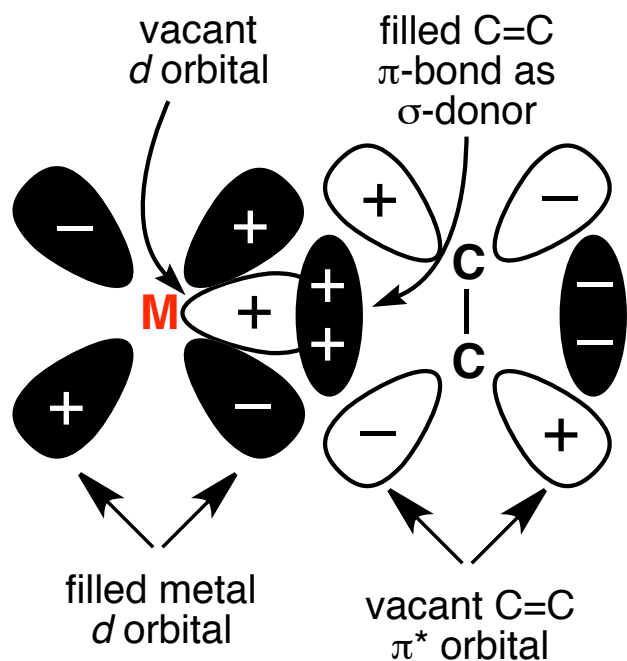


Additions to Metal-Alkene and -Alkyne Complexes

Recal that alkenes, alkynes and other π -systems can be excellent ligands for transition metals. As a consequence of this binding, the nature of the π -system changes from weakly nucleophilic to electrophilic.

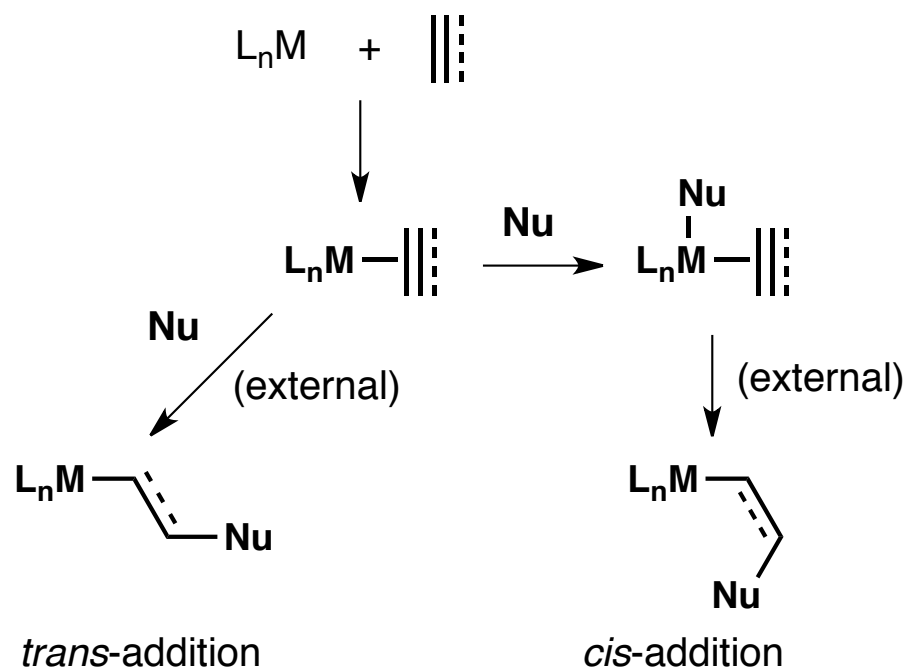


Attack on ligand favored by:

- saturated metal center
- π -accepting ligands
- electron-poor metal centers
- cationic complexes
- soft nucleophiles

A lot of very rich chemistry here. We will focus our attention on reactions promoted by Pd(II) and Au(I).

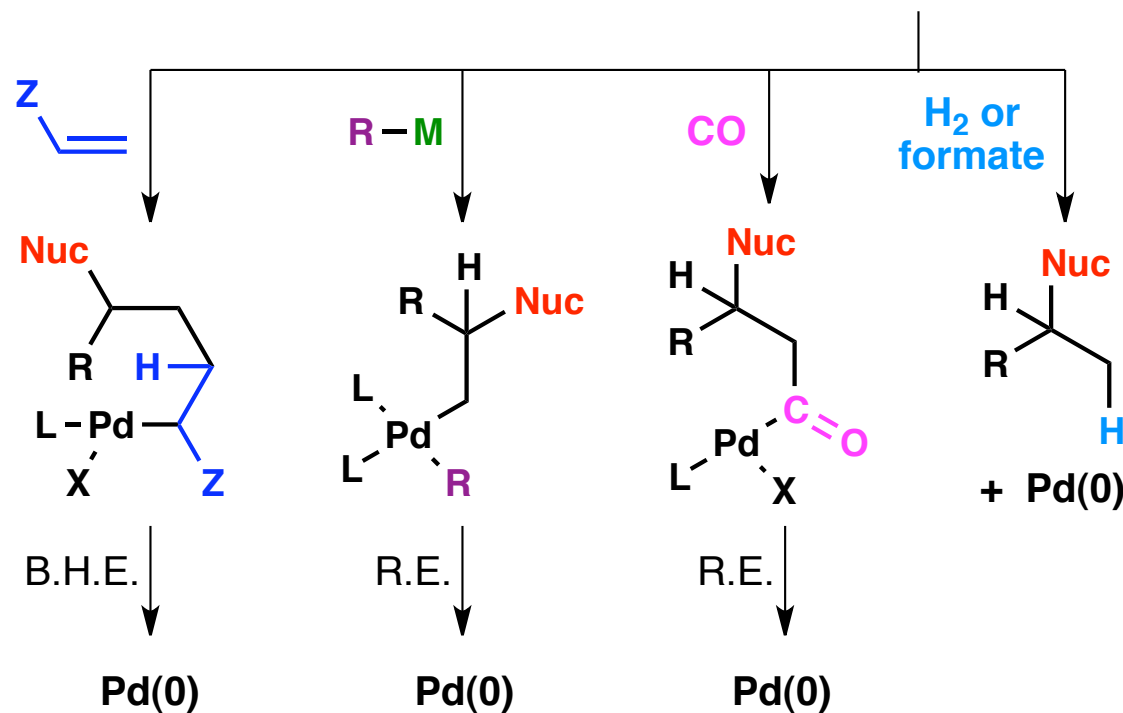
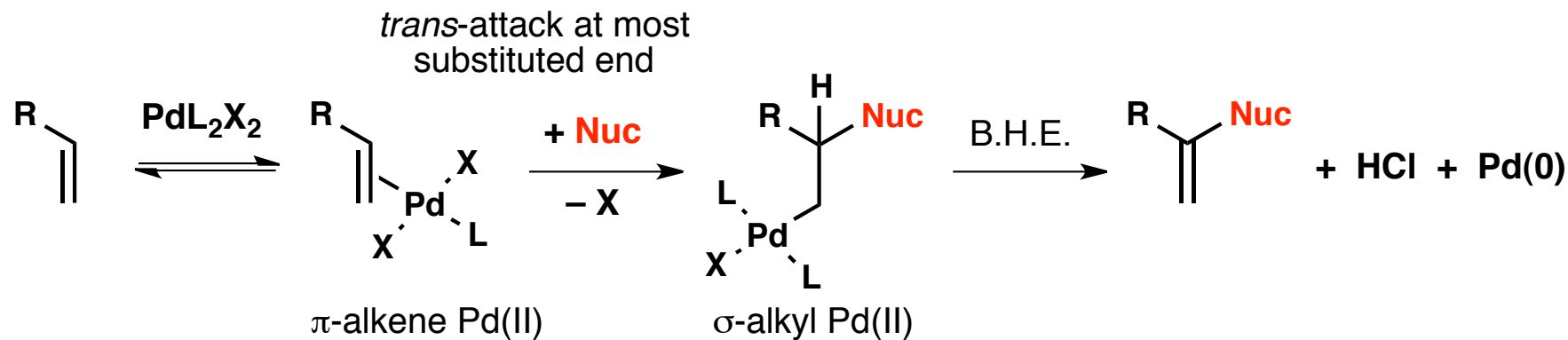
The addition of the nucleophile can be external or internal.



