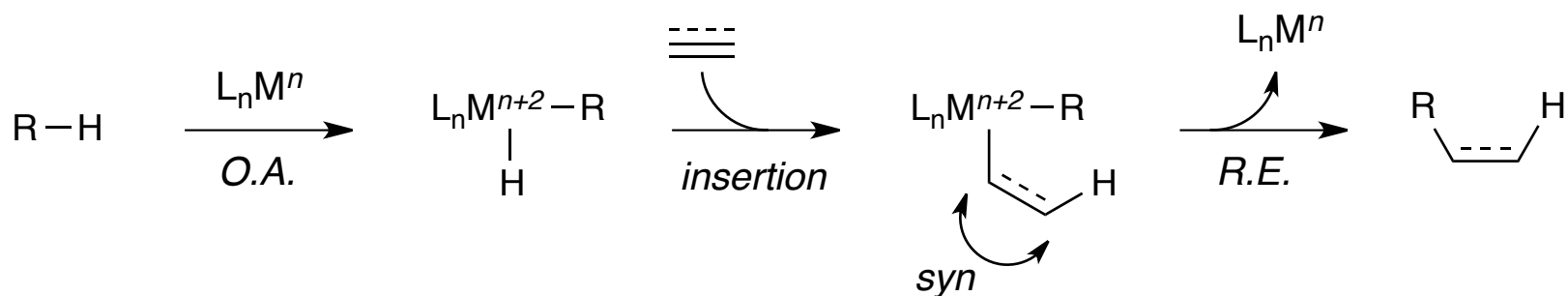


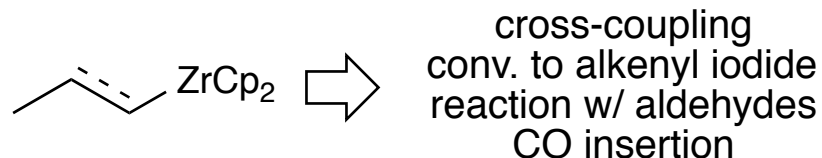
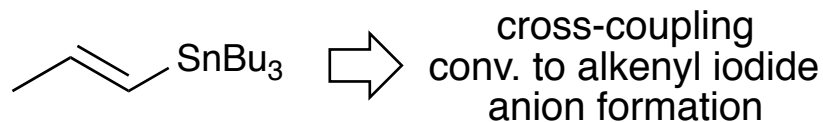
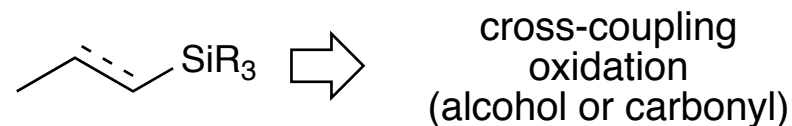
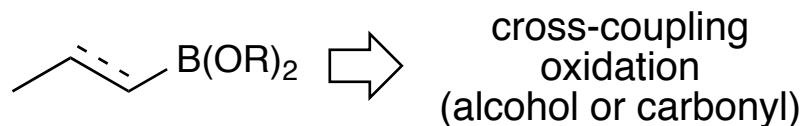
Hydrofunctionalizations

Certain transition metal hydrides (and main group hydrides) are useful for delivering more than just "H₂" to olefins and alkynes. In these cases the net transformation is the addition of a hydrogen and another function group.

When the process is catalytic, the following general scheme is likely involved.



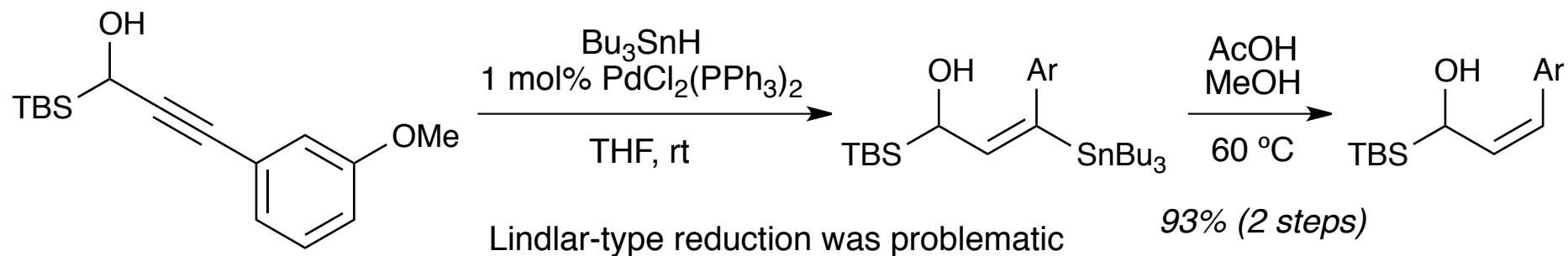
$R-H = \text{"H-Sn", "H-B", "H-Si", "H-C=O", "H-Zr" (non-catalytic)}$



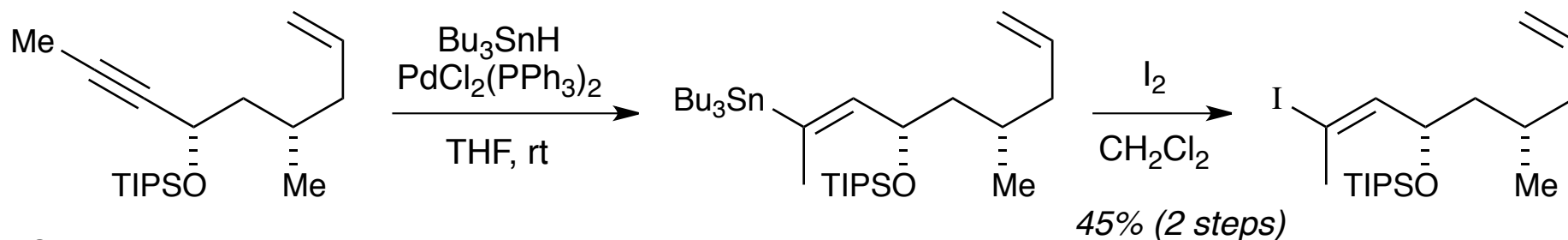
Hydrostannation

Addition of Sn–H across alkyne. Bu_3SnH is most commonly used. Palladium catalysis is quite common.

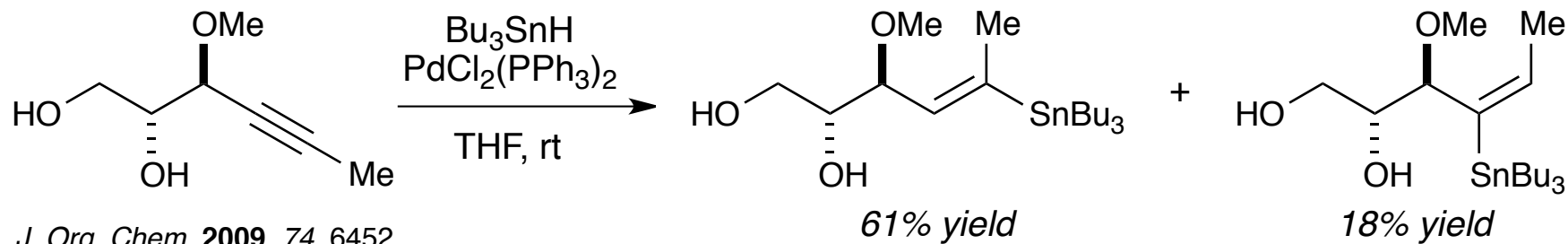
Mixtures of regioisomers can often be a problem. " Bu_3Sn " usually ends up on less hindered end of alkyne, but electronic factors can win out as well.



Tetrahedron **2009**, 65, 10355.



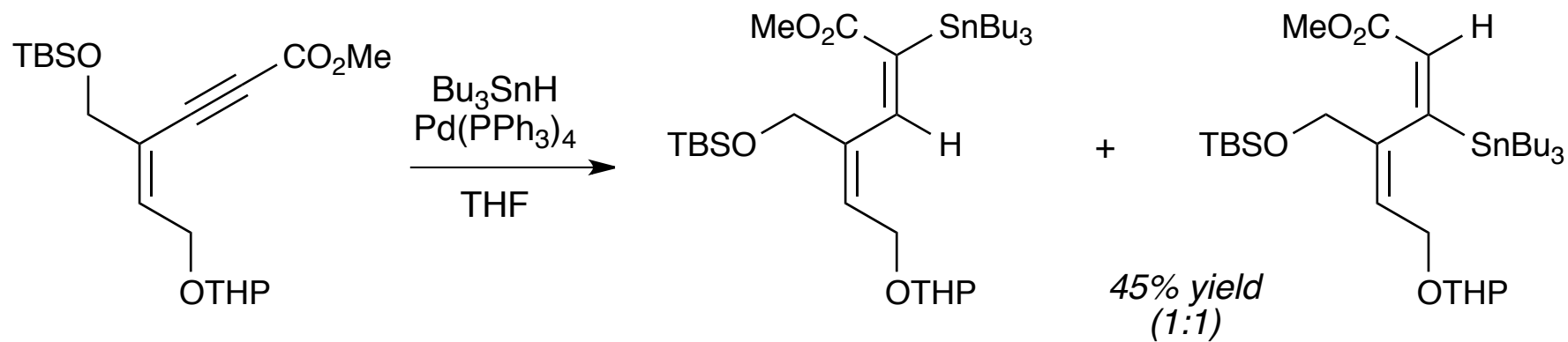
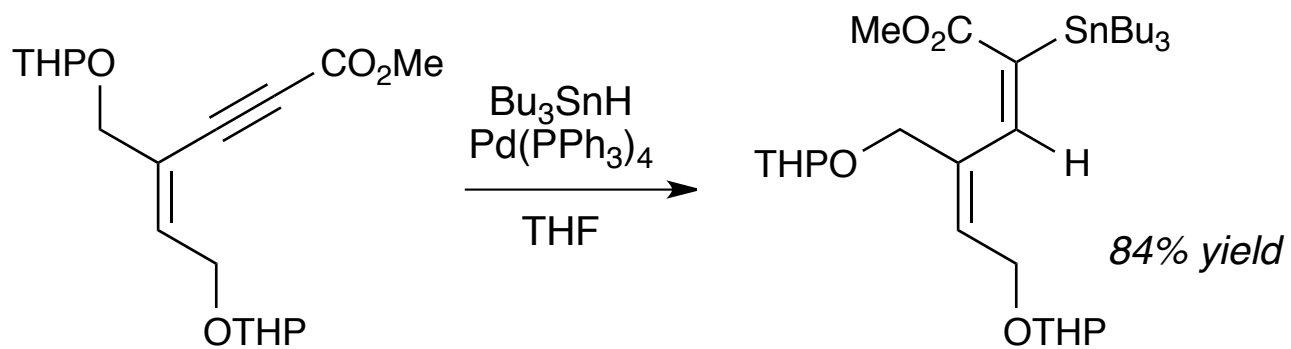
Org. Lett. **2009**, 11, 3282.



