

# The Chemistry of Cobalt and Iridium

Baran Group Meeting – 30 November 2005

Carlos Guerrero

Some useful reference texts:

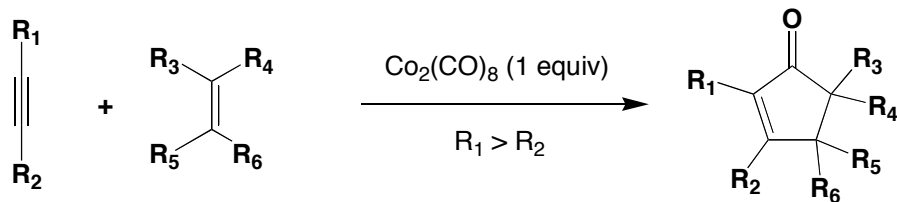
**Crabtree, Robert H.** *"The Organometallic Chemistry of the Transition Metals"* 3rd Ed., Wiley Interscience, **2001**.

**Czako, Barbara; Kurti, Laszlo.** *"Synthetic Applications of Named Reactions in Organic Synthesis"* Elsevier Academic Press, **2005**.

**Dyker, Gerald,** editor. *"Handbook of C–H Transformations"* Vols. 1 and 2, Wiley-VCH, **2005**.

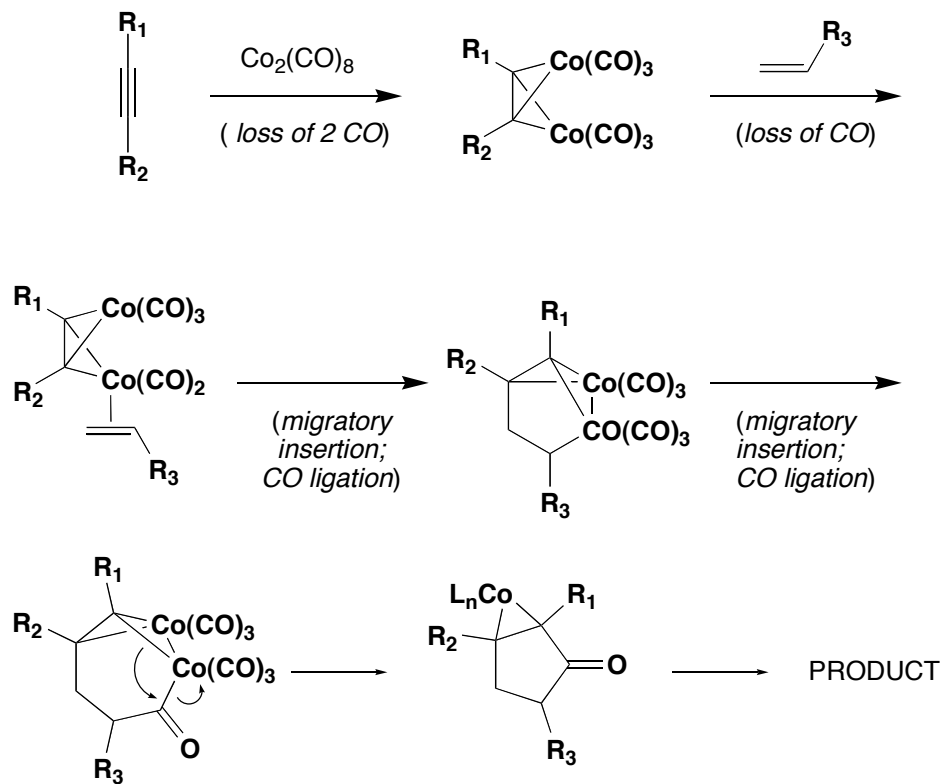
**Tsuji, Jiro.** *"Transition Metal Reagents and Catalysts: Innovations in Organic Synthesis"* Wiley, **2000**.

## Pauson-Khand Reaction

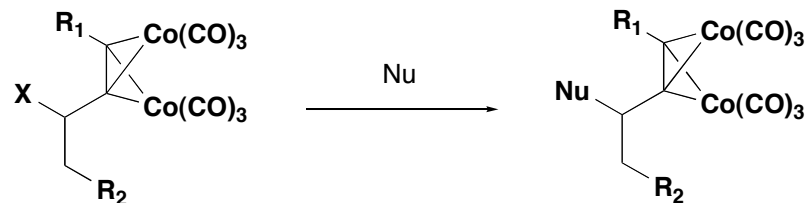


- The reaction can be mediated by a variety of metal complexes. In order to render the reaction catalytic, one must use a high pressure atmosphere of CO.
- The reaction can be accelerated by the addition of various promoters that accelerate the rate of dissociation of CO ligands on metal centers.
- The required alkyne-metal complex does not need to be prepared *in situ*. The complex can be formed several steps in advance in the context of a synthetic sequence and can even be subjected to silica gel chromatography, but exposure to oxidizing agents will return the starting alkyne.
- The reaction can be performed intramolecularly. Tetrasubstituted alkenes do not react.
- Somewhat incompatible functionalities include halides and vinyl ethers/esters.
- The mechanism has not been fully elucidated.