The resulting σ -alkyl or σ -alkenyl complexes can proceed to do other reactions.

Palladium (II)-Catalyzed Additions

PdCl_2 and Pd(OAc)_2 are commonly used. Strong donor ligands (phosphines) tend to shut down reactivity. Weaker donor ligands (pyridines) can be used. Acceptor ligands (nitriles) also good.

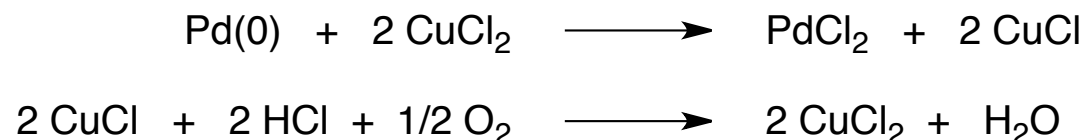


All transformations involving the σ -alkyl palladium intermediate will eventually generate Pd(0) . Either stoichiometric amounts of metal are needed or a reoxidant must be present.

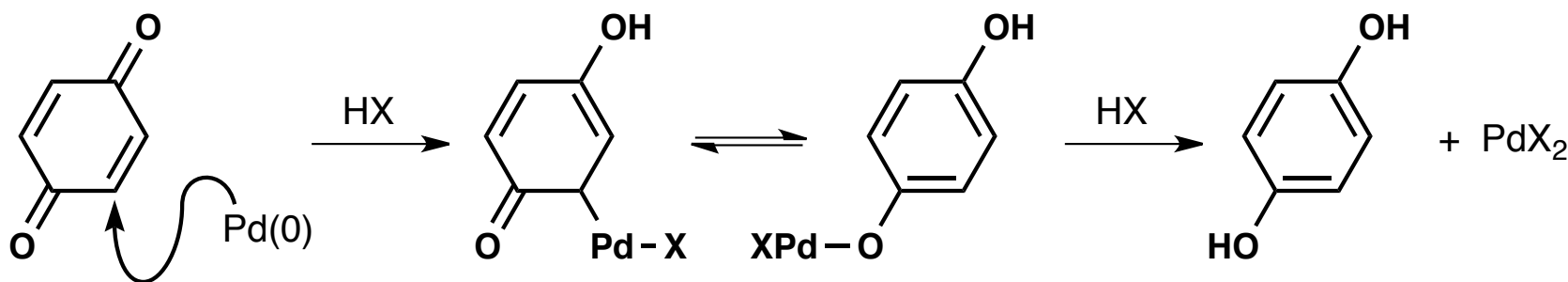
Stoichiometric Oxidants for Generating Pd(II)

Several stoichiometric reoxidant systems have been developed for converting Pd(0) back to Pd(II). There are advantages/disadvantages with each. Choice determined by what else is going on the system and the stability of starting material/products toward the oxidant.

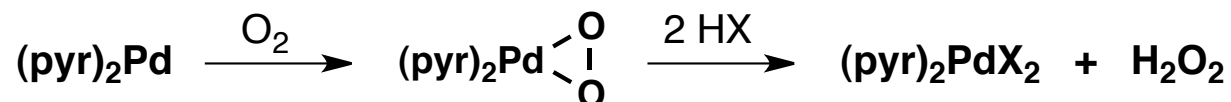
CuCl₂ or CuCl₂ w/ O₂: likely involves sequential SET reactions. Catalytic in Cu if O₂ (1 atm) is used.



Benzoquinone (BQ): Very mild and compatible with lots of functional groups. Stoichiometric organic impurity that must be removed.

