

The Chemistry of Cobalt and Iridium

Baran Group Meeting – 30 November 2005

Carlos Guerrero

Some useful reference texts:

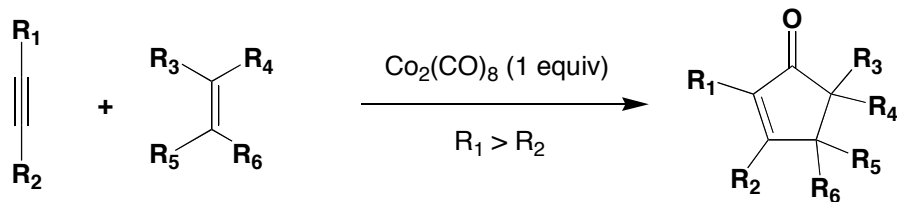
Crabtree, Robert H. *"The Organometallic Chemistry of the Transition Metals"* 3rd Ed., Wiley Interscience, **2001**.

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**.

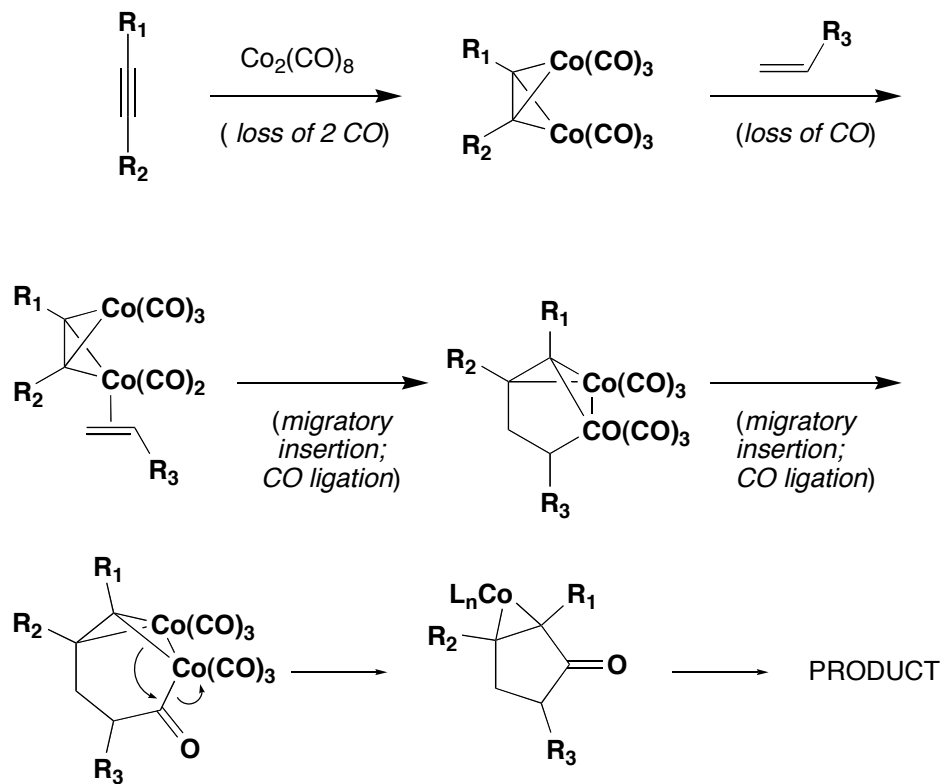
Tsuji, Jiro. *"Transition Metal Reagents and Catalysts: Innovations in Organic Synthesis"* Wiley, **2000**.