## Proposed mechanism:



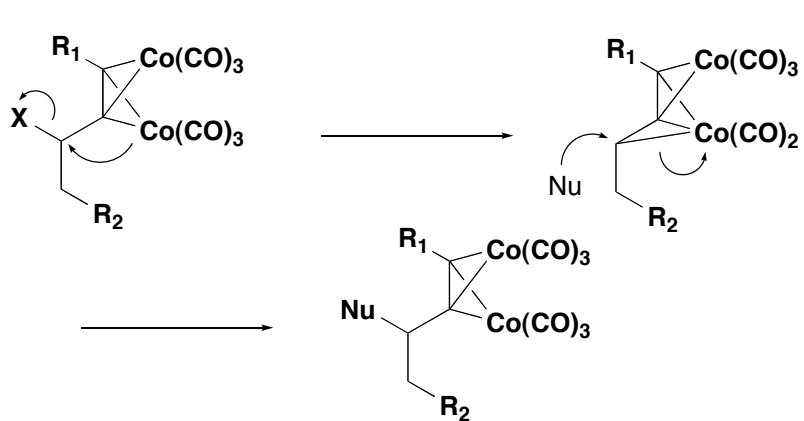
## Nicholas Reaction



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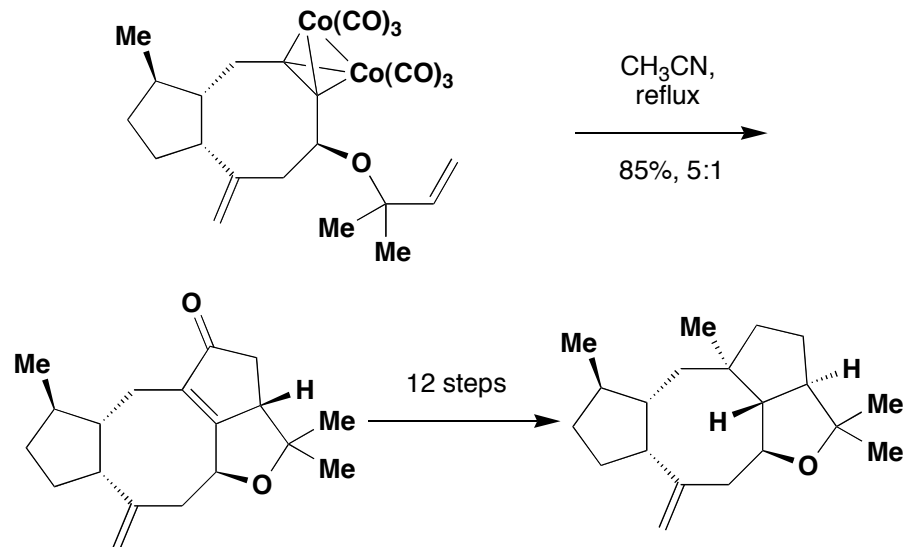
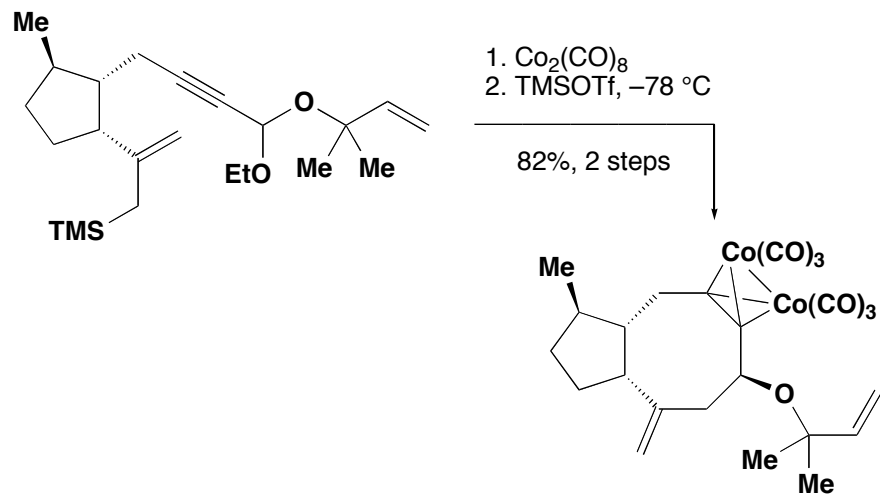
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- C, O, N, and S-nucleophiles are all suitable for the Nicholas reaction.
- The reaction can be conducted intramolecularly.
- No allene side products are observed.