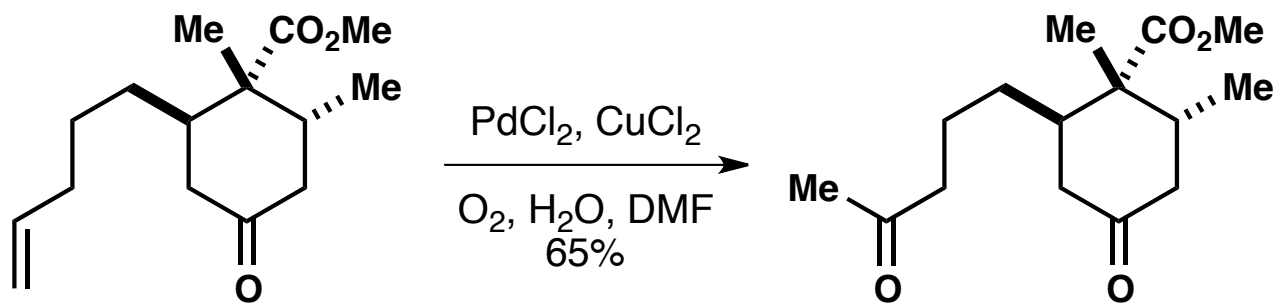
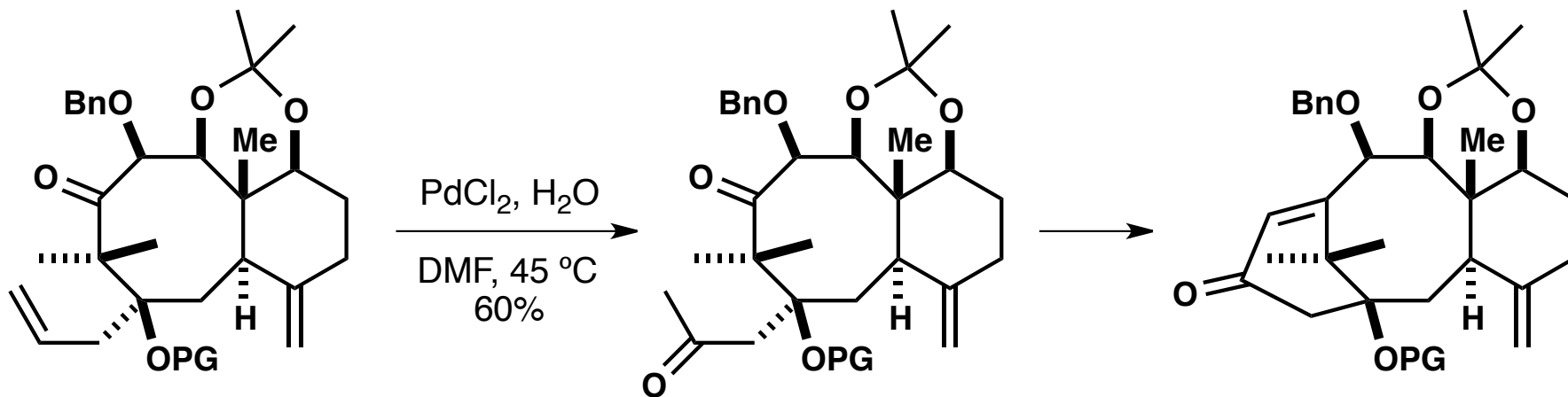
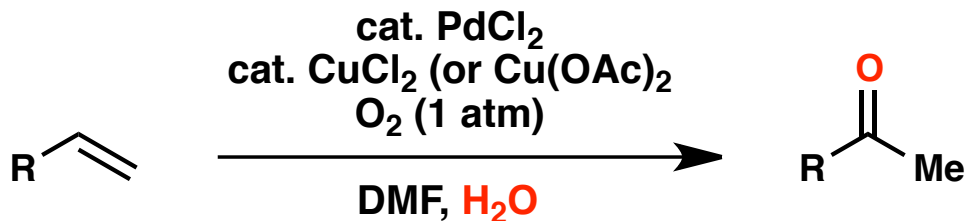


O₂ (1 atm): If the reaction is carried out in DMSO or with pyridine ligand, then O₂ can be used by itself.



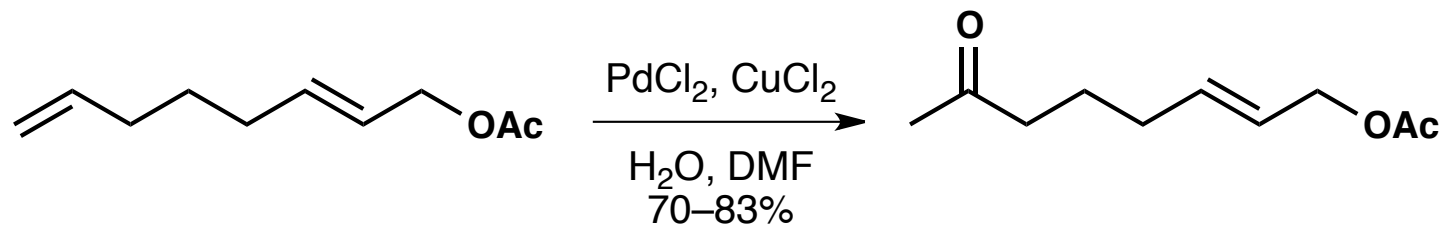
Wacker Oxidation

One of the first palladium-catalyzed reactions. Discovered by the process group at Wacker Chemie (*Angew. Chem. Int Ed. Engl.* **1962**, 1, 80). Originally developed to convert ethylene into acetaldehyde. Has since become a general way to convert a monosubstituted olefin into a methyl ketone.

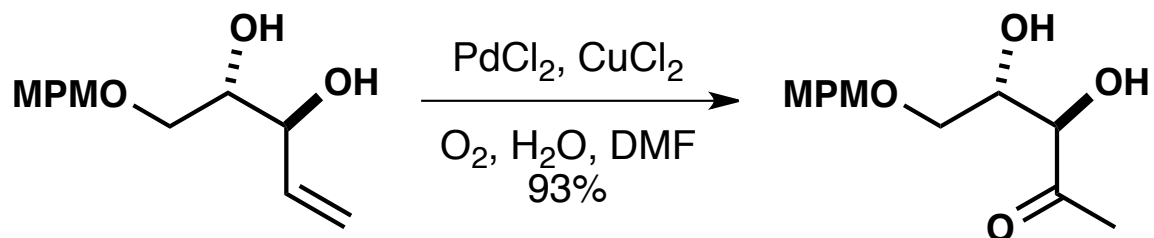
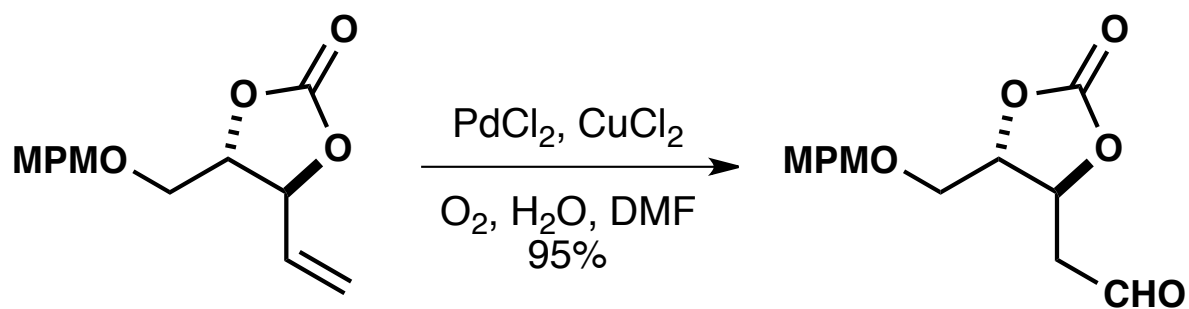