Pauson-Khand Reaction

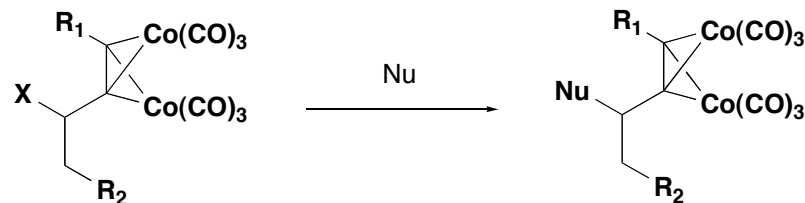


- The reaction can be mediated by a variety of metal complexes. In order to render the reaction catalytic, one must use a high pressure atmosphere of CO.
- The reaction can be accelerated by the addition of various promoters that accelerate the rate of dissociation of CO ligands on metal centers.
- The 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:



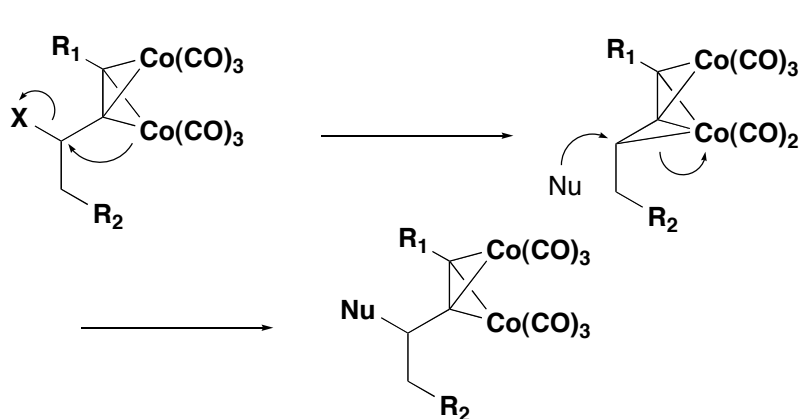
Nicholas Reaction



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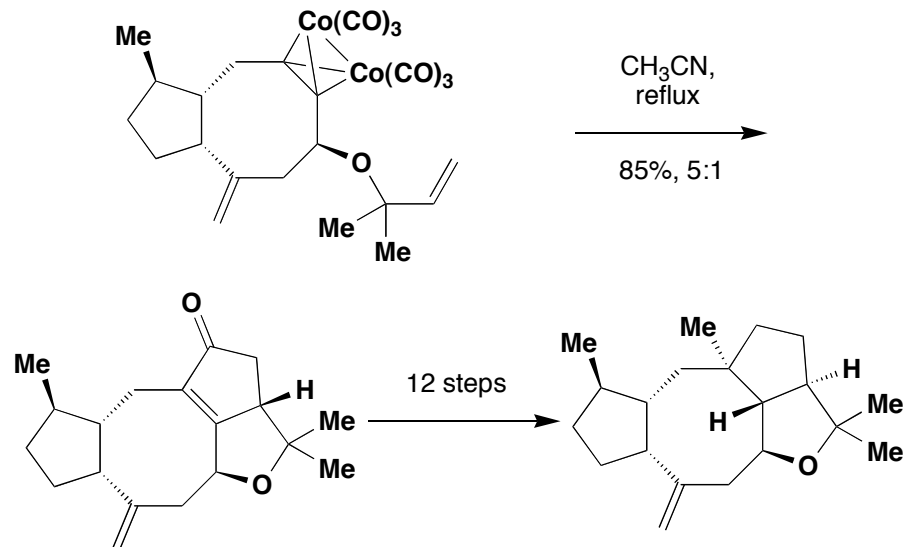
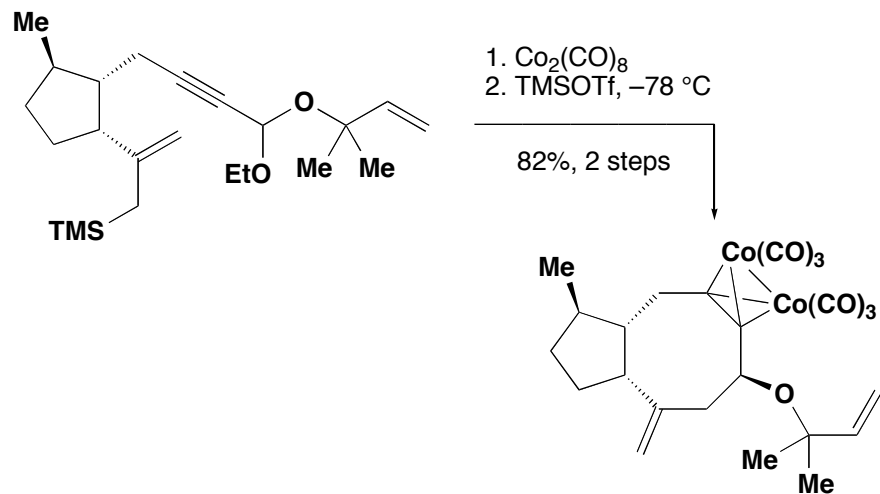
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- C, O, N, and S-nucleophiles are all suitable for the Nicholas reaction.
- The reaction can be conducted intramolecularly.
- No allene side products are observed.

