/Cycloalkenylation Approach

Wang, J.; Hong, B.; Hu D.-C.; Kadonaga, Y.; Tang, R.-Y.; Lei, X.-G.

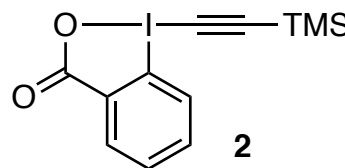
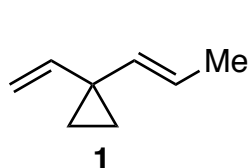
*J. Am. Chem. Soc.* **2020**, *142*, 2238–2243.



1-3



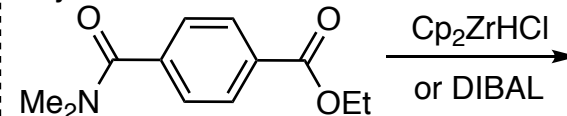
5-7



- 1) **1**,  $\text{Cp}_2\text{ZrHCl}$ , then  $\text{CuBrMe}_2\text{S}$ , then enone,  $\text{TMSCl}$ ,  $\text{BF}_3\text{Et}_2\text{O}$
- 2)  $t\text{-BuOK}$ , TBAF, **2**
- 3)  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ , CO
- 4) TIPSOTf, DBU, then  $\text{Pd}(\text{OAc})_2$

- 5)  $\text{Mn}(\text{dpm})_3$ ,  $\text{PhSiH}_3$ ,  $\text{O}_2$
- 6)  $\text{SOCl}_2$ ,  $\text{Et}_3\text{N}$
- 7)  $\text{NaBH}_4$ ,  $-78^\circ\text{C}$

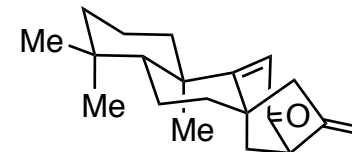
1) The name of the Zr reagent. What's the product of the reaction below, explain why?



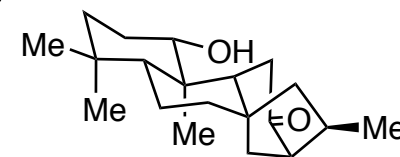
- 2) The mechanism?
- 3) The mechanism? *hint: [3+2+1] cycloaddition*. What's the name of the homologous [2+2+1] reaction that also involves CO?
- 5) Name and mechanism of the reaction? What reaction can achieve oppsite regioselectivity?

Hint:

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



**12-oxo- 9,11-dehydrokaurane**



**ent-1α-hydroxykauran-12-one**

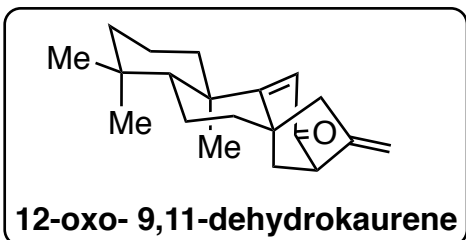
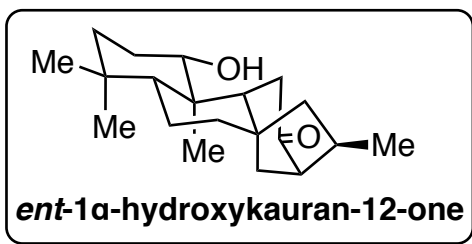


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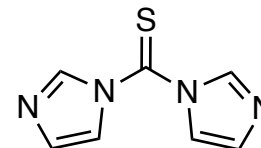
from B  
8

from C  
9-12



- 8) TCDI, DMAP, *then*  $n\text{-Bu}_3\text{SnH}$ , AIBN
- 9)  $\text{NaBH}_4$ ,  $\text{CeCl}_3$
- 10) Raney Ni,  $\text{H}_2$
- 11)  $\text{MnO}_2$ ,  $\text{CH}_2\text{Cl}_2$
- 12)  $\text{Li}/\text{NH}_3$ , EtOH,  $-78^\circ\text{C}$

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



TCDI