Wacker Oxidation

Internal olefins are typically much slower to react

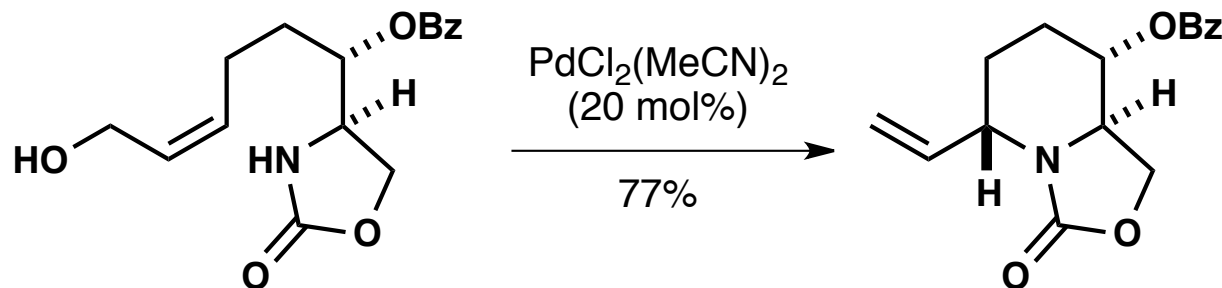
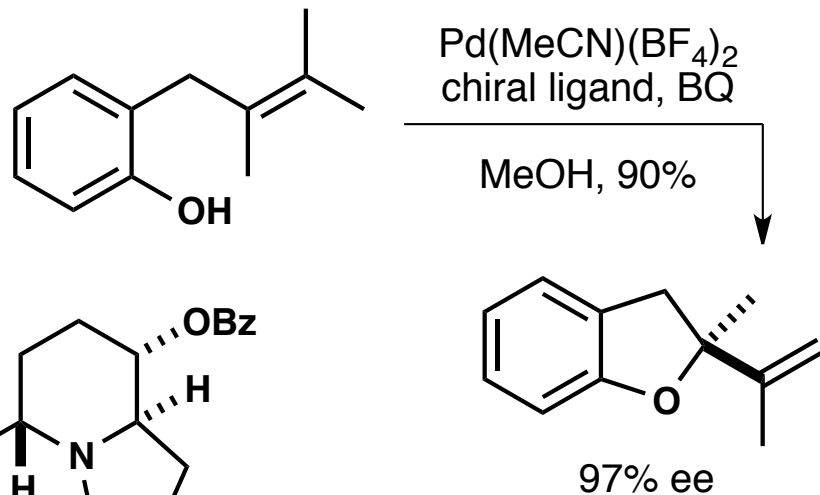
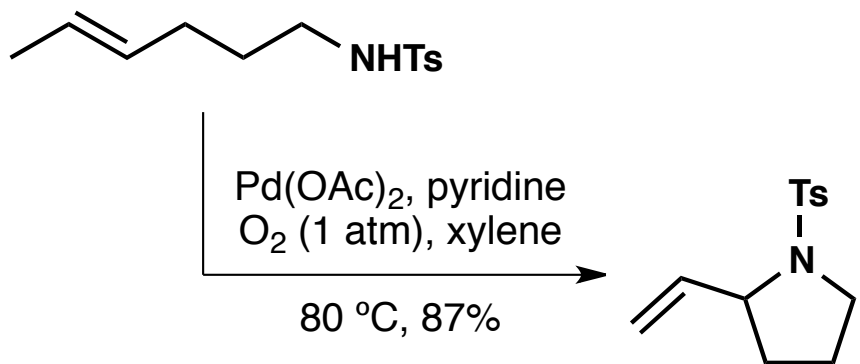
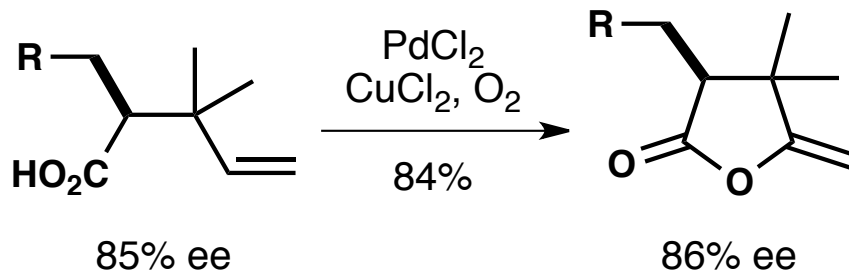
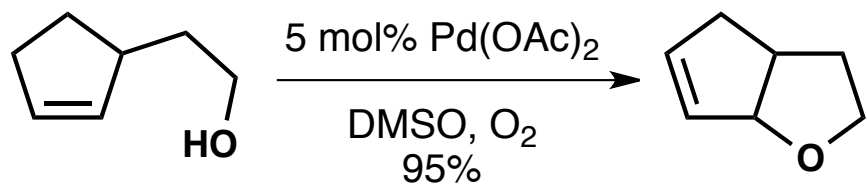


In some cases a neighboring group, can alter the regioselectivity and form an aldehyde