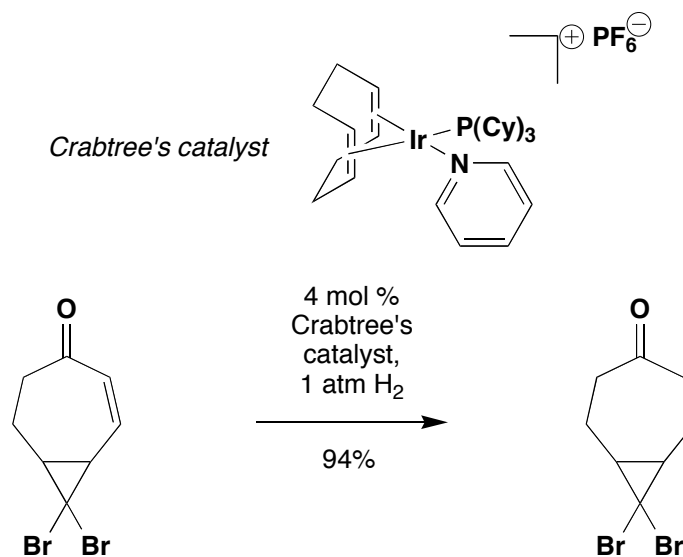
## Cobalt-Mediated Total Synthesis of (+)-Epoxydictymene

Schreiber, JACS, 1994, p. 5505.



## Homogenous Hydrogenations Using Ir(I)-based Catalysts

Crabtree, TL, 1981, p. 303.