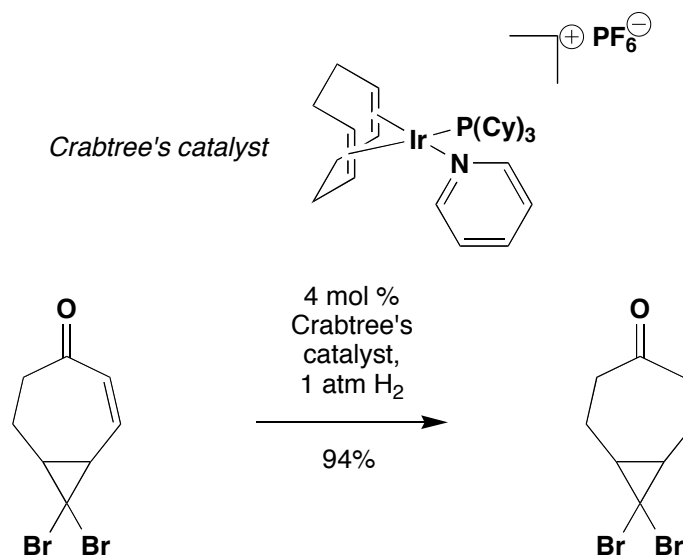
Cobalt-Mediated Total Synthesis of (+)-Epoxydictymene

Schreiber, JACS, 1994, p. 5505.



Homogenous Hydrogenations Using Ir(I)-based Catalysts

Crabtree, TL, 1981, p. 303.