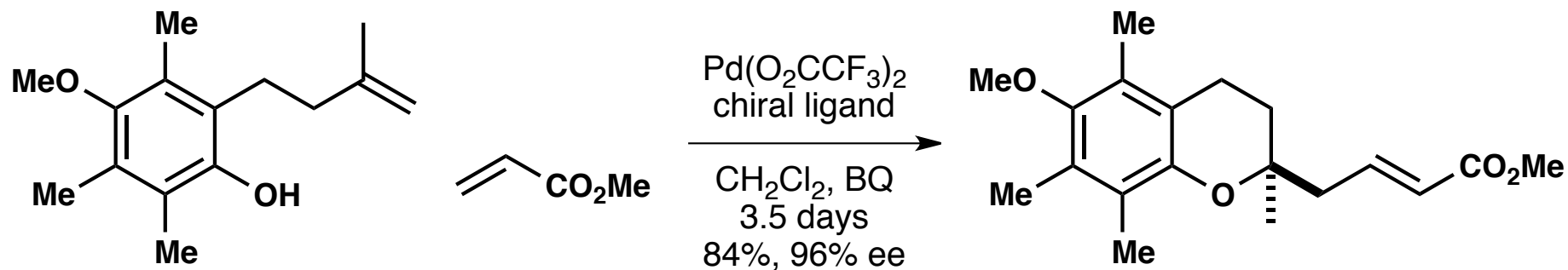
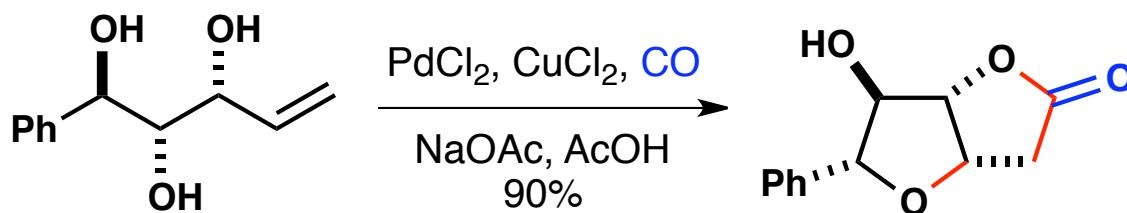
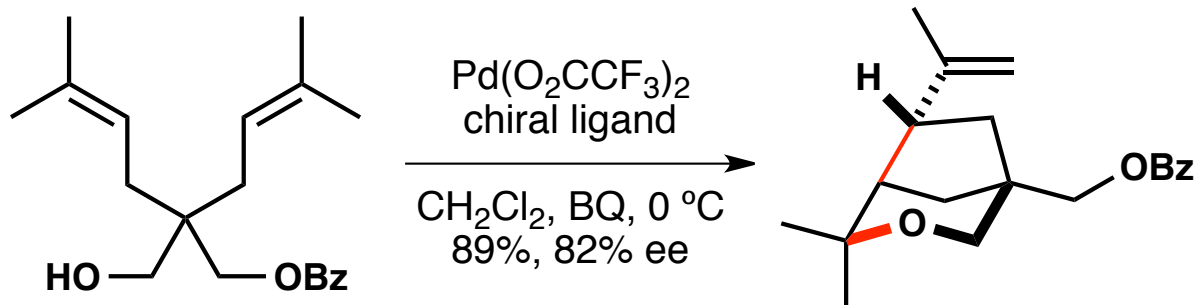
Wacker-Type Cyclizations

Tethered nucleophiles (typically O and N) can be used to form heterocycles. Both terminal and internal olefins work well. Can be coupled with other processes.



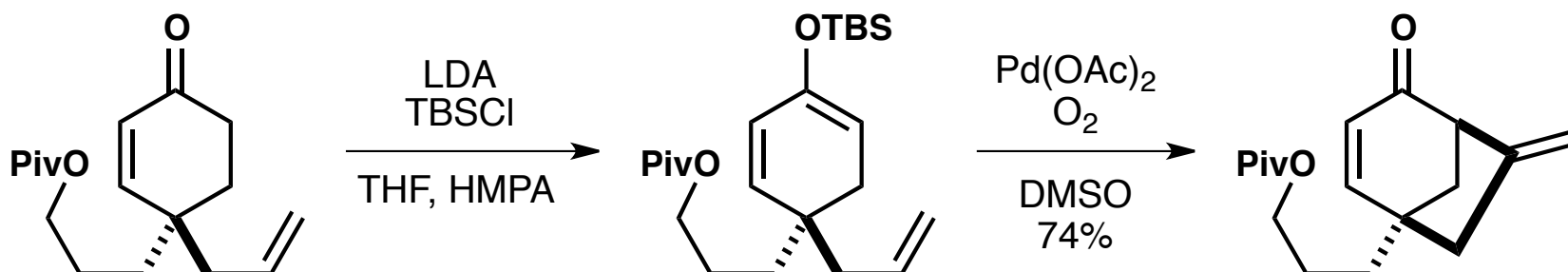
Note catalysis without oxidant

Wacker-Type Cascades

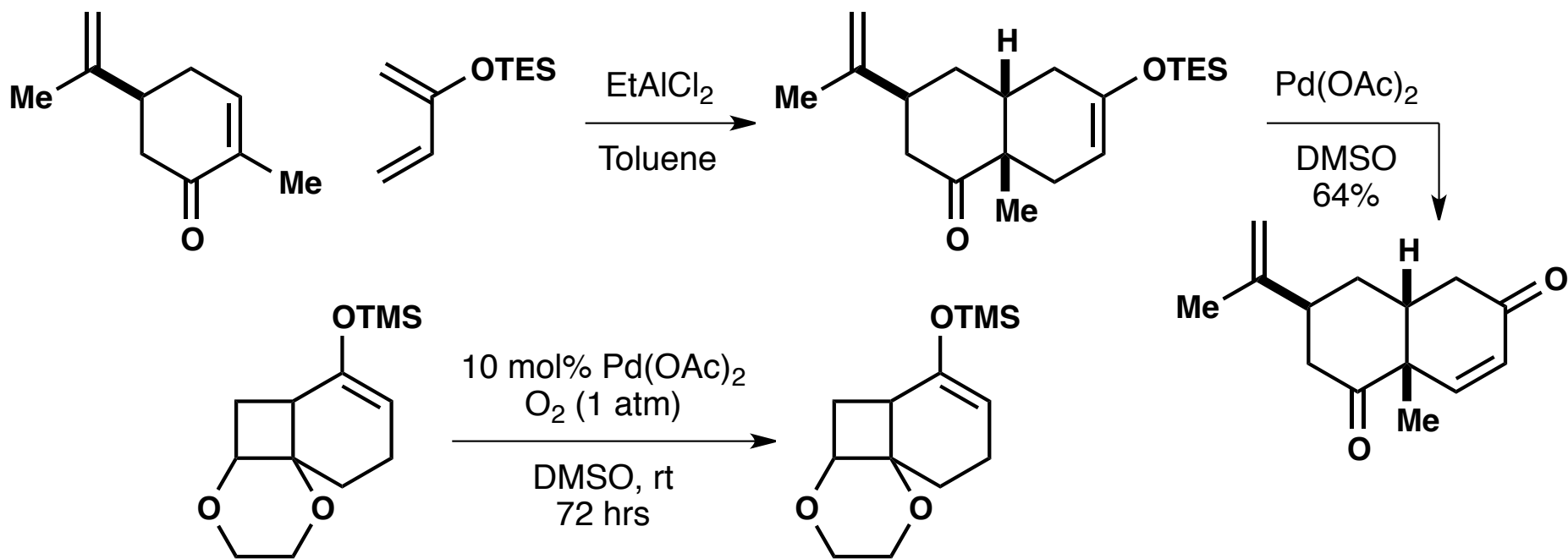


Enol Ether Substrates (Saegusa Oxidation)

Useful C–C bond formations can be accomplished with silyl enol ether nucleophiles