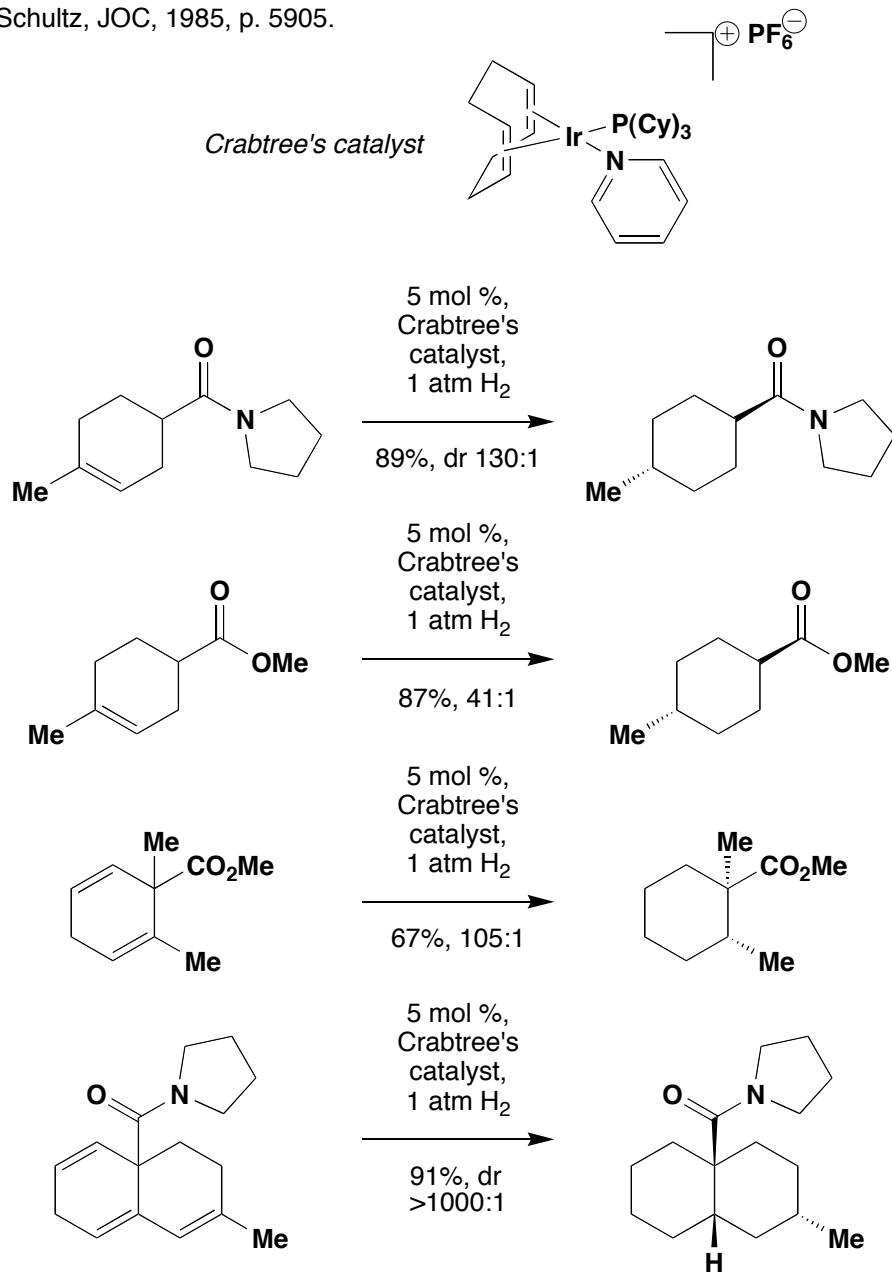


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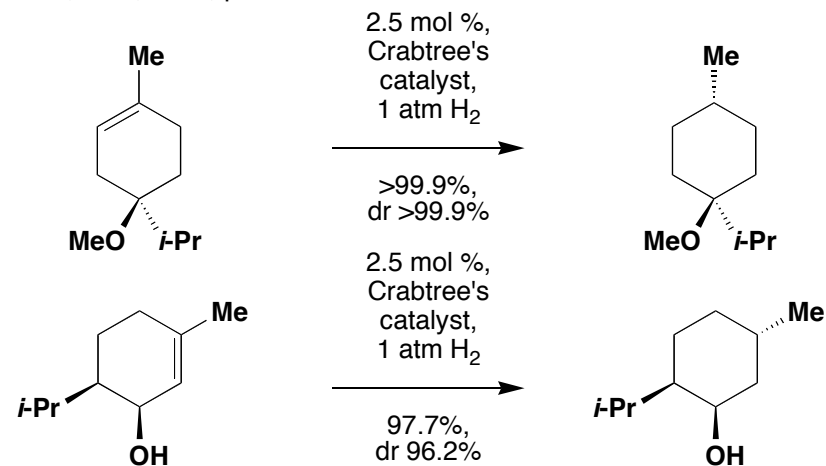
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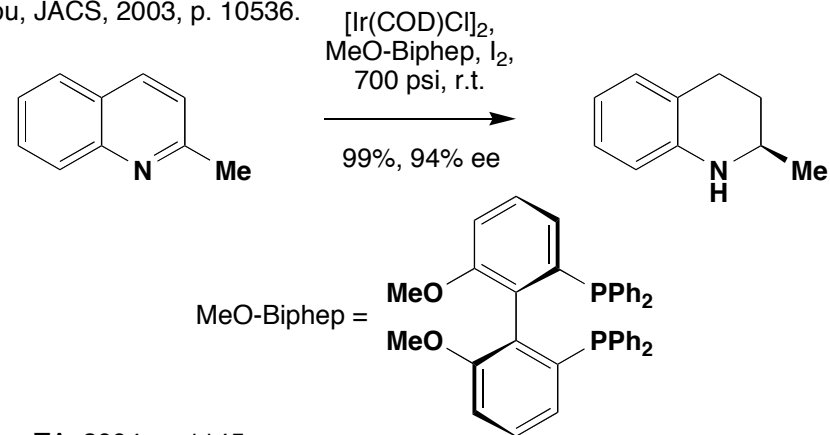
Schultz, JOC, 1985, p. 5905.



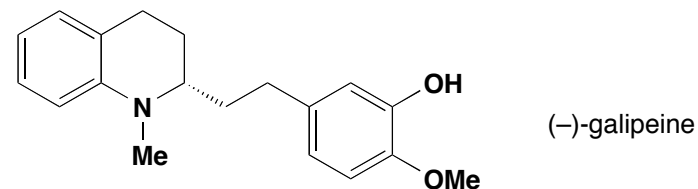
Crabtree, JOC, 1986, p. 2655.



Zhou, JACS, 2003, p. 10536.



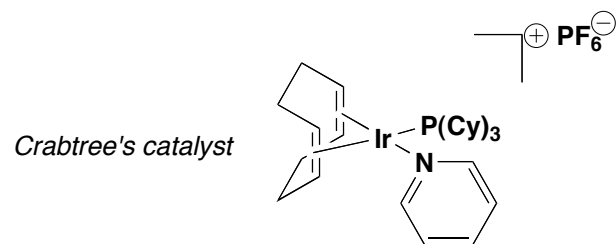
Zhou, TA, 2004, p. 1145.



