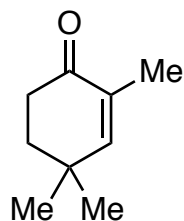


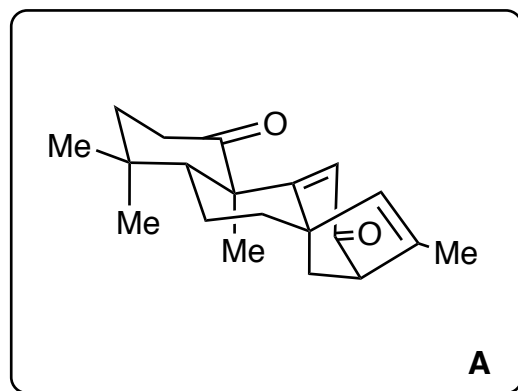
Protecting-Group-Free Syntheses of ent-Kaurane Diterpenoids: [3+2+1] Cycloaddition/Cycloalkenylation Approach

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

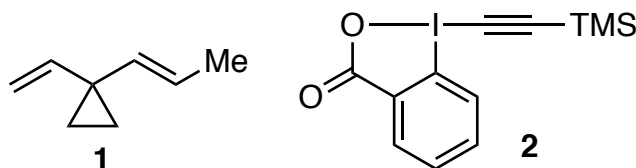
J. Am. Chem. Soc. **2020**, *142*, 2238–2243.



1-3



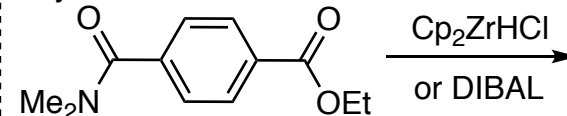
5-7



- 1) **1**, Cp_2ZrHCl , then CuBrMe_2S , then enone, 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) $\text{Mn}(\text{dpm})_3$, PhSiH_3 , O_2
- 6) SOCl_2 , Et_3N
- 7) NaBH_4 , -78°C

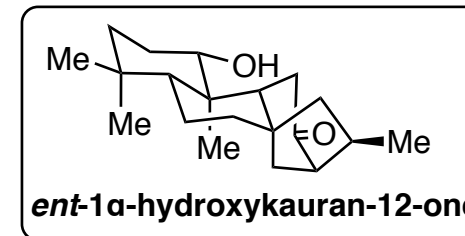
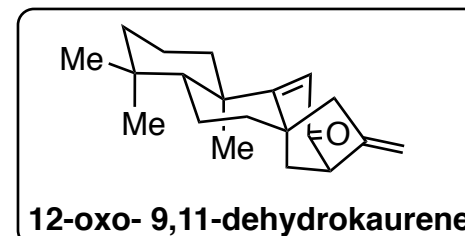
1) The name of the Zr reagent. What's the product of the reaction below, explain why?

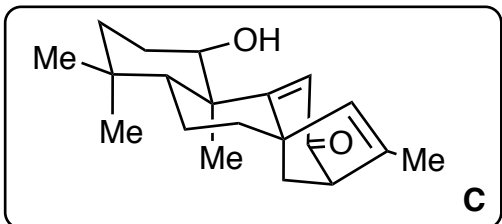
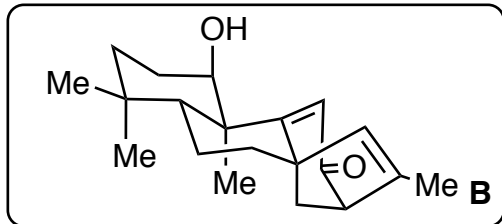


- 2) The mechanism?
- 3) The mechanism? *hint: [3+2+1] cycloaddition*. What's the name of the homologous [2+2+1] reaction that also involves CO?
- 5) Name and mechanism of the reaction? What reaction can achieve oppsite regioselectivity?