J. Org. Chem. **2009**, 74, 6452.

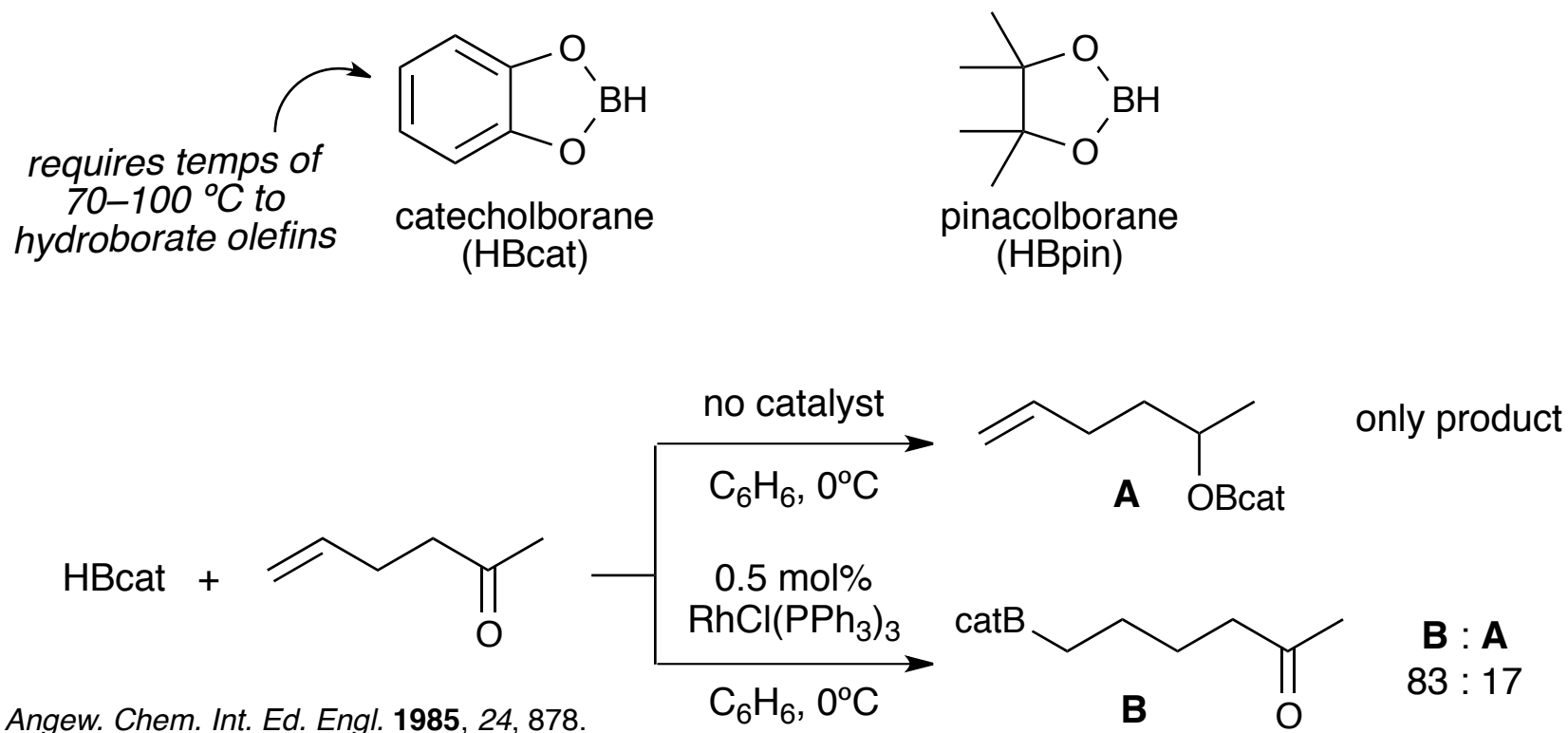
Hydrostannation

With alkynoates the tin usually ends up on the α -position ("conjugate addition of hydride").



Hydroboration

Metal catalysed hydroboration of alkenes and alkynes can be accomplished with dialkoxyboranes, most commonly catecholborane and pinacolborane. Dialkoxyboranes not as sensitive as dialkylboranes.



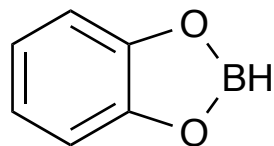
Mechanism is quite similar to hydrogenation by Wilkinson's cat.

J. Am. Chem. Soc. **1992**, 114, 9350.

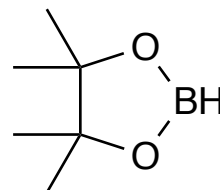
J. Am. Chem. Soc. **1992**, 114, 6679.

Hydroboration

Metal catalysed hydroboration of alkenes and alkynes can be accomplished with dialkoxyboranes, most commonly catecholborane and pinacolborane. Wilkinson's catalyst is commonly employed, but other can be used as well.

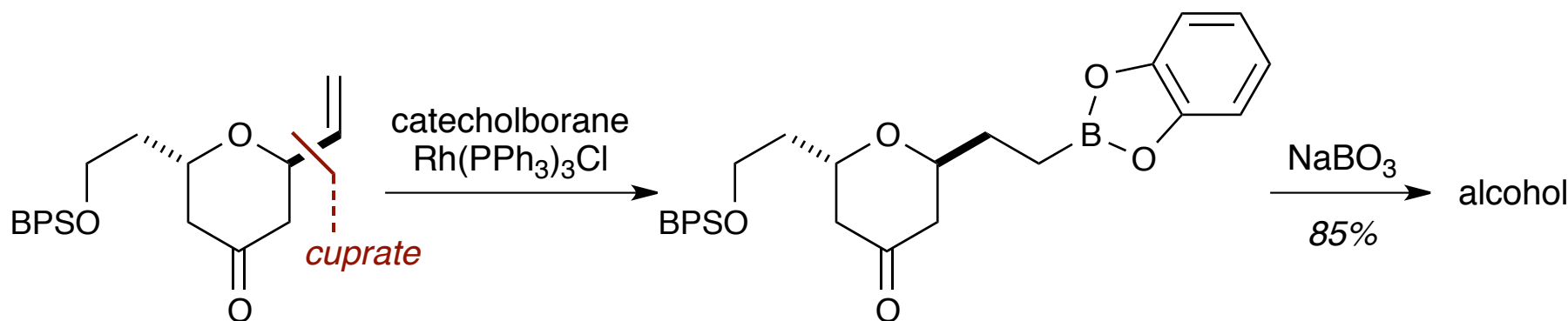


catecholborane



pinacolborane

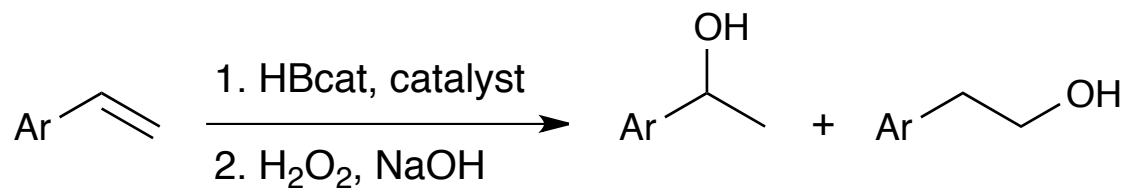
Stereoselectivity and regioselectivity can be higher than "traditional" hydroborations. Dialkoxyboranes not as sensitive as dialkylboranes. Chemoselectivity toward olefins/alkynes over ketones/aldehydes much higher.



J. Am. Chem. Soc. **2001**, *123*, 10942.

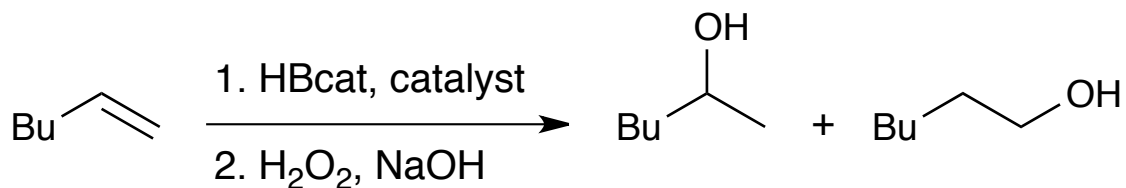
Hydroboration

Wilkinson's catalyst is commonly employed, but other can be used as well. The regioselectivity of the process can be quite dependent on both substrate and catalyst identity.

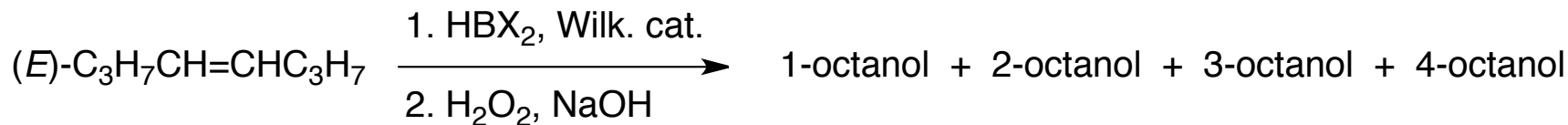


RhCl(PPh ₃) ₃ (argon)	> 99	< 1
RhCl(PPh ₃) ₃ (in air)	24	76
[Rh(COD) ₂]BF ₄ /dppb	99	1
Cp ₂ TiMe ₂	0	100