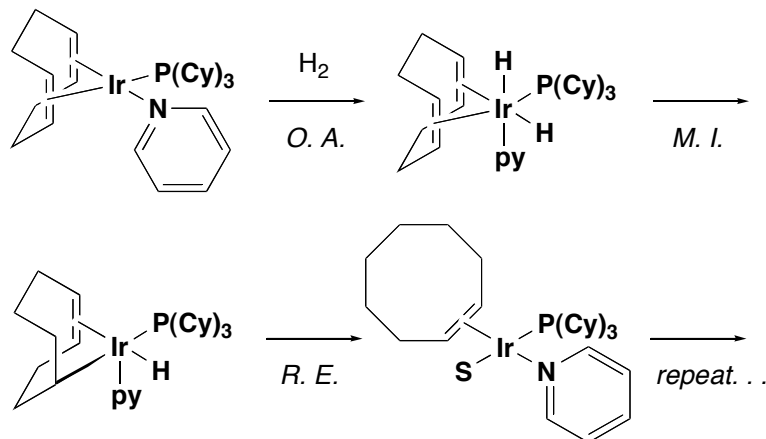
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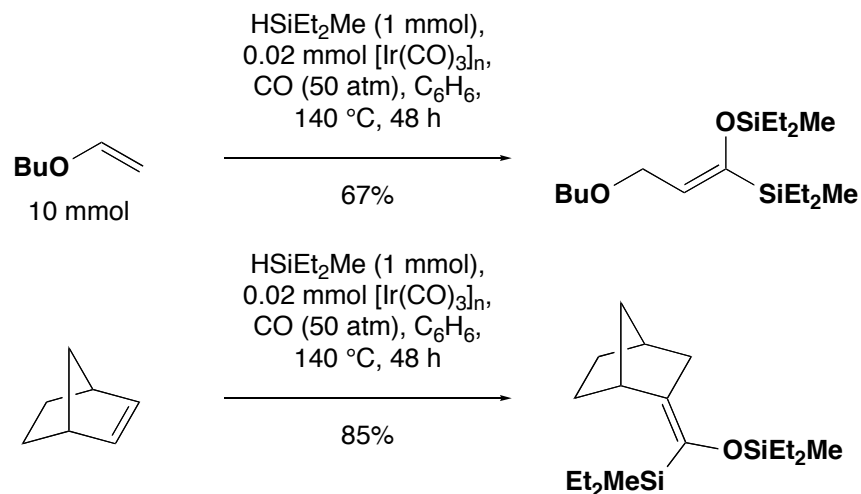
General dihydride mechanism for homogenous hydrogenation:



- This mechanism is applicable to a wide range of homogenous hydrogenation catalysts with small modifications.

- Excess catalyst leads to erosion of yields and selectivities (when applicable) presumably due to the formation of dimeric and trimeric metallic species that are inactive toward hydrogenation.

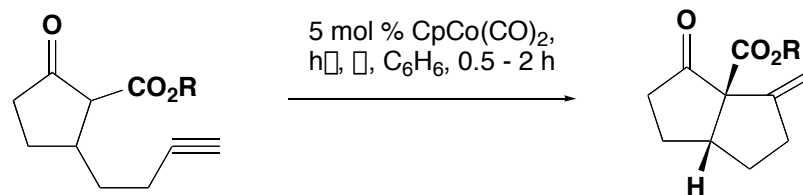
**Conversion of Alkenes to Enol Silyl Ethers of Acyl Silanes by Iridium-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide**  
Murai, JACS, 1992, p. 9710.



The mechanism of this transformation has not been elucidated. Mixtures of *E* and *Z* olefins are produced. The products can be hydrolyzed to give acyl silanes.

**Cycloisomerization Reactions**

Malacria, Synlett, 1997, p. 931.