Hint:

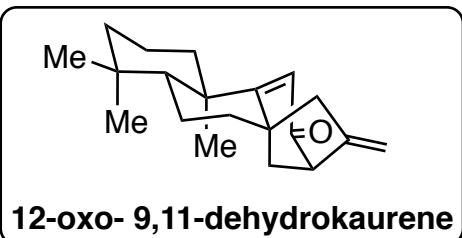
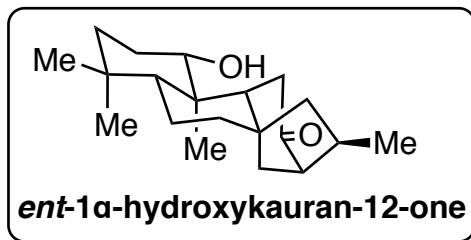
- 5) and 6) to isomerize one double bond;
- 7) both are desired products





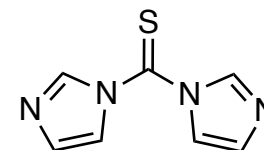
from B
8

from C
9-12

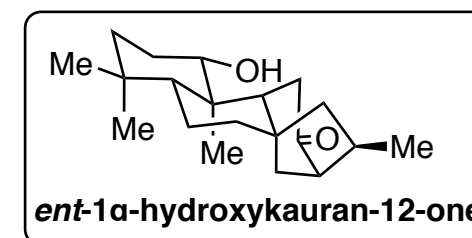
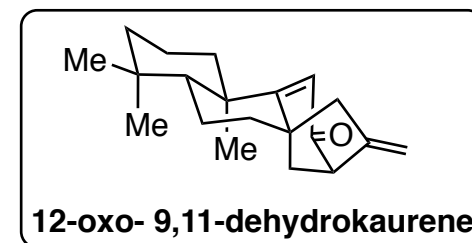


- 8) TCDI, DMAP, *then* $n\text{-Bu}_3\text{SnH}$, AIBN
- 9) NaBH_4 , CeCl_3
- 10) Raney Ni, H_2
- 11) MnO_2 , CH_2Cl_2
- 12) Li/NH_3 , EtOH, -78°C