J. Am. Chem. Soc. **1992**, *114*, 9350.
J. Am. Chem. Soc. **1996**, *118*, 1696.



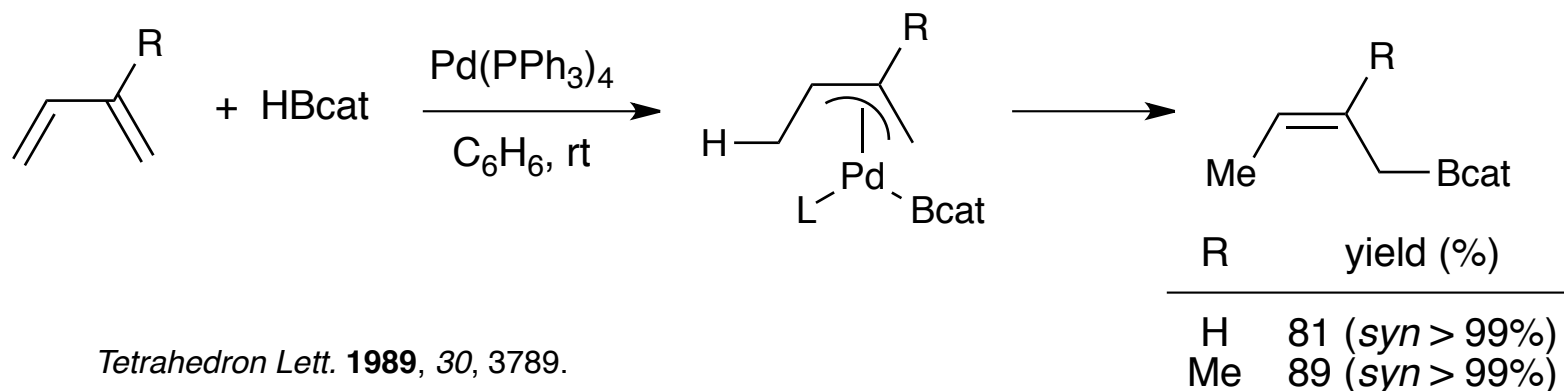
RhCl(PPh ₃) ₃	1	99
Cp* ₂ Sm(THF)	< 1	> 99



HBcat	THF	0	0	0	100
HBpin	CH ₂ Cl ₂	100	0	0	0

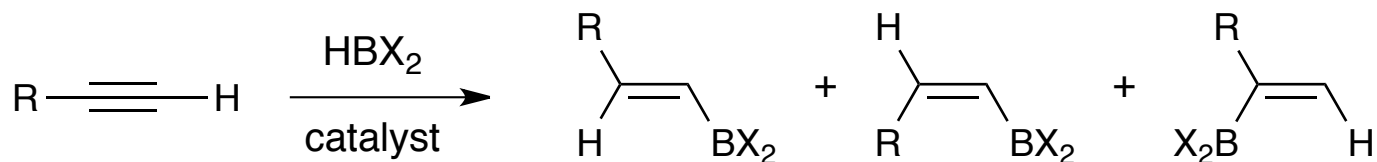
Hydroboration

Palladium catalyzed hydroboration of dienes provides access to allyl boronates.



Tetrahedron Lett. **1989**, 30, 3789.

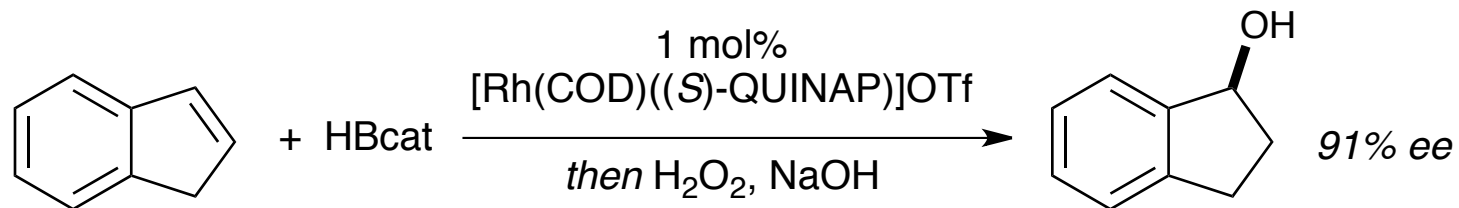
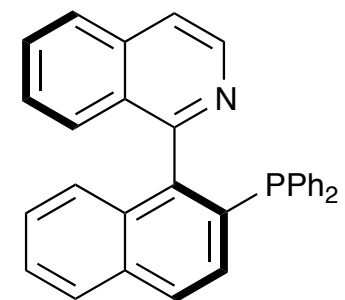
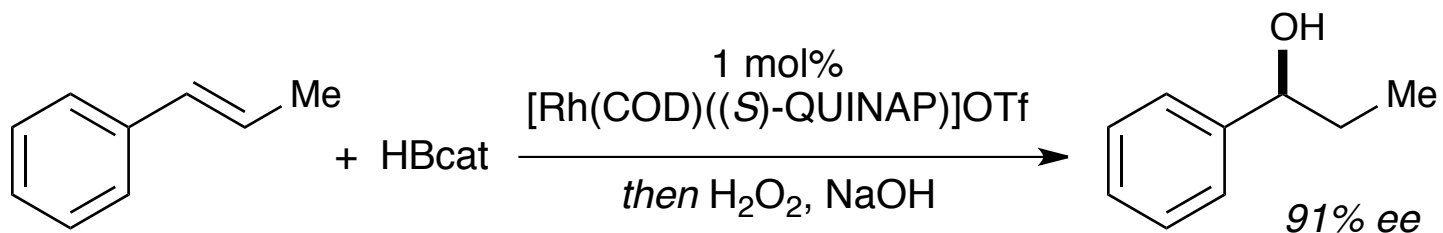
Alkynes can also be substrates. Not only is regioselectivity a problem, but stereoselectivity can also be a factor (net *syn* hydroboration not guaranteed).



<i>p</i> -Tol	HBcat	Cp ₂ Ti(CO) ₂	100	0	0
C ₄ H ₉	HBpin	Rh(CO)(PPh ₃) ₂ Cl	99	0	1
<i>p</i> -Tol	HBpin	RhCl(PPh ₃) ₃	48	0	52
Ph	HBcat	[Rh(cod)Cl ₂]/4 <i>Pi</i> -Pr ₃	1	99	0

Asymmetric Hydroboration

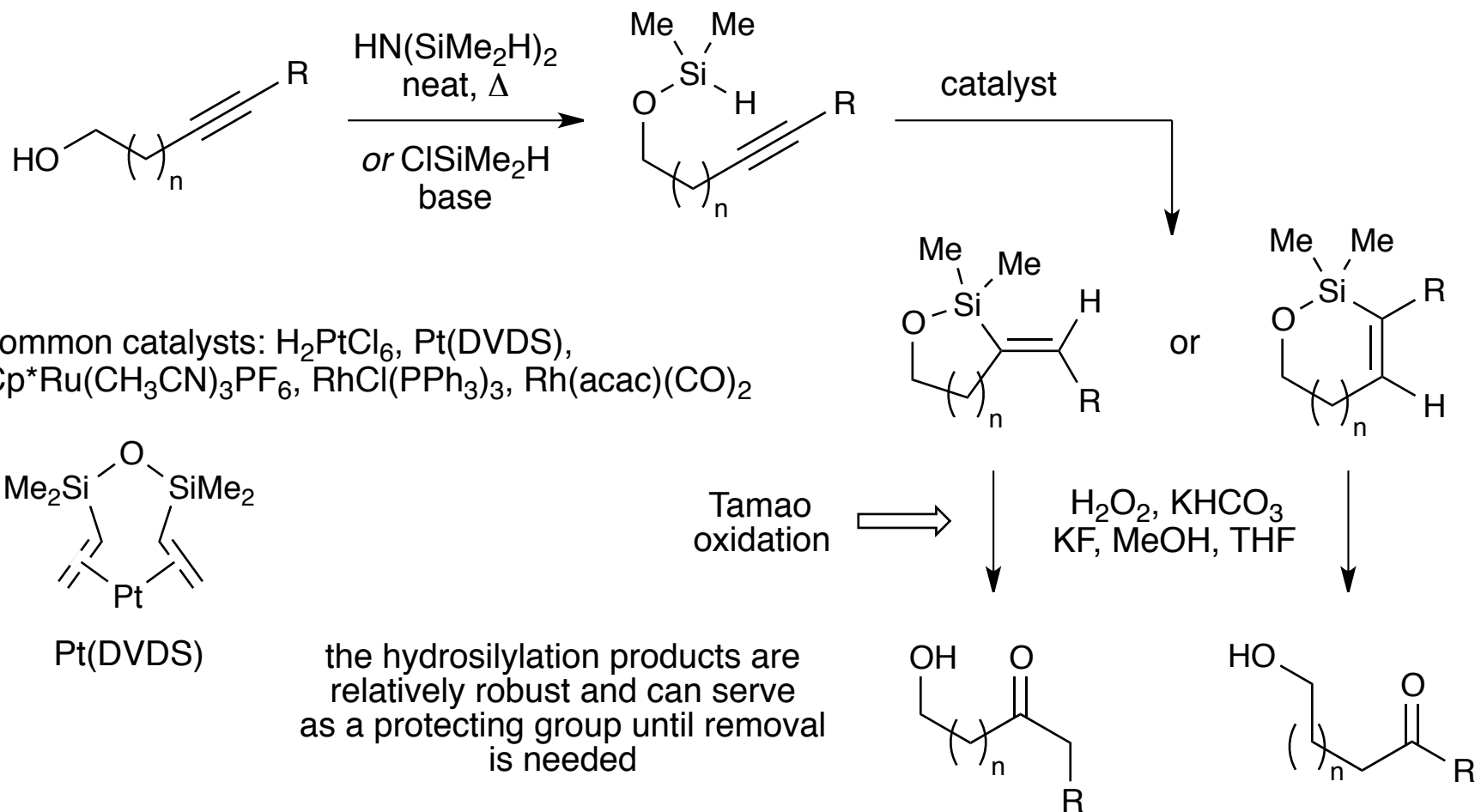
Enantioselective hydroborations are possible, but are quite limited at this time.