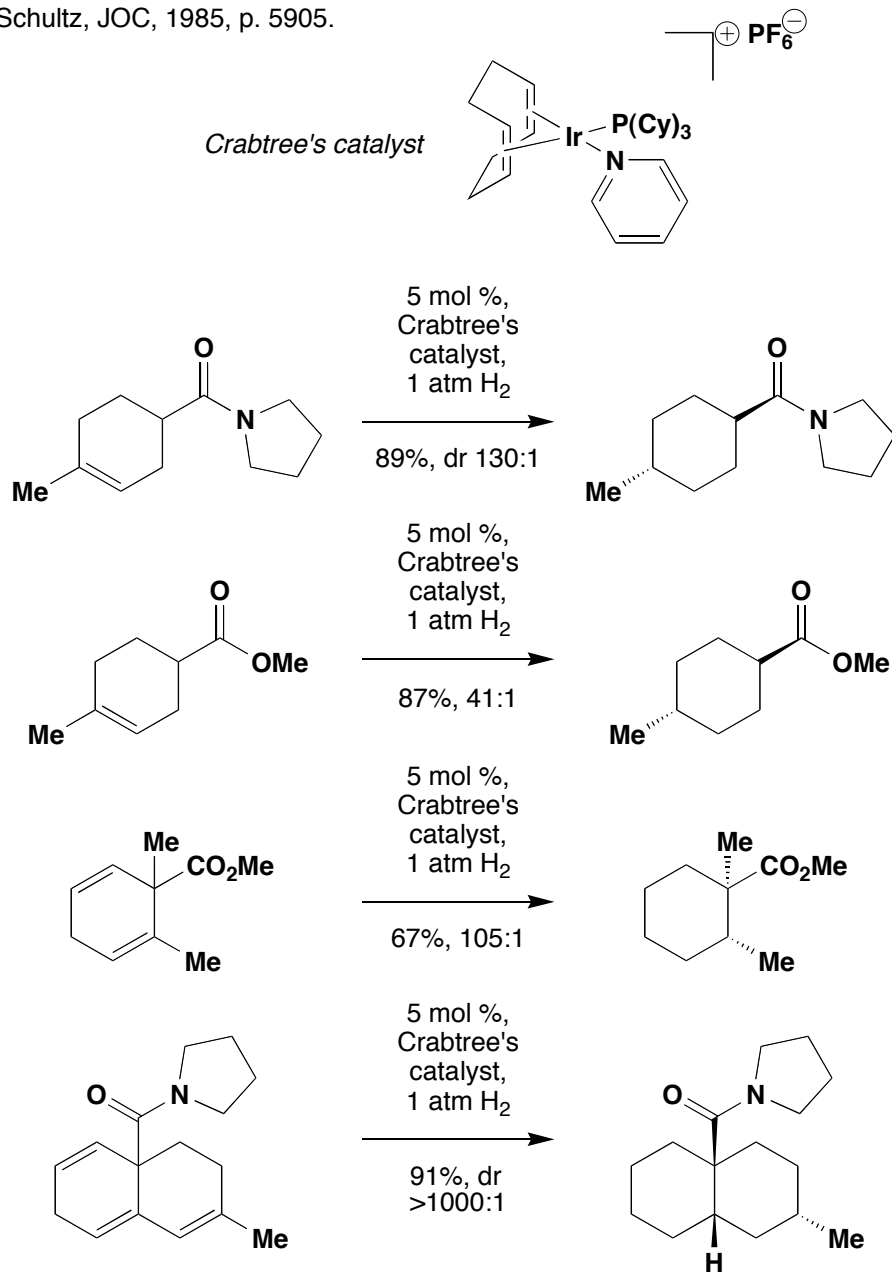


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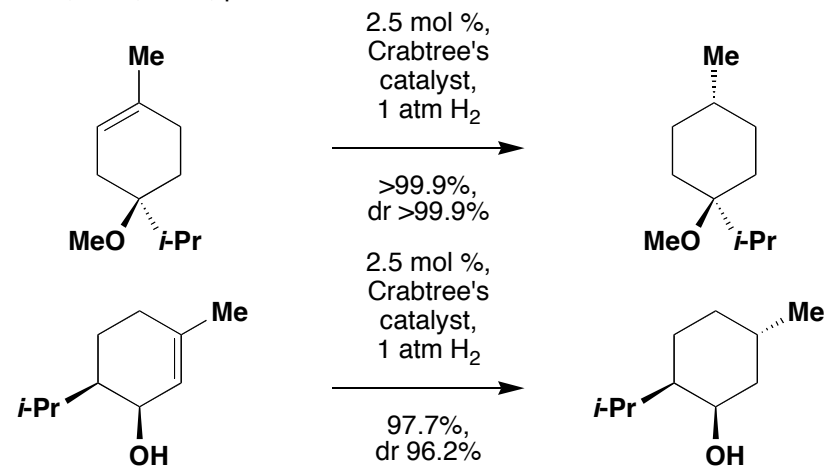
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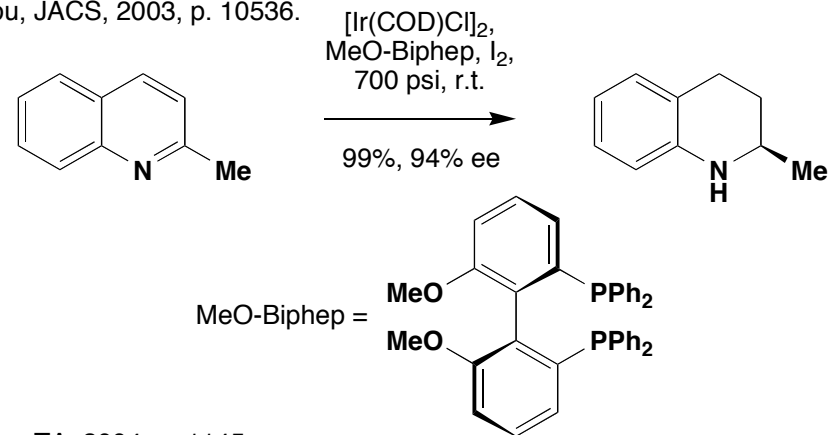
Schultz, JOC, 1985, p. 5905.