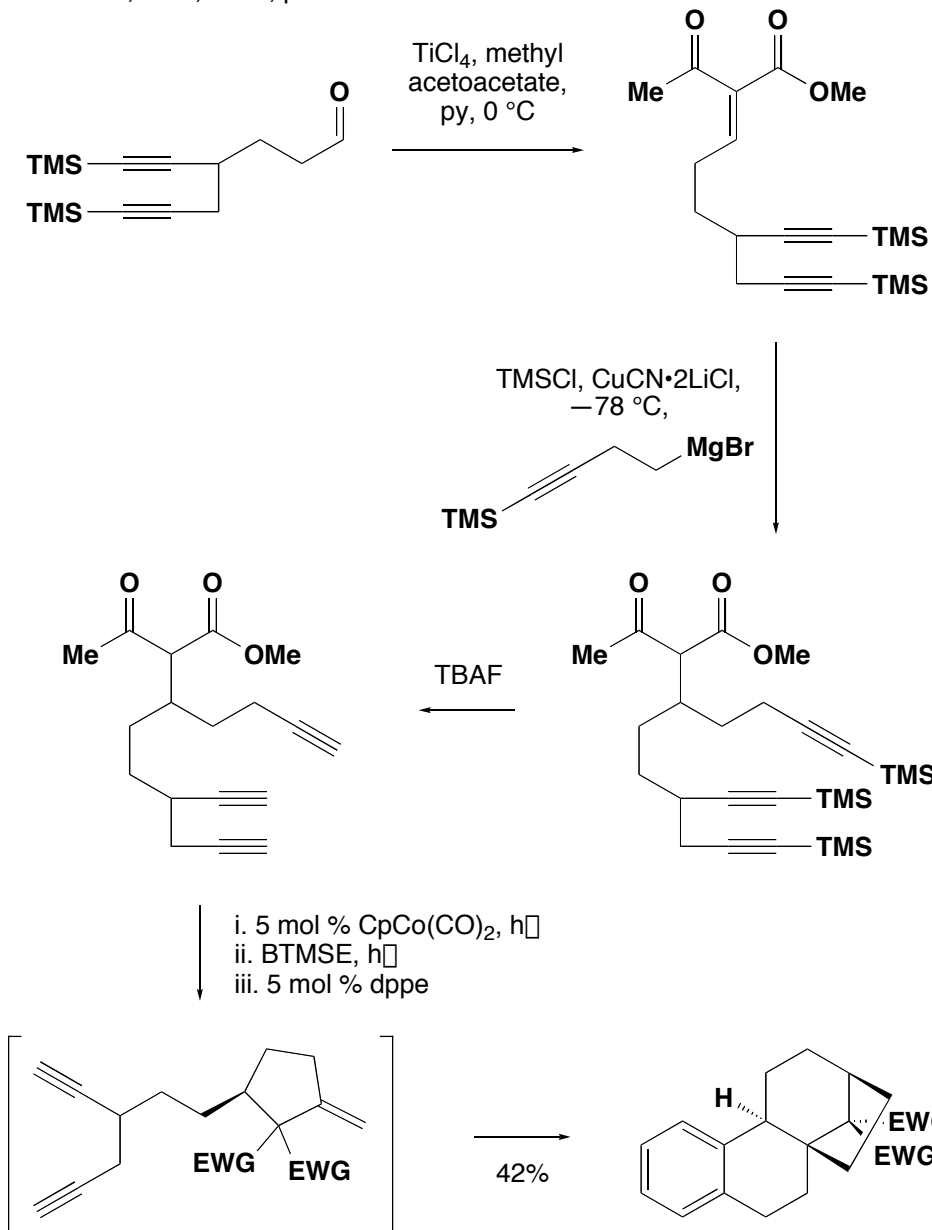
ring size:	5	6	7	8
yield:	73%	81%	70%	73%

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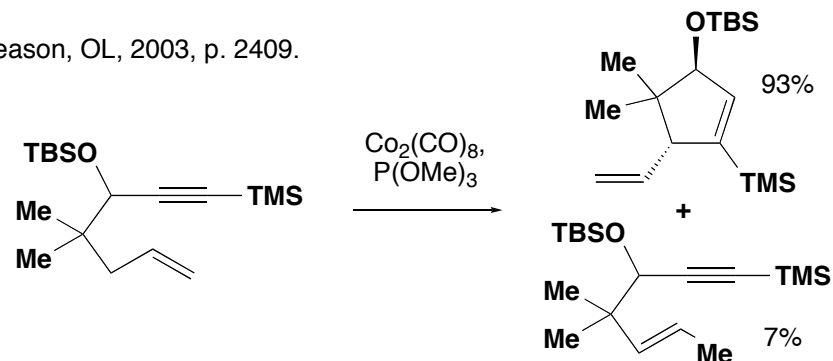
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Malacria, JOC, 1996, p. 2699.



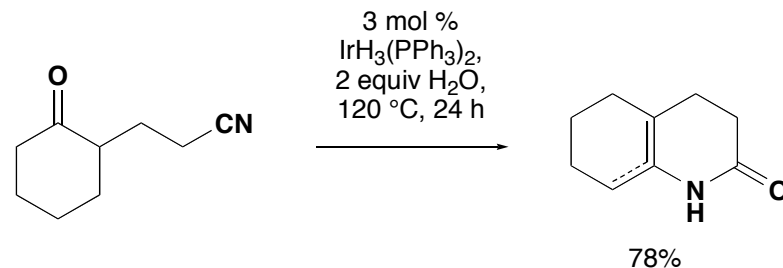
Gleason, OL, 2003, p. 2409.



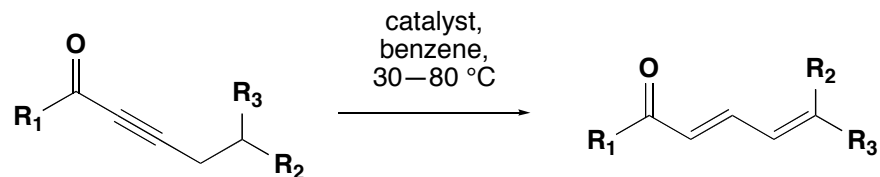
Note that the alkyne terminus is incorporated into the new cyclopentene. The terminal alkyne must be subject to the reaction conditions in its protected form.