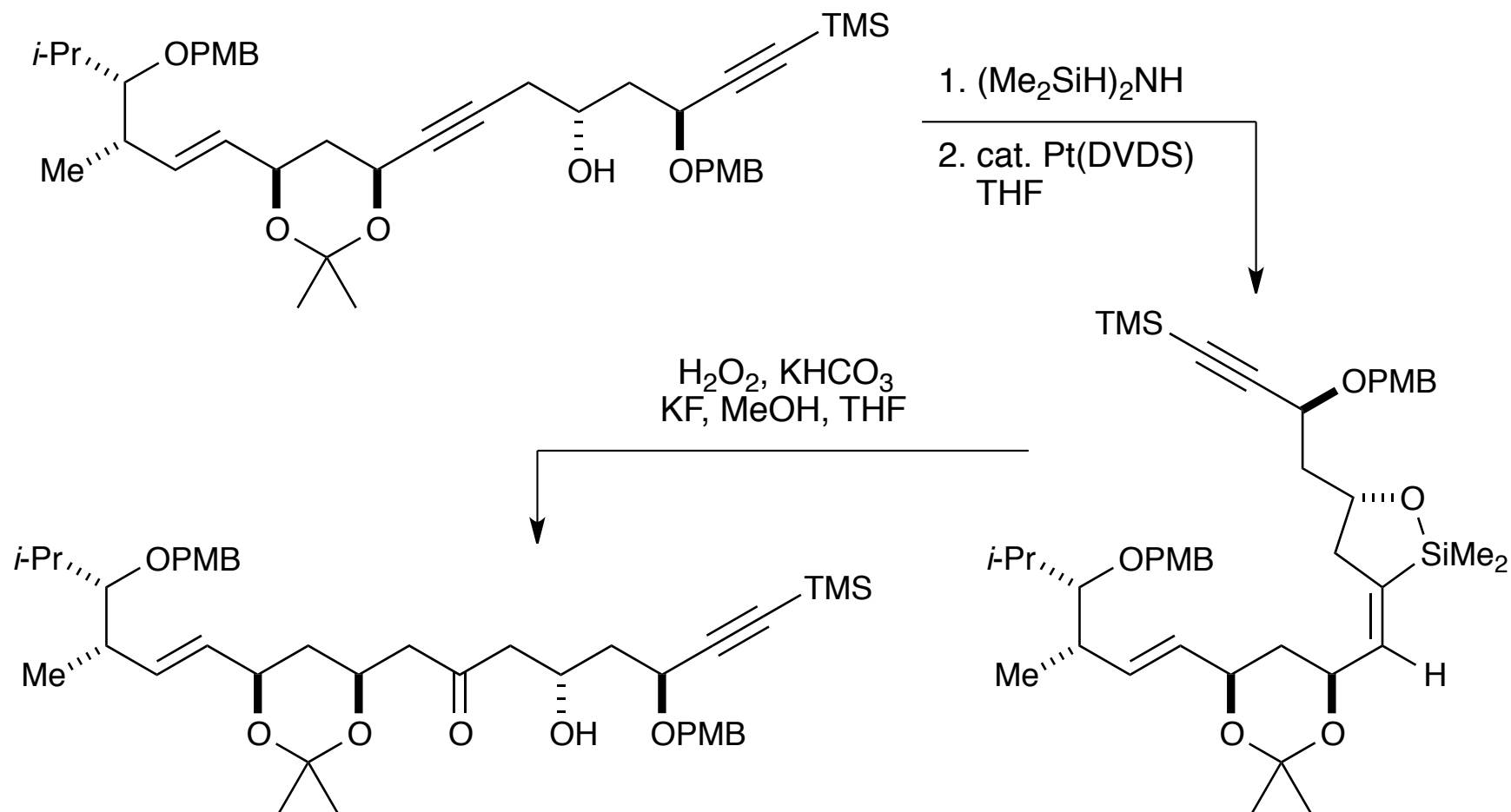
Hydrosilylation

Unlike borohydrides, silicon hydrides generally do not add to olefins or alkynes without a catalyst. Hydrosilylation is an important industrial reaction for generating silicon-containing materials. While there are a number of intermolecular examples that use simple silanes, the real synthetic utility is with intramolecular hydrosilylations.

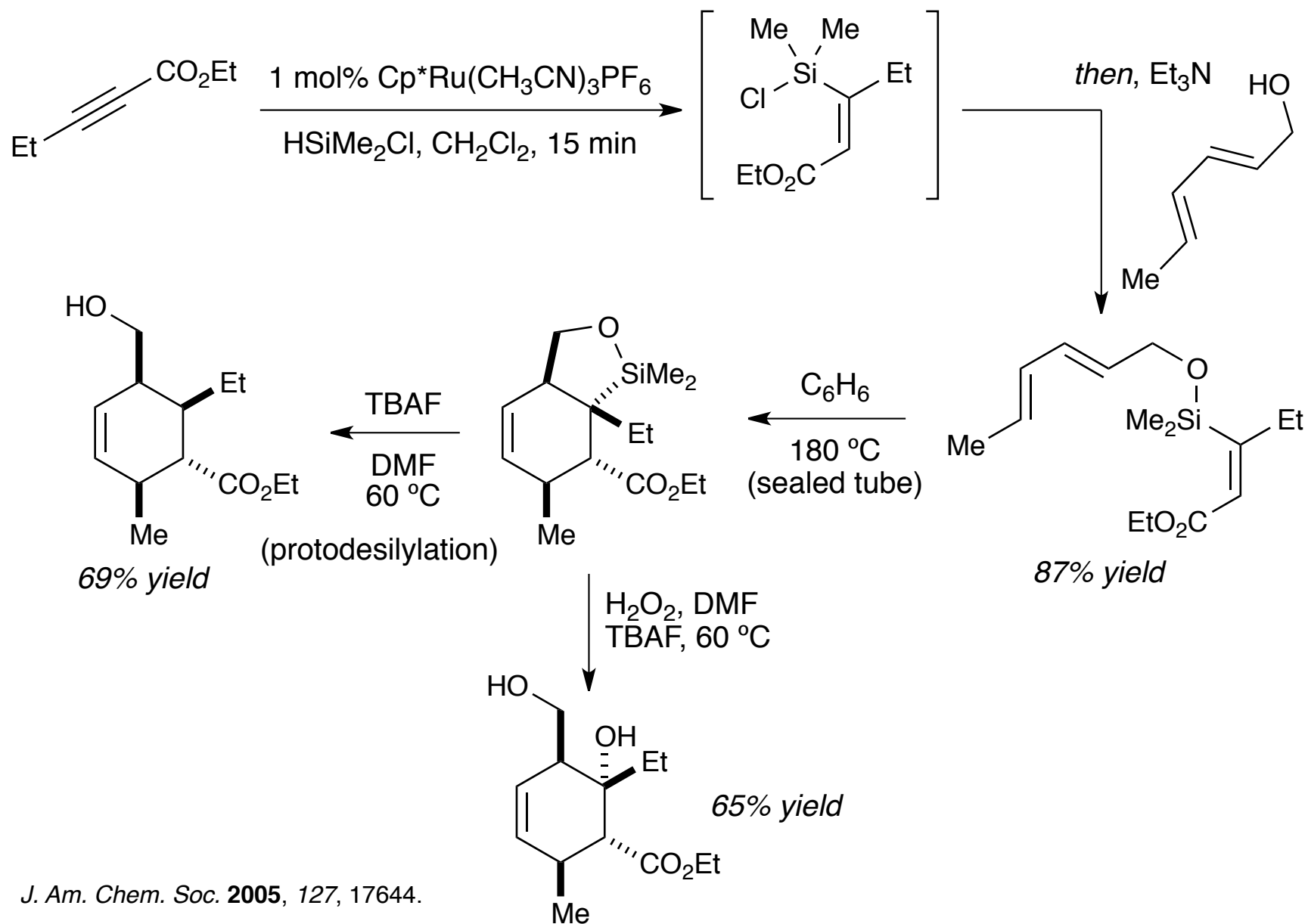
Alkynes are very common, but olefins can also be used.



Hydrosilylation

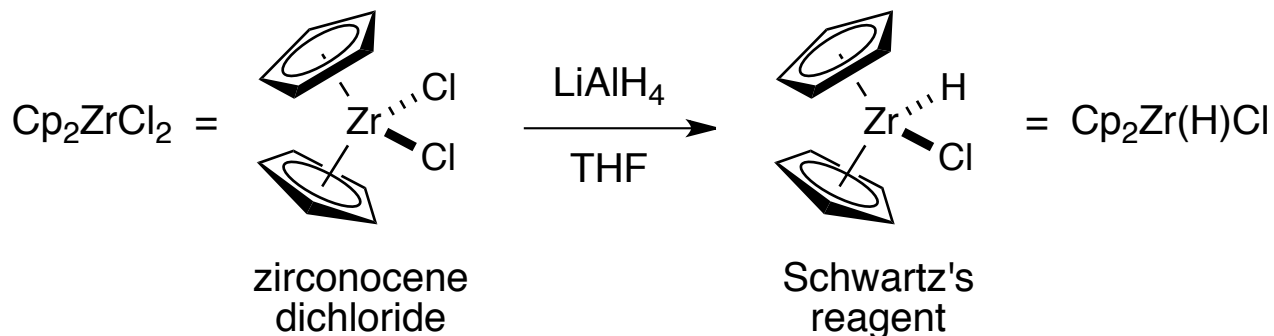


Hydrosilylation

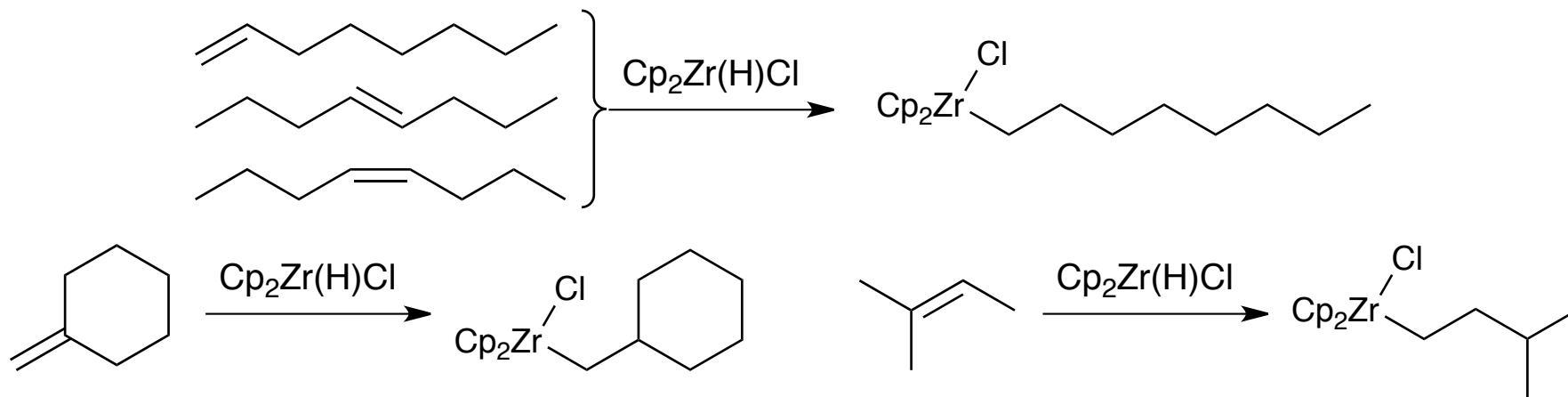


Hydrozirconation

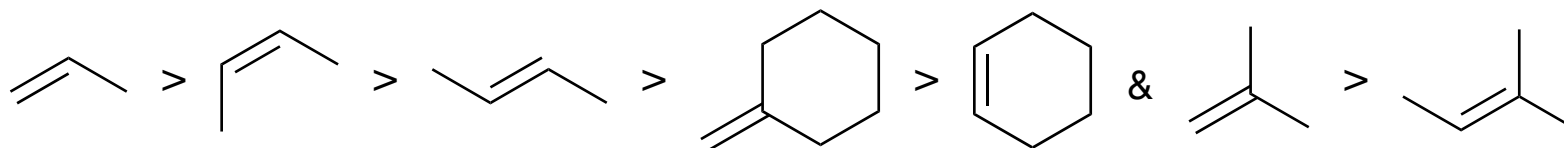
Not catalytic, but still highly useful.