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

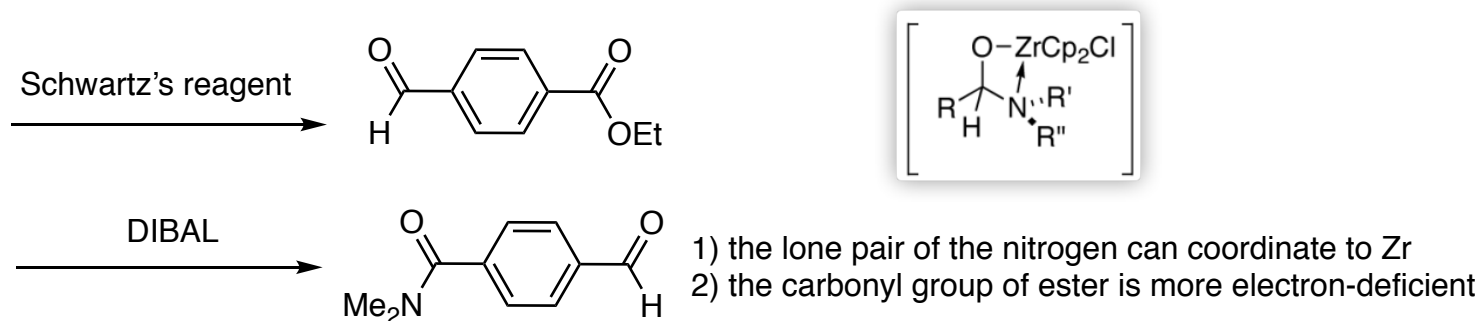


TCDI

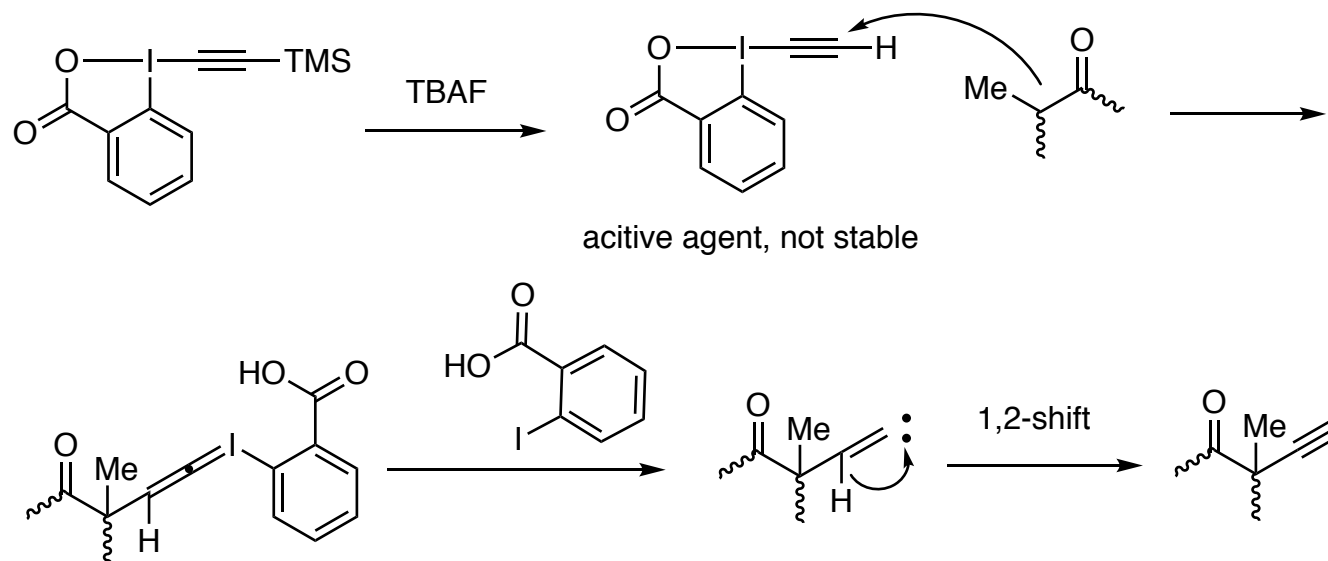


Key:

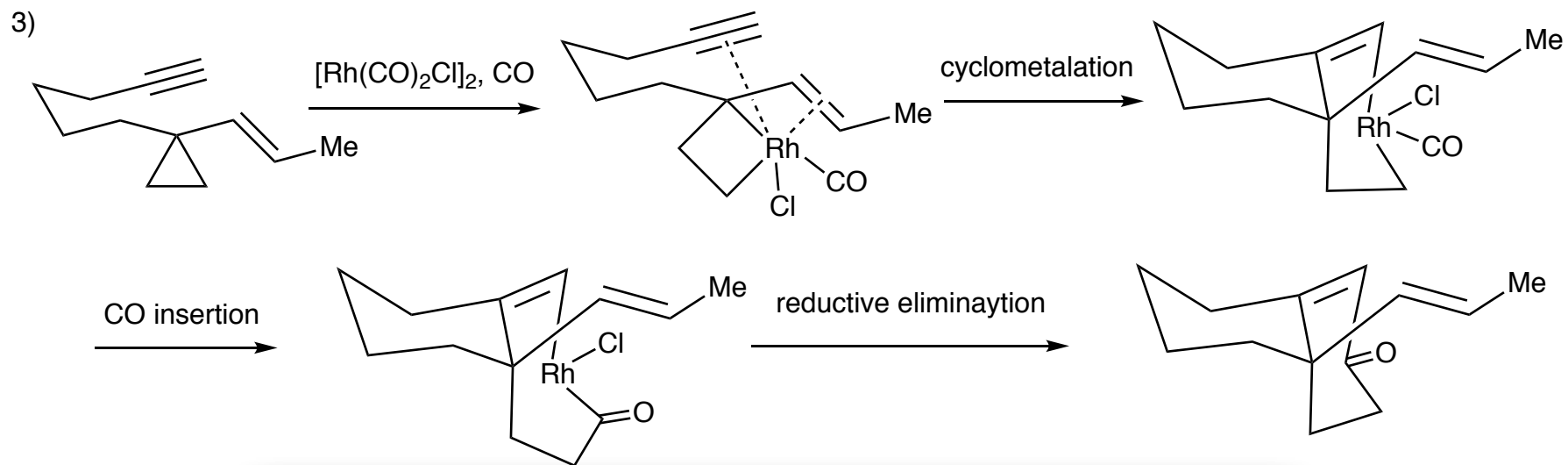
1) Schwartz's reagent. Hydrometallation of alkene and alkyne, reduction of amide (tertiary).