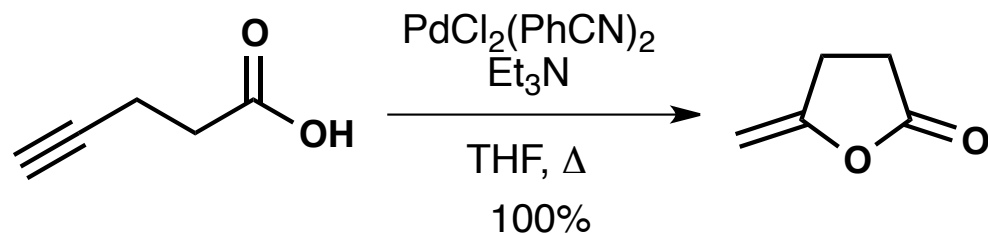
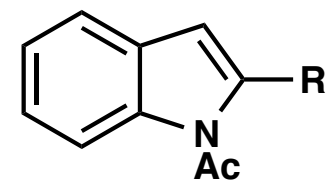
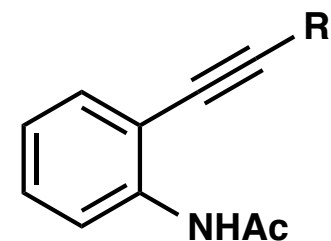
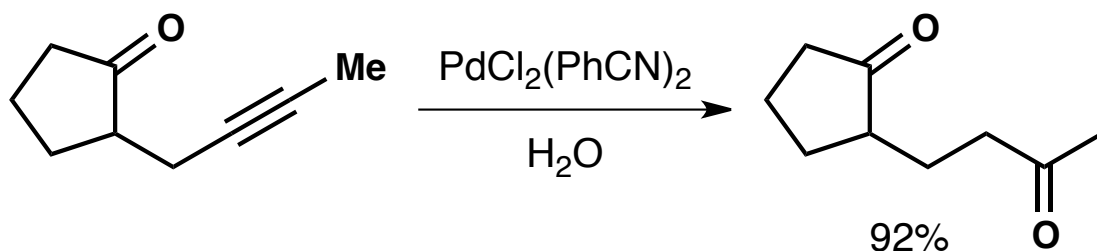
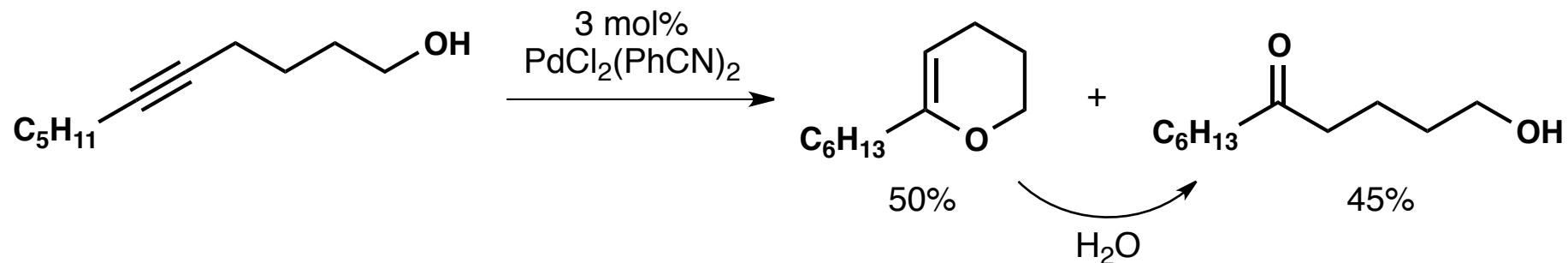


More commonly, silyl enol ethers are oxidized to enones. Originally used stoichiometric amounts of Pd because turnover was not observed with BQ. Catalysis can be achieved with O₂ and DMSO.



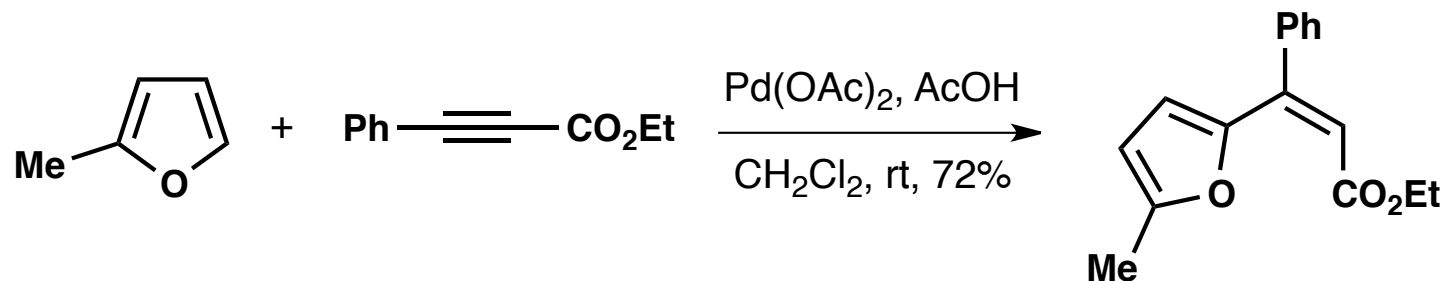
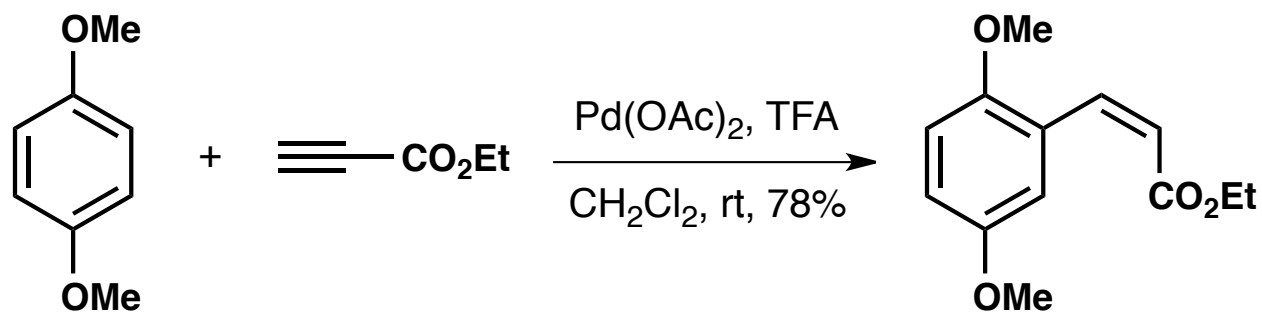
Additions to Alkynes

Alkynes are also excellent π -ligands for Pd(II). Nucleophilic addition produces an alkenyl Pd intermediate that is more stable than the alkyl Pd intermediates generated from alkenes (B.H.E. not a problem). This can be intercepted by other processes or undergo protodemetalation (regenerates Pd(II)).