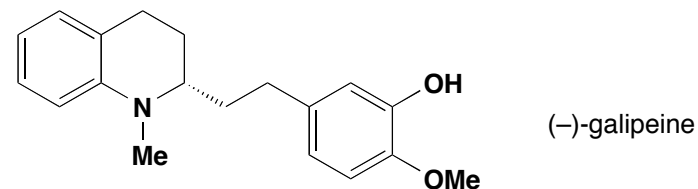
Crabtree, JOC, 1986, p. 2655.



Zhou, JACS, 2003, p. 10536.



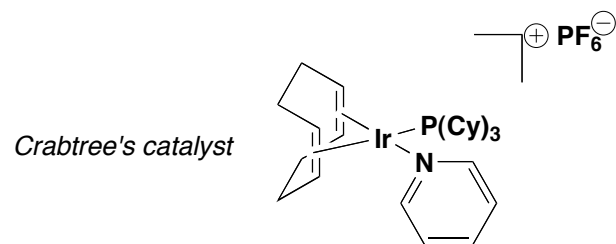
Zhou, TA, 2004, p. 1145.



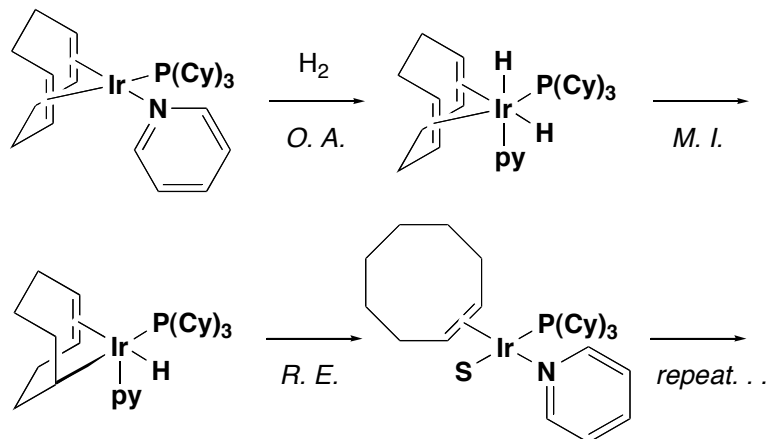
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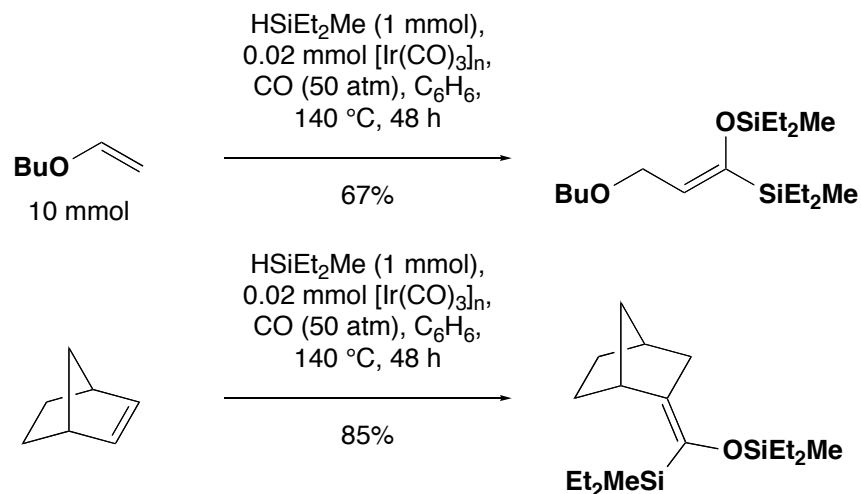
General dihydride mechanism for homogenous hydrogenation:



- 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.