Reaction with olefins results in formation of the terminal alkylzirconium species. This can be through direct reaction of a terminal olefin, or by initial reaction with an internal olefin followed by a series of eliminations/isomerizations to the terminal species.

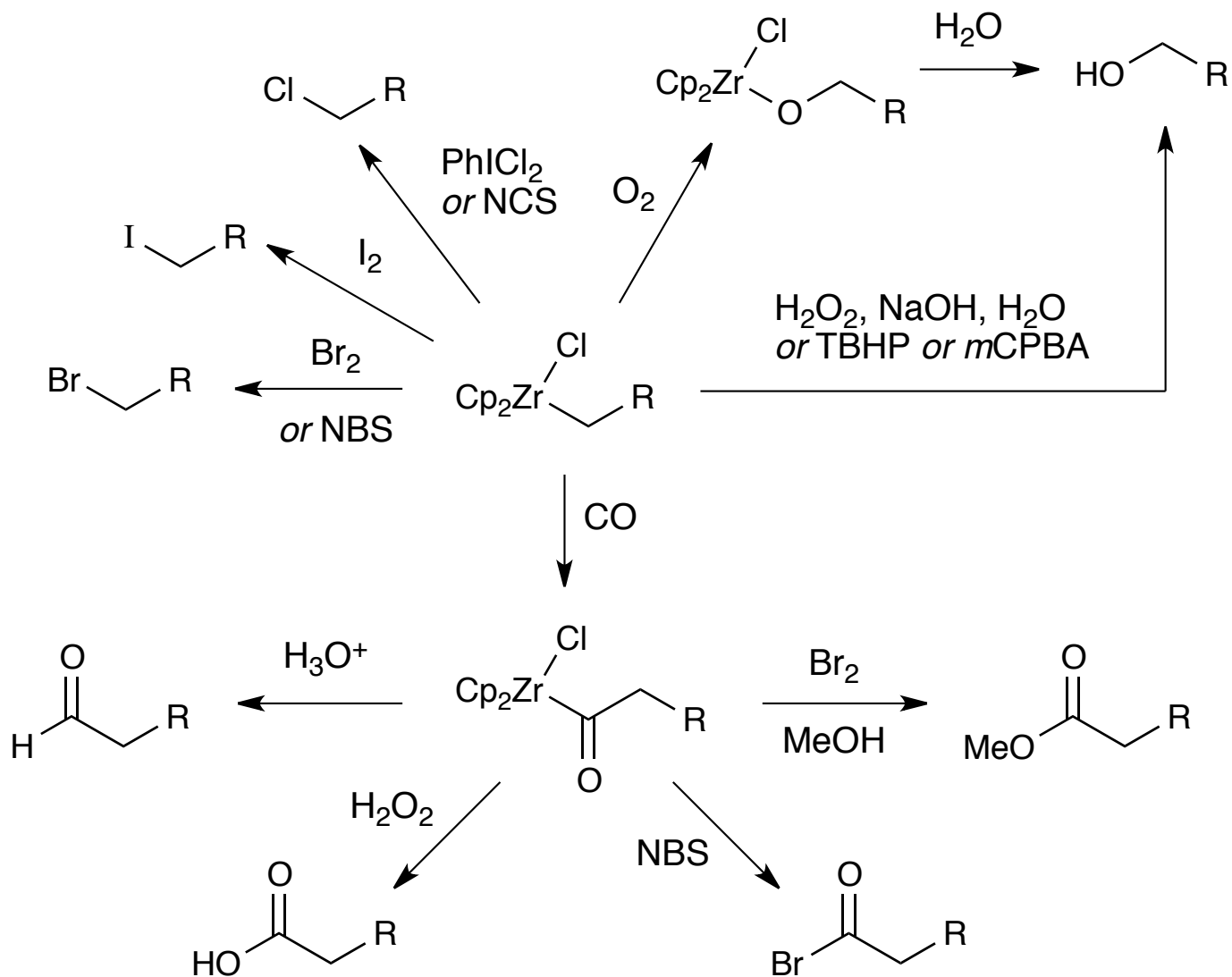


order of reactivity (tetrasubstituted and trisubstituted cyclic do not react)



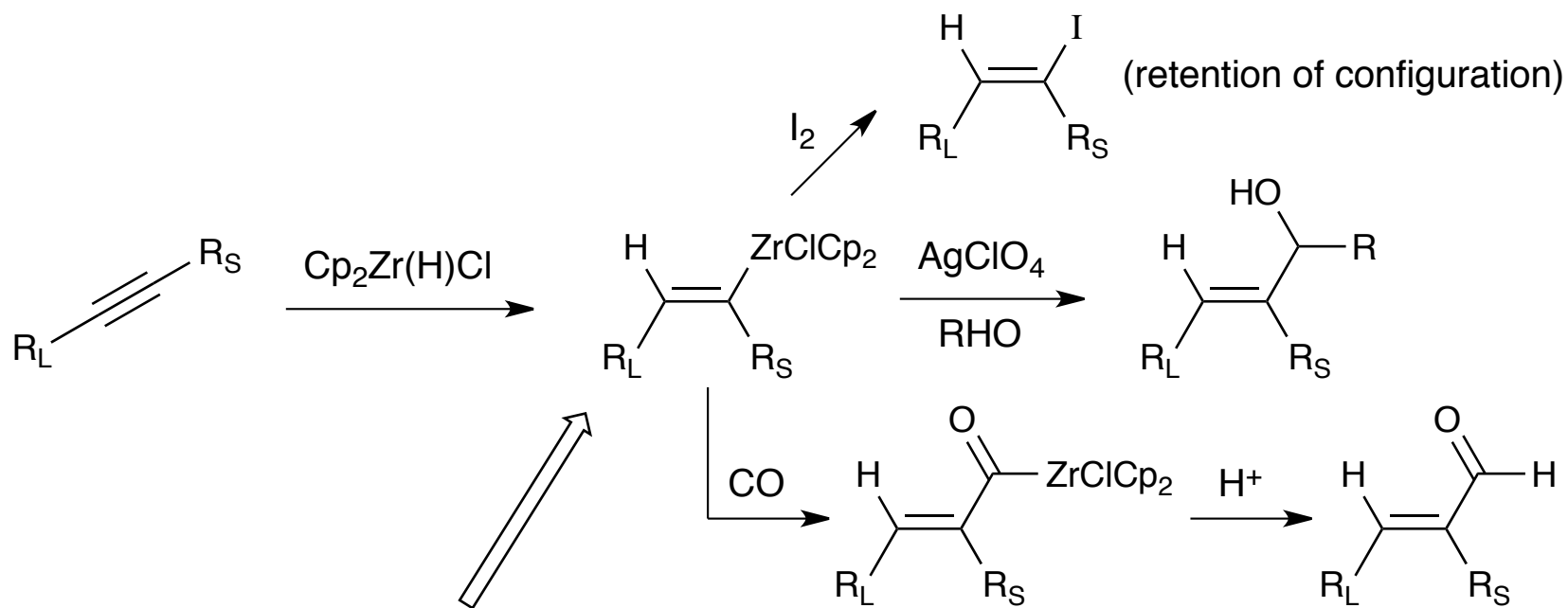
Hydrozirconation

The alkylzircononium products can be readily converted into many different functional groups.



Hydrozirconation

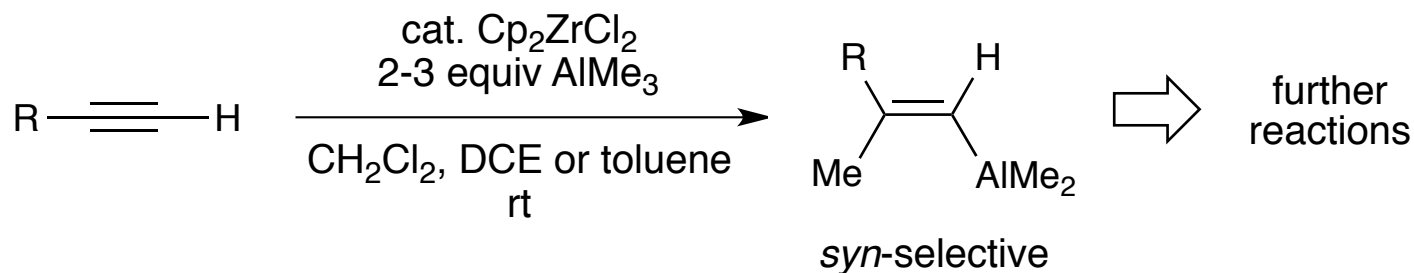
Schwartz's reagent also reacts readily with alkynes to give alkenylzirconium intermediates. *Syn* addition is observed. React with aldehydes in the presence of a Lewis acid and are useful in transmetalation reactions and cross couplings.