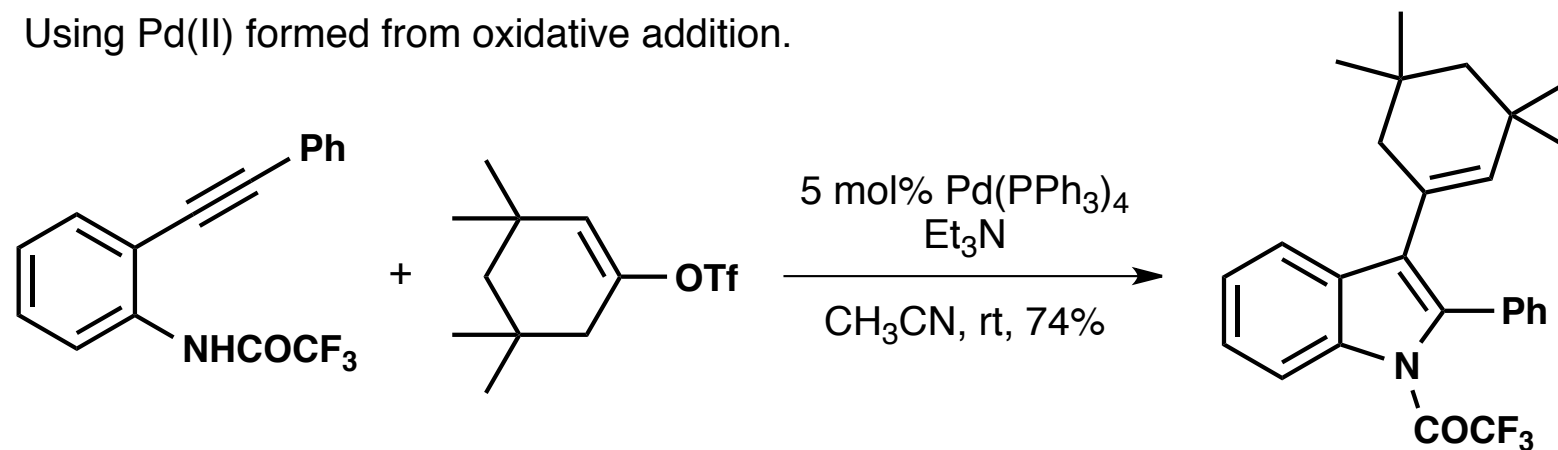


Arylations of Alkynes

Hydroarylation of alkynes – likely involves initial palladation of aromatic. Similar reactions with alkenes.

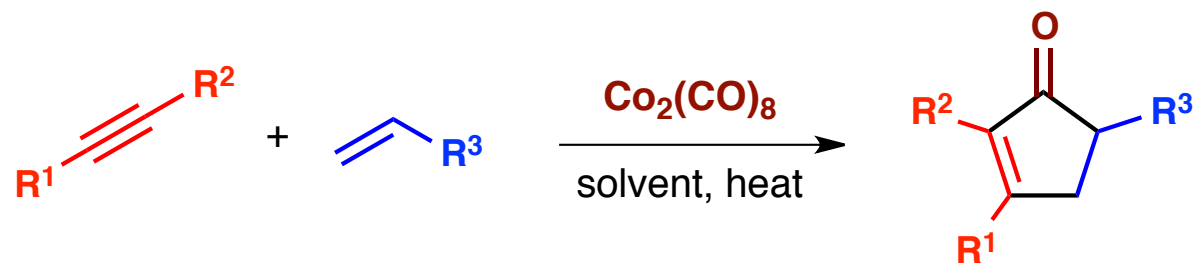


Using Pd(II) formed from oxidative addition.