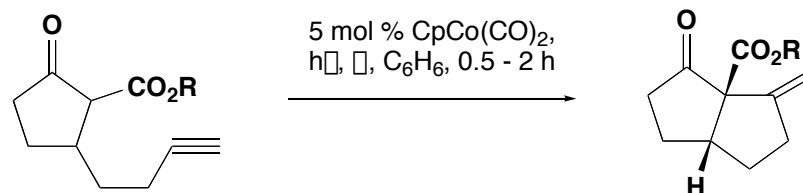
Conversion of Alkenes to Enol Silyl Ethers of Acyl Silanes by Iridium-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide
Murai, JACS, 1992, p. 9710.



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.



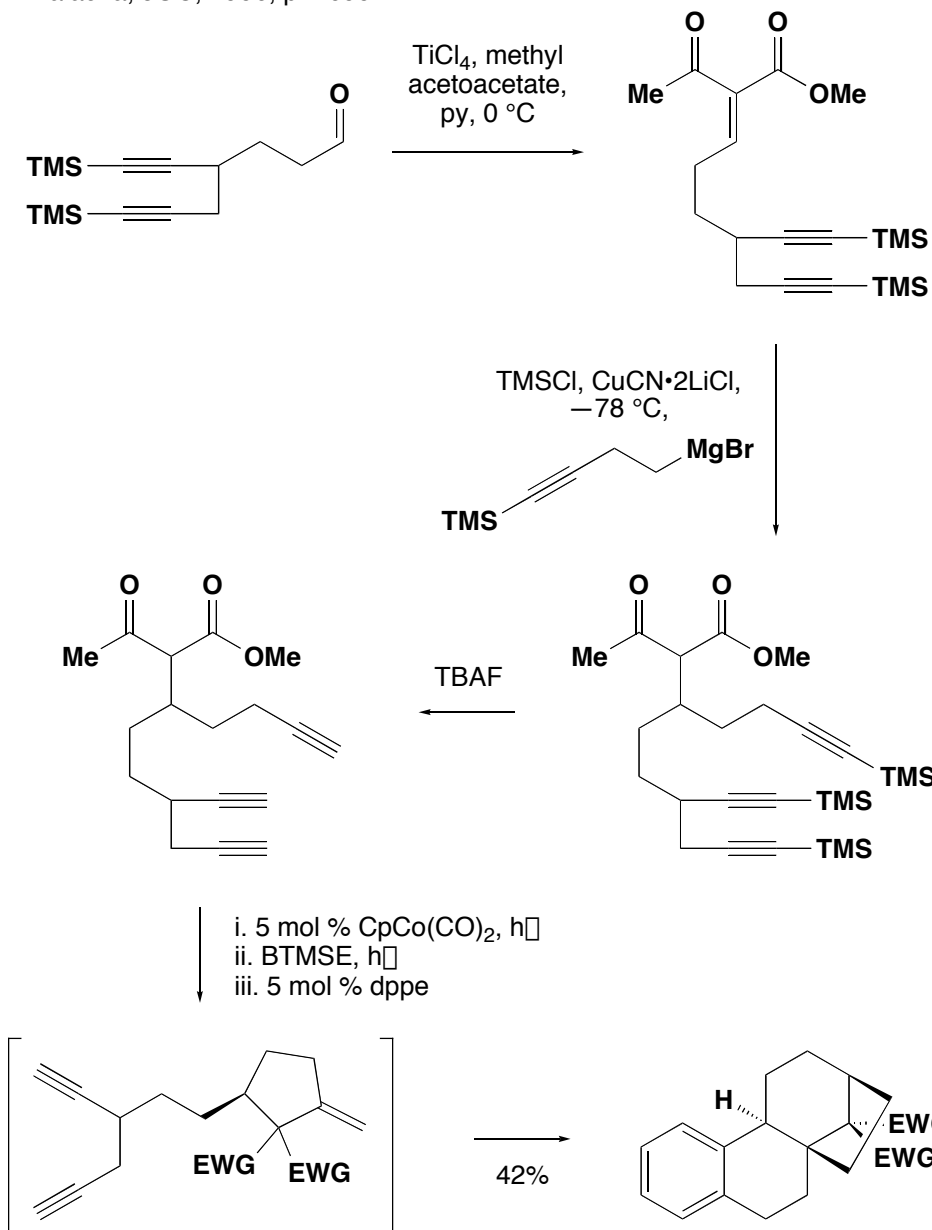
ring size:	5	6	7	8
yield:	73%	81%	70%	73%