2)



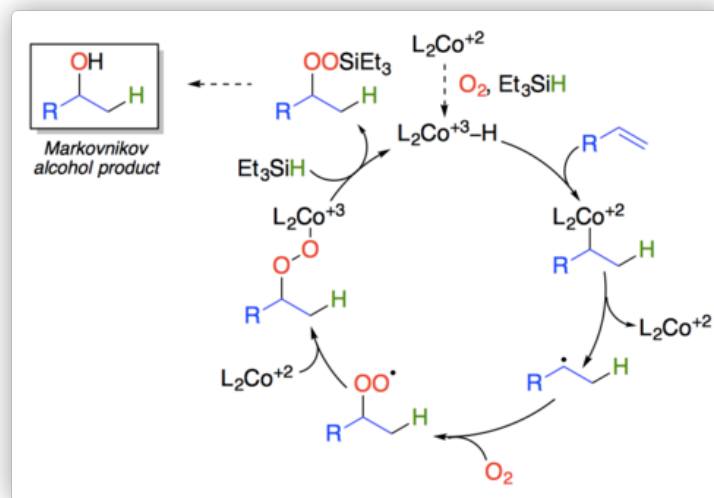
Waser *et. al.* **Chem. Eur. J.** 2010, 16, 9457 – 9461



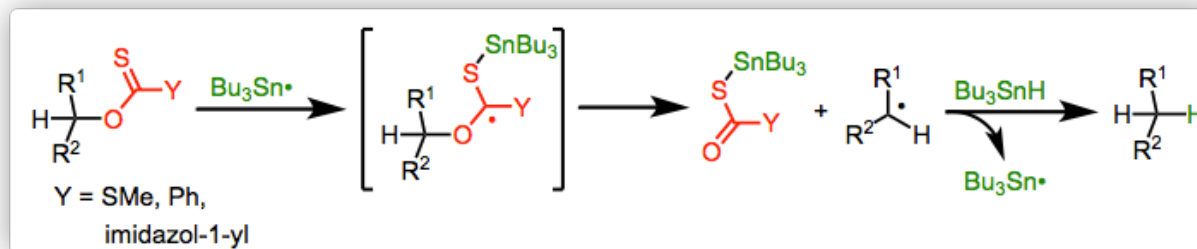
+ 2] cycloadditions.⁷ The **vinyl group** was found to act as an **activating group** that facilitates the ring opening of cyclopropane under much **milder conditions**.^{7,8} We hope to

Org. Lett. 2010, 12, 11, 2528–2531

5) Mukaiyama hydration. Alternative selectivity can be achieved from hydroboration-oxidation



8) Barton-McCombie reaction



10) The author mentioned the directing effect of the OH group (other hydrogenation reaction on the ketone compound gave the wrong diastereoisomer). And this is reason that they do the reduction and reoxidation.