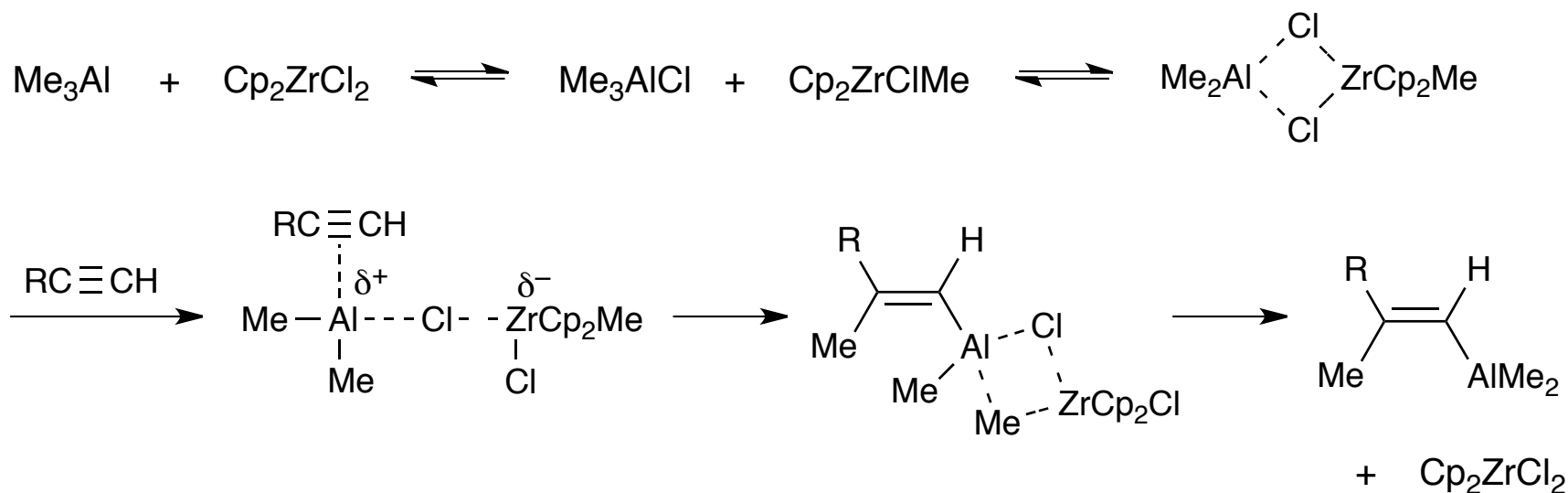
Zirconation on less substituted side predominates. By using a slight excess of $Cp_2Zr(H)Cl$ the mixture can be equilibrated to enrich this preference.

Zirconium-Catalyzed Carboalumination

Alkylzirconocenes do "carbozirconate" alkynes. But zirconocene dichloride (Cp_2ZrCl_2) can catalyze "carboaluminations" of alkynes with high *syn* selectivity. AlMe_3 is most commonly used.



Mechanism still not entirely clear. The one most consistent with data:

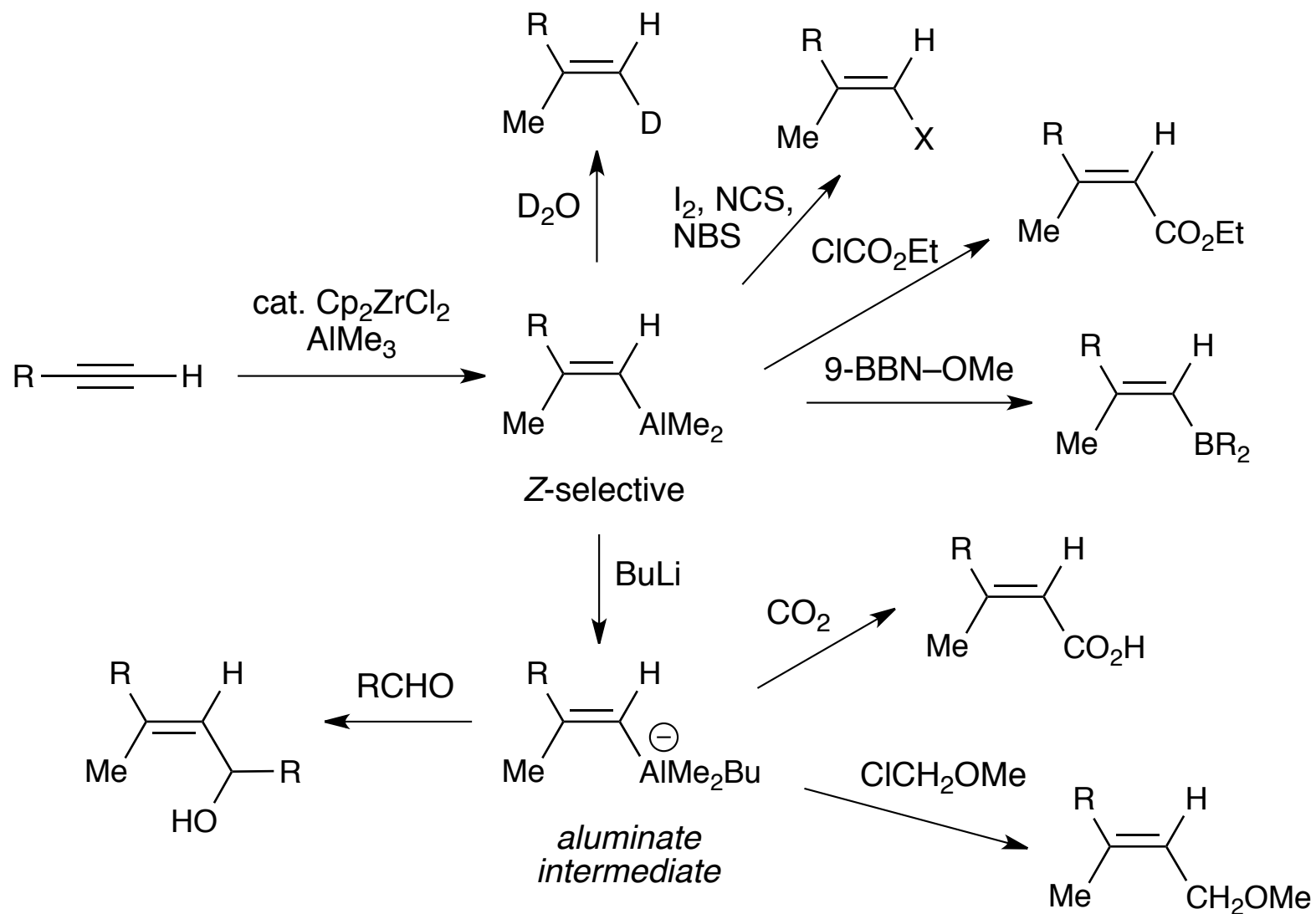


J. Am. Chem. Soc. **1978**, *100*, 2252.
J. Am. Chem. Soc. **1985**, *107*, 6639.
 H_2O promoted: *Angew. Chem. Int. Ed.* **1993**, *32*, 1068.

Mechanism discussion:
J. Am. Chem. Soc. **1983**, *103*, 4985.
J. Am. Chem. Soc. **1996**, *118*, 9577.

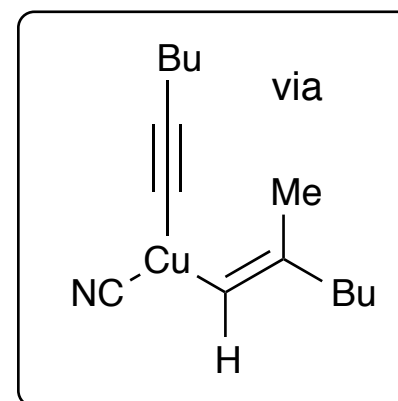
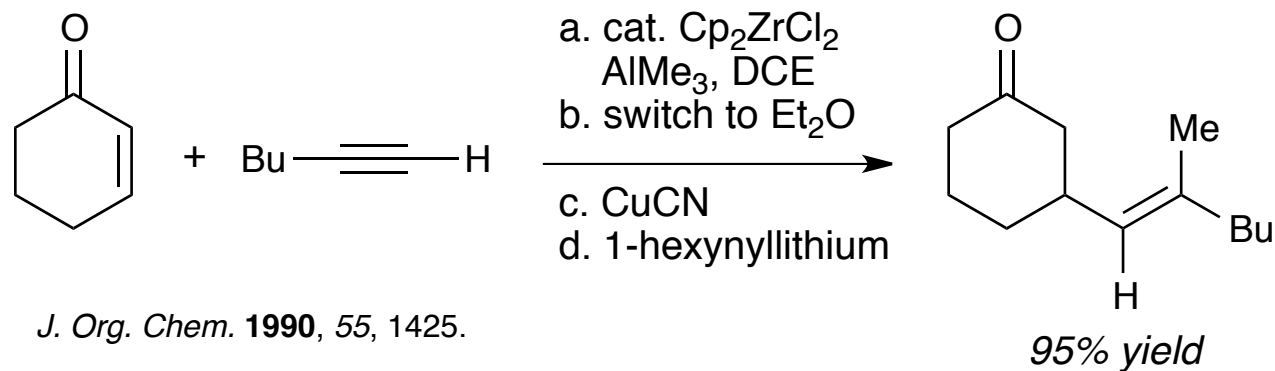
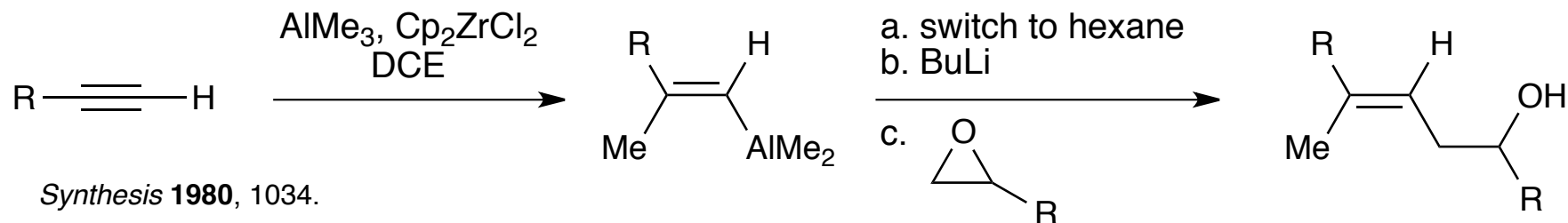
Zirconium-Catalyzed Carboalumination

The resulting σ -alkenylaluminum intermediate can undergo several transformations. Retention of configuration is generally observed.