## Functional Group Interconversions

Murahashi, T, 1993, p8805.



Note: this transformation has been demonstrated as shown, but Ru catalysts are superior in this setting.



catalyst:  $\text{IrH}_5(i\text{-Pr}_3\text{P})_2$ ,  $\text{RuH}_2(n\text{-Bu}_3\text{P})_4$ , or  $\text{RuCl}_2(\text{PPh}_3)_3/\text{PPh}_3$

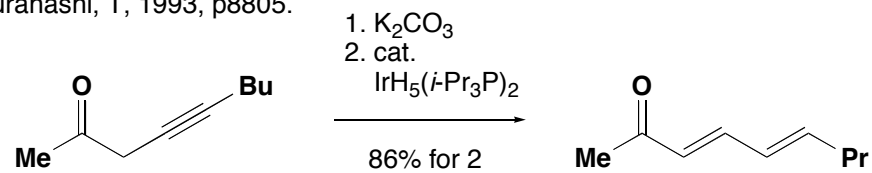
Yields are high; ynals are viable substrates.

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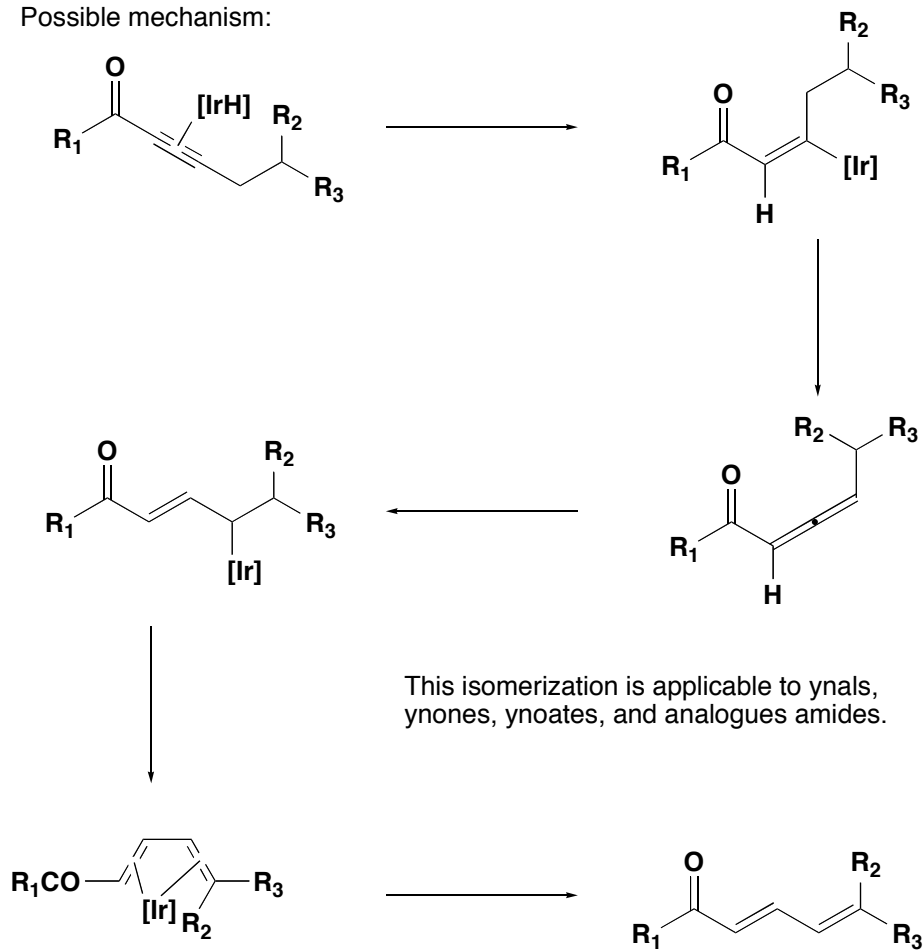
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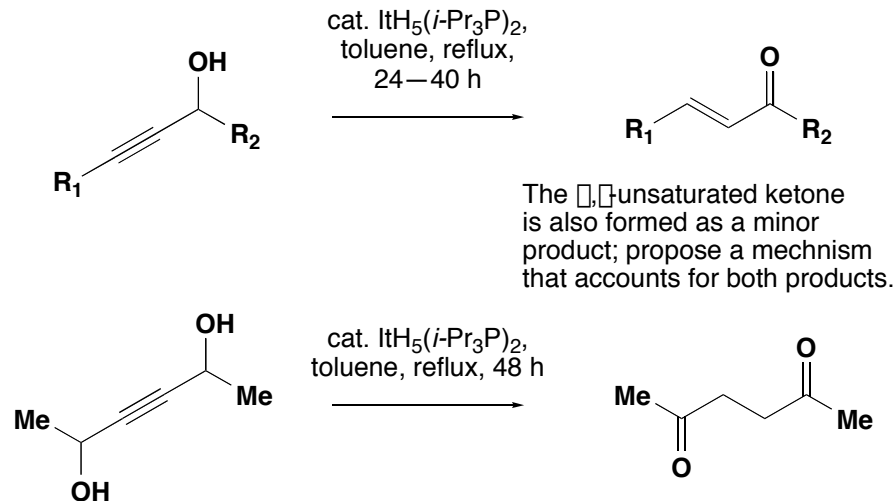
Murahashi, T, 1993, p8805.