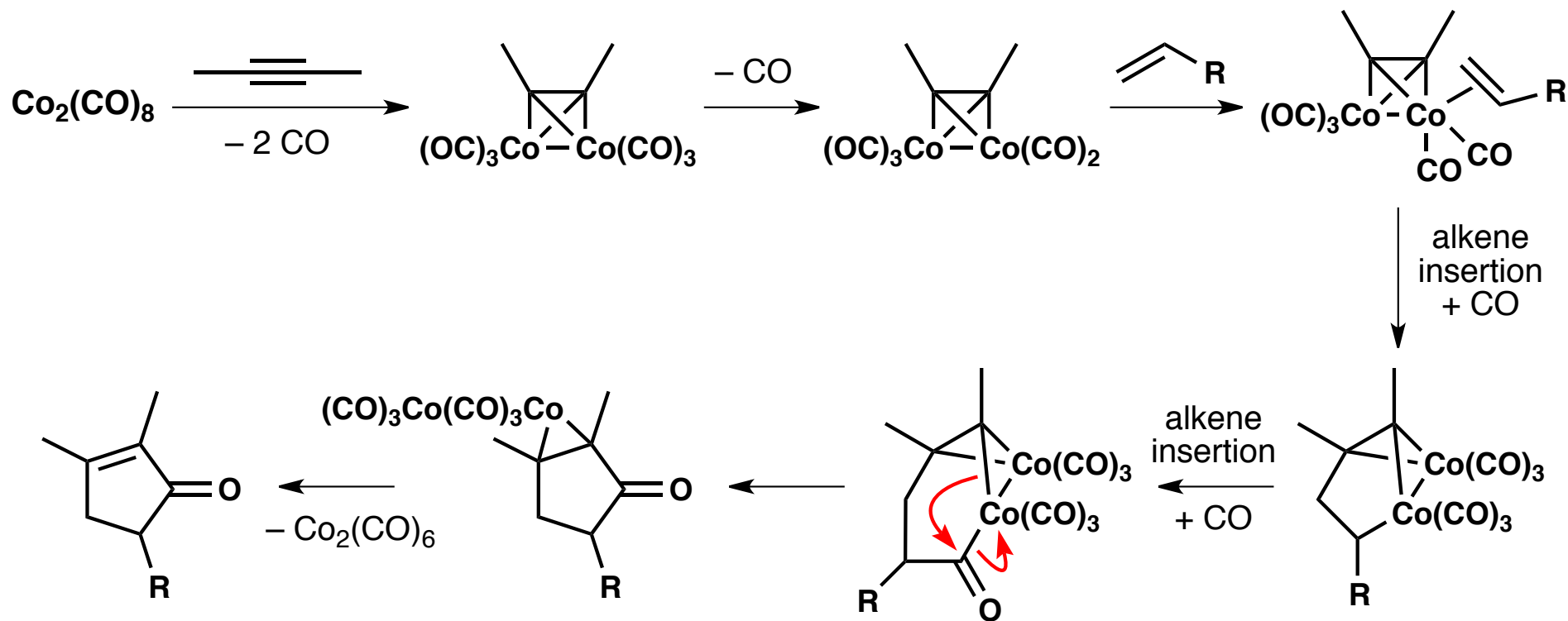


The Pauson-Khand Reaction

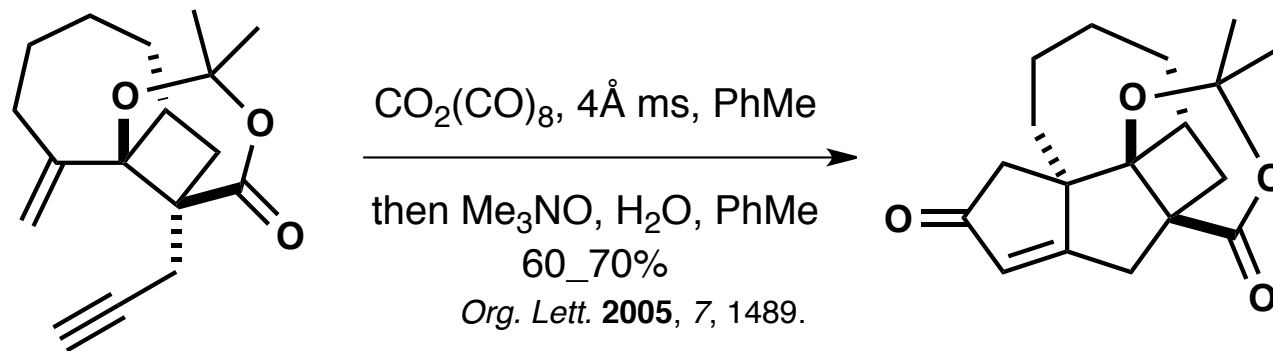
Coupling of an alkyne, alkene, and CO to give a cyclopentenone. Both inter- and intramolecular variants are possible. Often use stoichiometric amounts of $\text{Co}_2(\text{CO})_8$, but catalytic versions are known as well as with other metals. Often requires high temperatures.



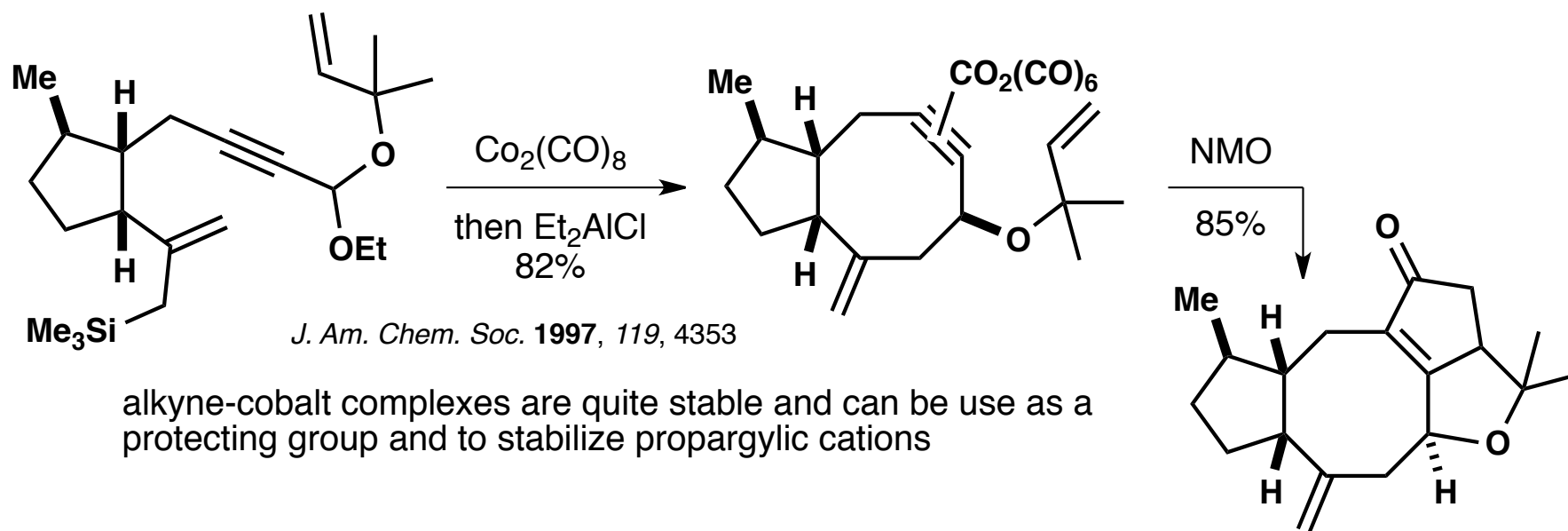
Plausible mechanism:



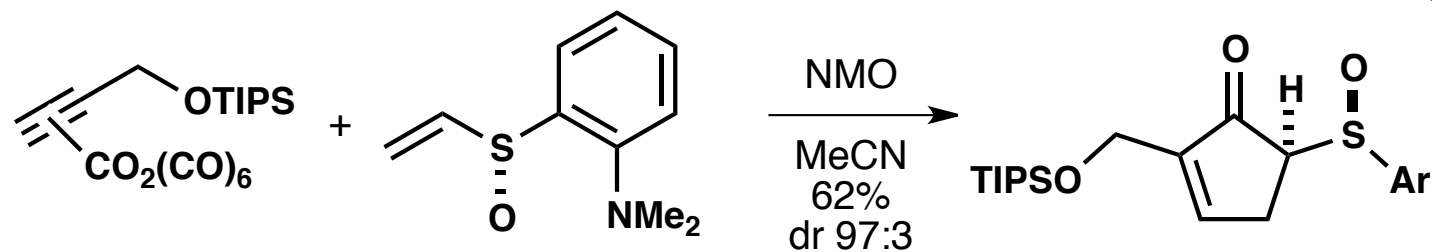
The Pauson-Khand Reaction



amine oxides and other Lewis bases can be used as a promoter



alkyne-cobalt complexes are quite stable and can be used as a protecting group and to stabilize propargylic cations



Chem. Eur. J. **2004**, 10, 5443.