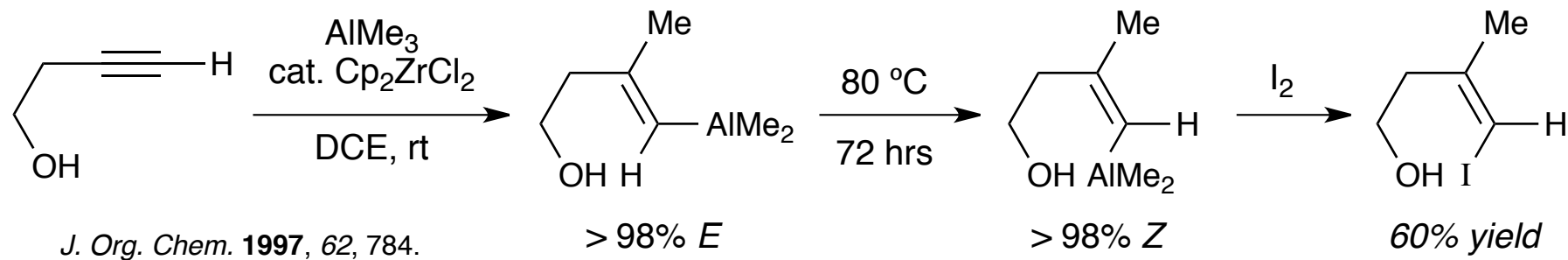


Zirconium-Catalyzed Carboalumination

More examples:



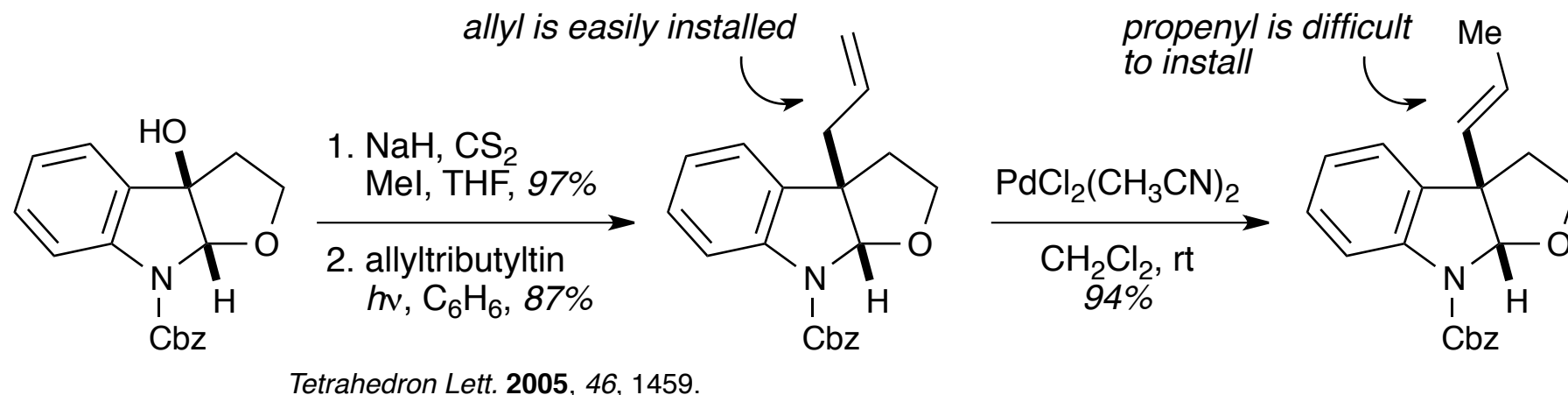
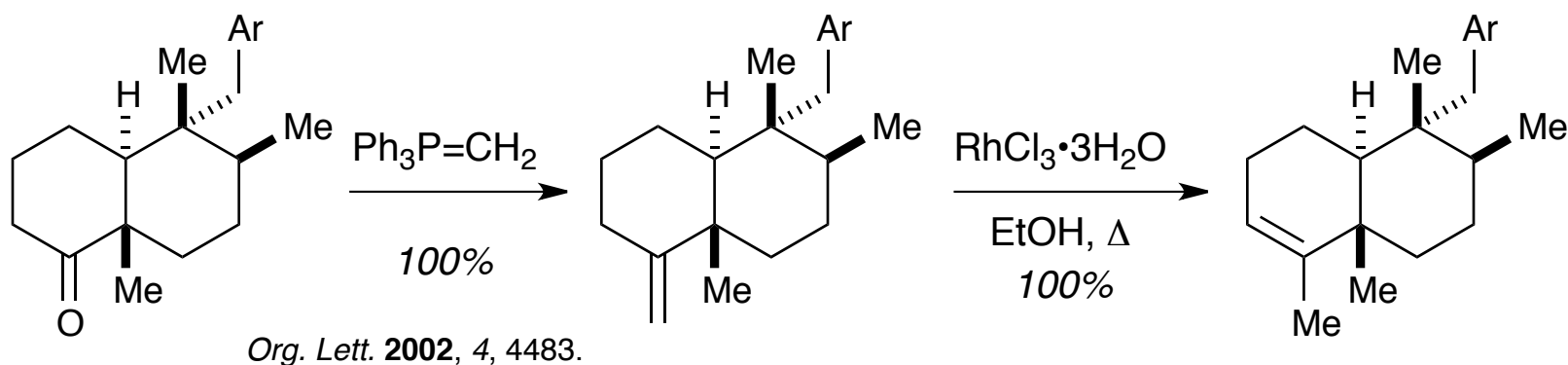
thermal isomerization of homopropargylic alcohols



Olefin Isomerizations

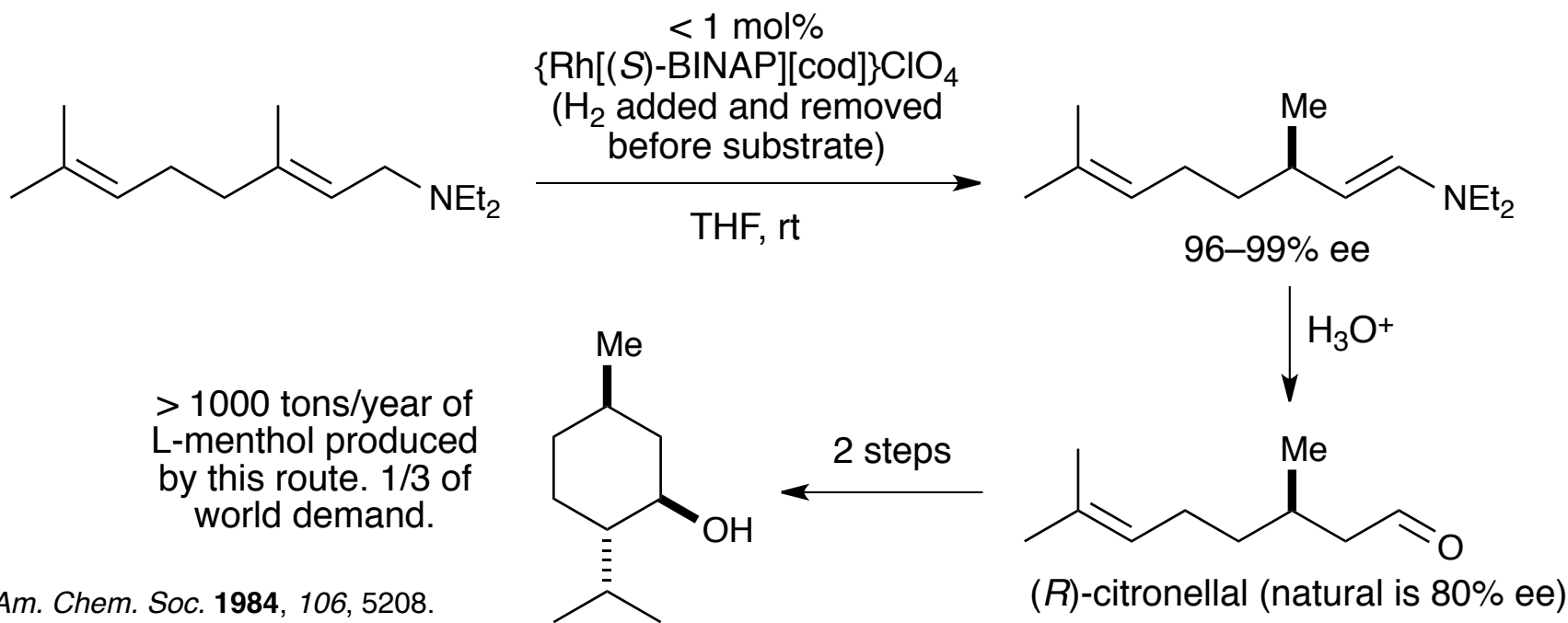
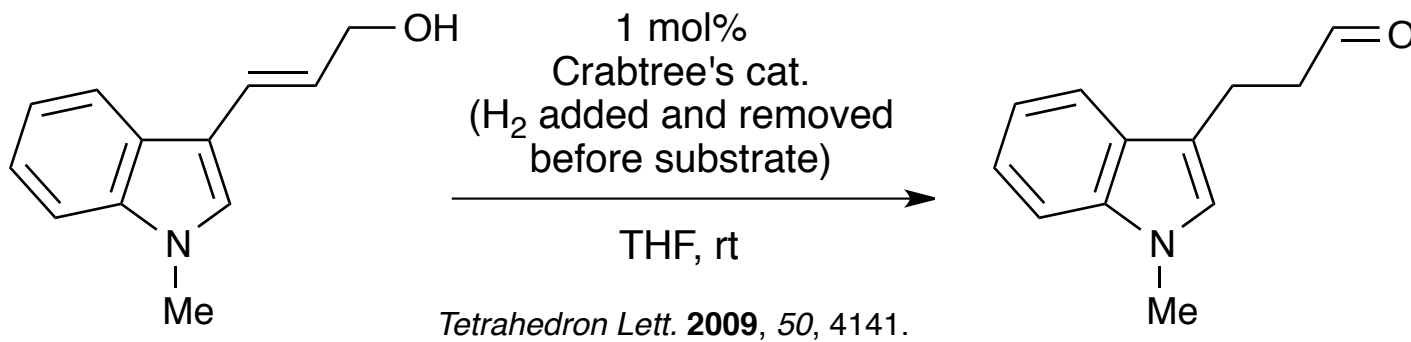
Initially considered a bit of a nuisance in olefin reductions, but has become a useful strategy if controlled properly. Typical catalysts are those used in hydrogenation reactions (Pd, Rh, Ru, Ir). Typically give the more substituted olefin. No one general catalyst.

Main utility lies in being able to isomerize terminal olefins into the more thermodynamically favorable internal olefins.



Olefin Isomerizations

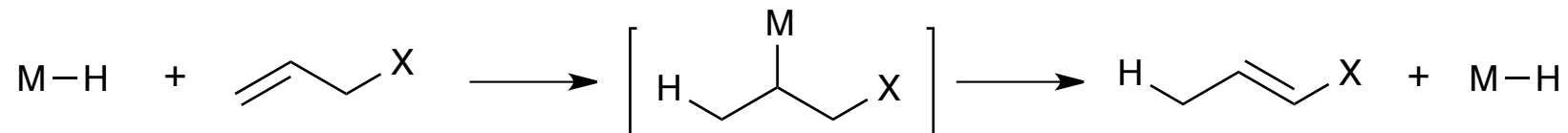
Isomerization of allylic alcohols, ethers, and amines also quite useful. Gives aldehydes, enol ethers, and enamines, respectively.