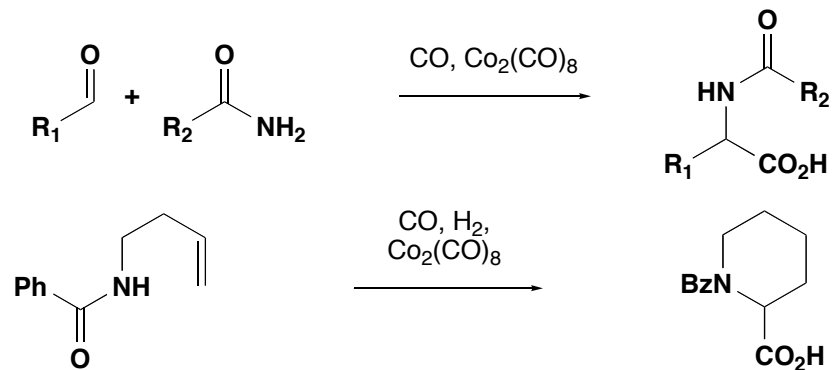
Possible mechanism:



This isomerization is applicable to ynals, ynones, ynones, and analogues amides.



Synthesis of *N*-Acyl Amino-acids by a Carbonylation Reaction  
Wakamatsu, JCS, CC, 1971, p. 1540.



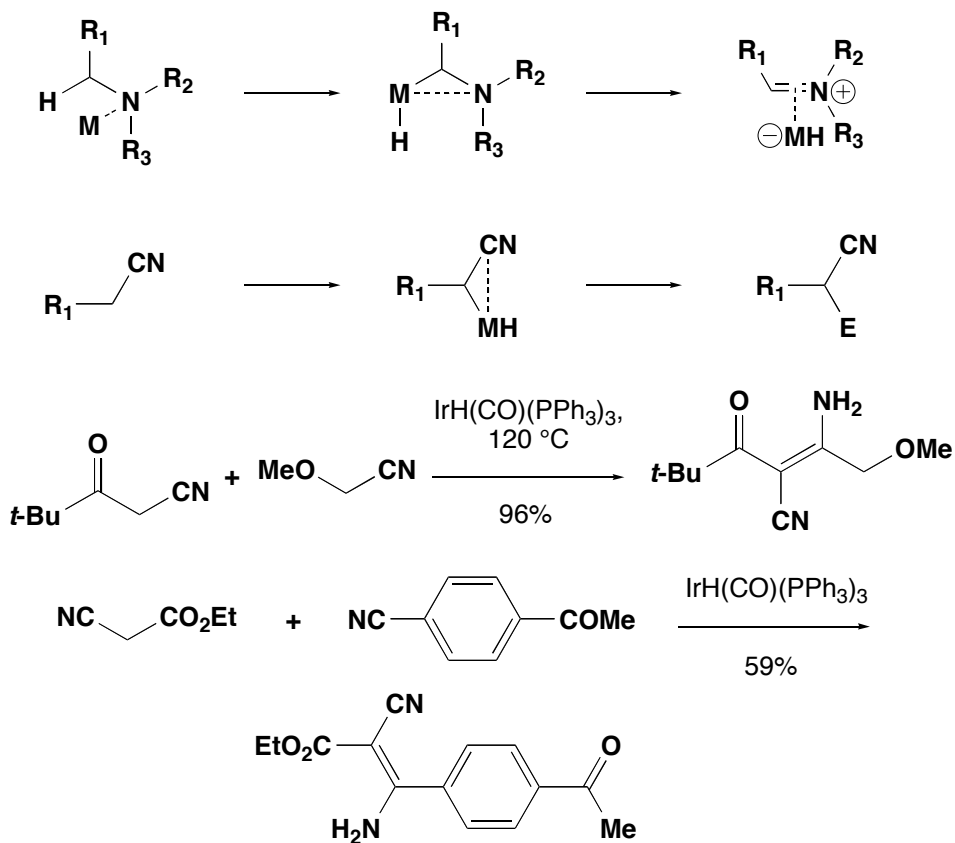
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## C–H Activation (i.e. C–H O. A.)

C–H activation of tertiary amines



## C–H borylation of arenes