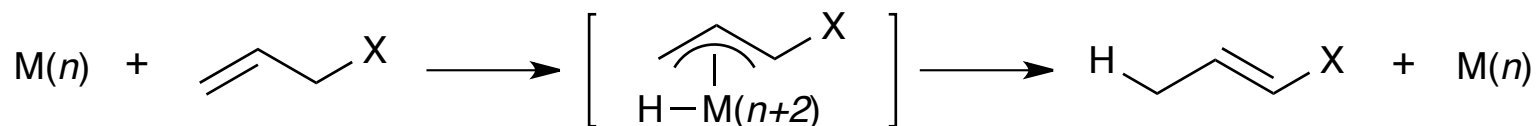
Olefin Isomerizations

Several different mechanisms are possible depending on catalyst and conditions.

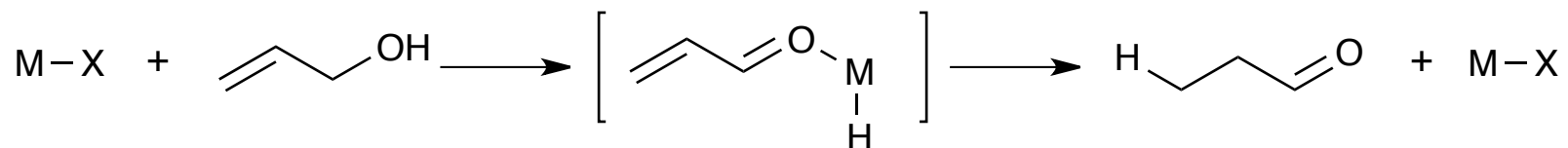
Isomerization by metal hydrides



Isomerization by low-valent metals

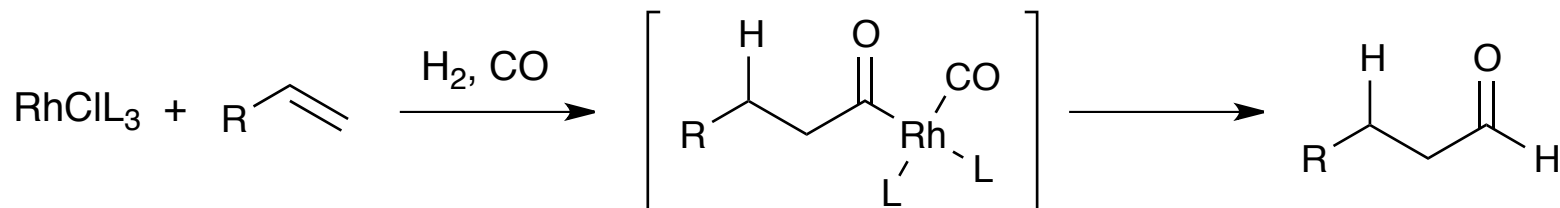


Isomerization by low-valent metals

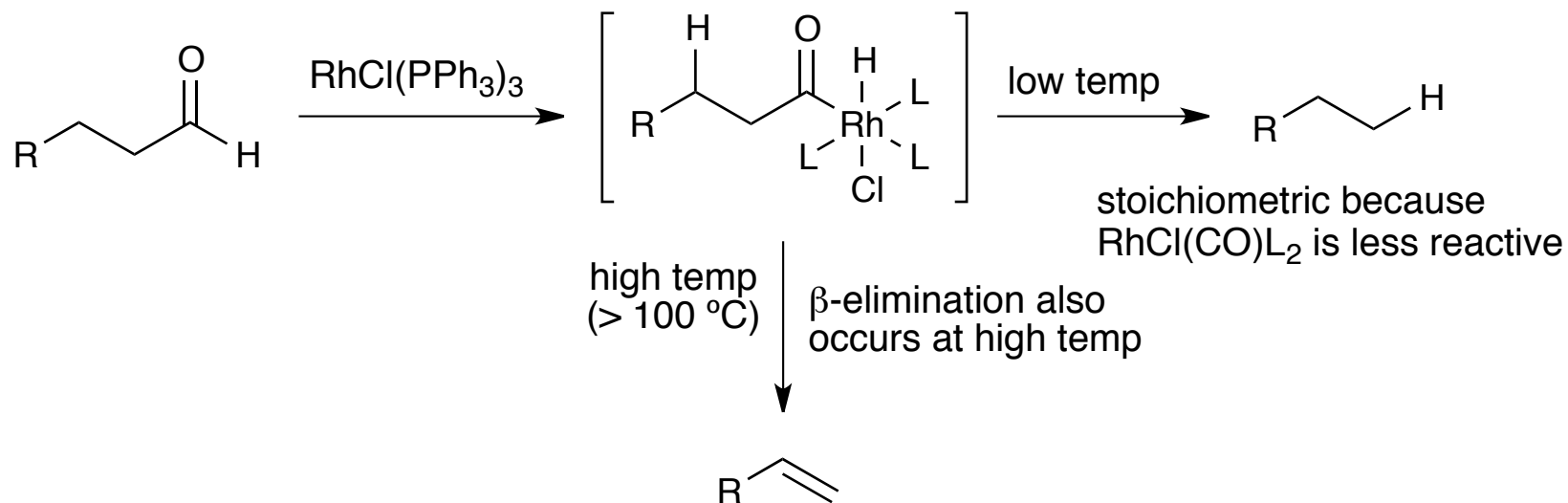


Hydroformylation

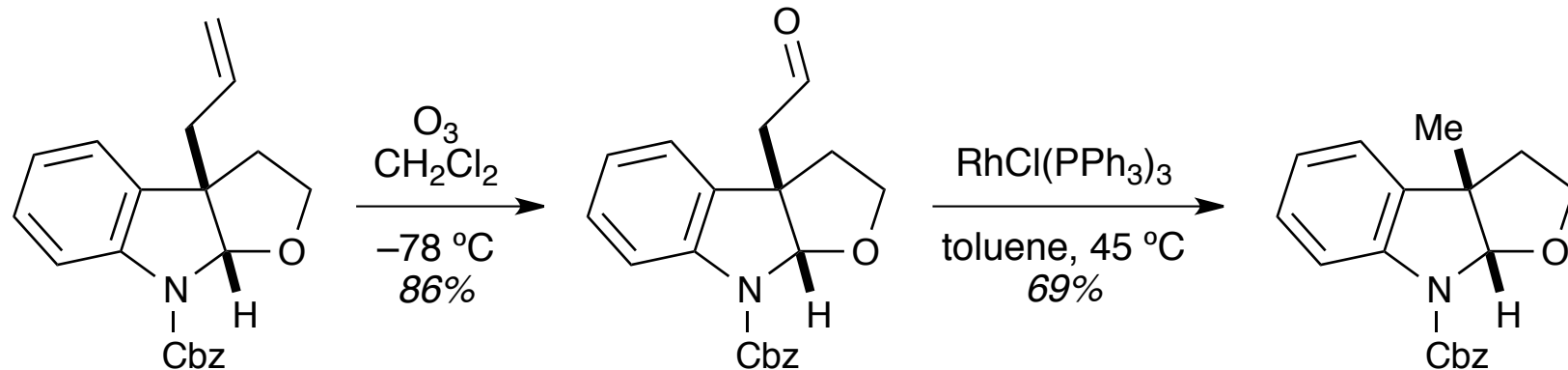
As the name implies, hydroformylation is the process of adding the components of H₂ and CO to an olefin. While other metals are possible, the use of Rh complexes is most common (usually Wilkinson's catalyst). Typically terminal olefins are used. Very important industrially.



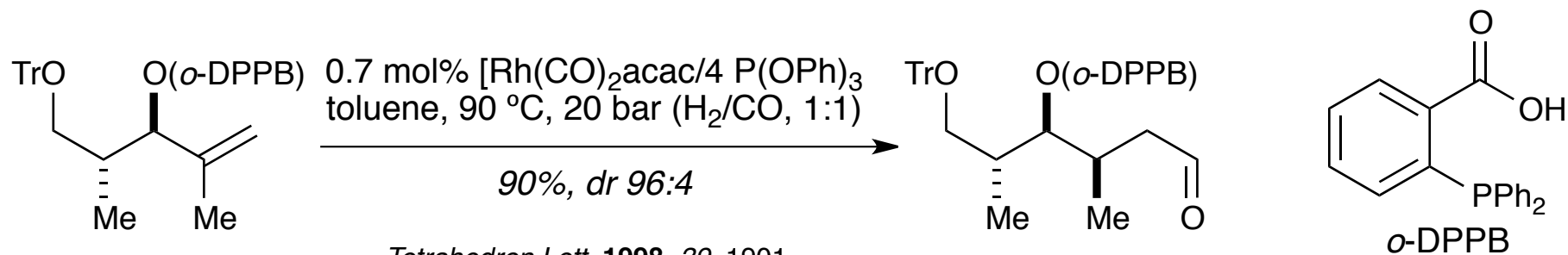
The reaction is reversible, so high pressures of CO must often be used. However, this can be a useful means of removing an aldehyde. Aldehydes on sp² and sp³ carbons both work. Retention of stereochemistry is observed.



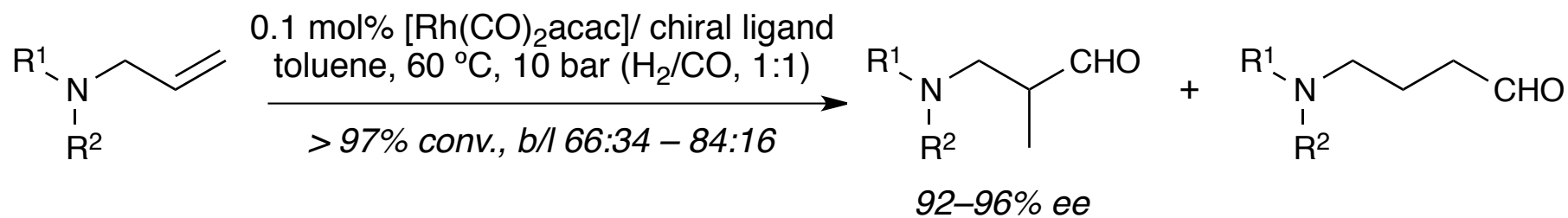
Hydroformylation



Tetrahedron Lett. **2005**, 46, 1459.



Tetrahedron Lett. **1998**, 39, 1901



Angew. Chem. Int. Ed. **2010**, 49, 4047

Hydroacylation

In some cases, the acylmetal intermediate can be intercepted by alkenes and alkynes before the decarbonylation occurs. Cyclic products result.