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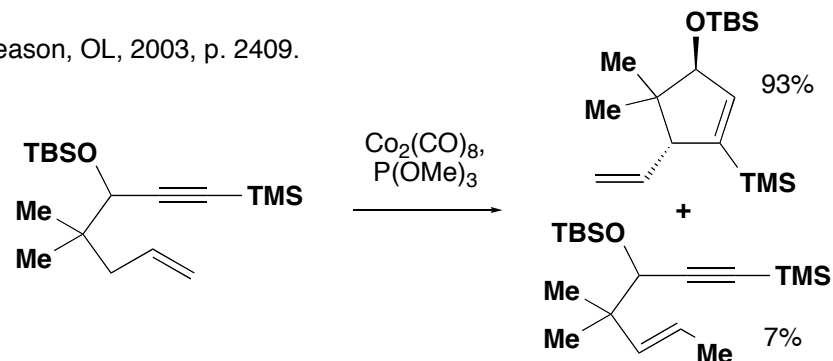
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Malacria, JOC, 1996, p. 2699.



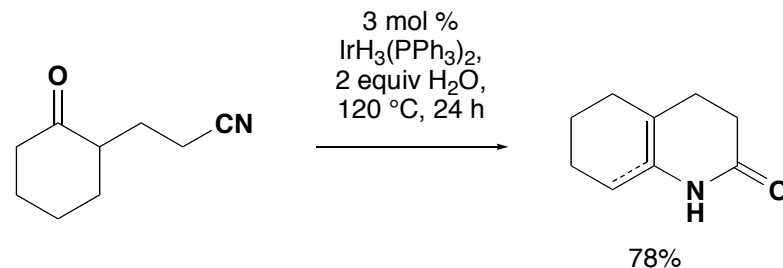
Gleason, OL, 2003, p. 2409.



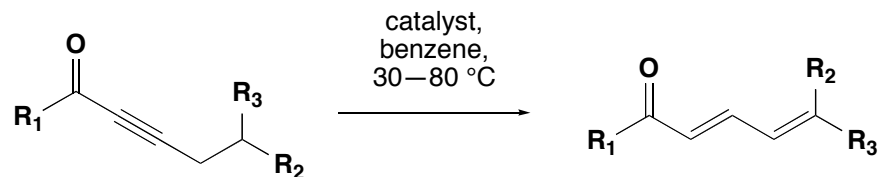
Note that the alkyne terminus is incorporated into the new cyclopentene. The terminal alkyne must be subject to the reaction conditions in its protected form.

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 $\text{RuCl}_2(\text{PPh}_3)_3/\text{PPh}_3$

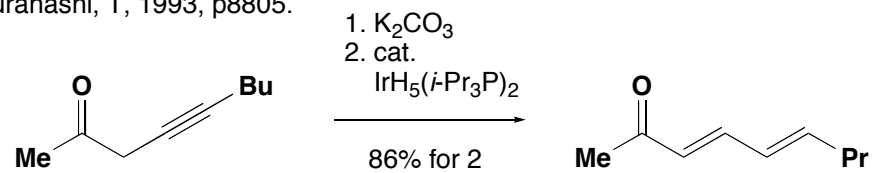
Yields are high; ynals are viable substrates.

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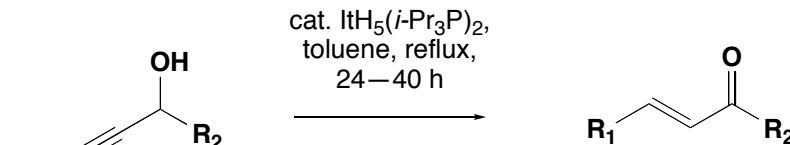
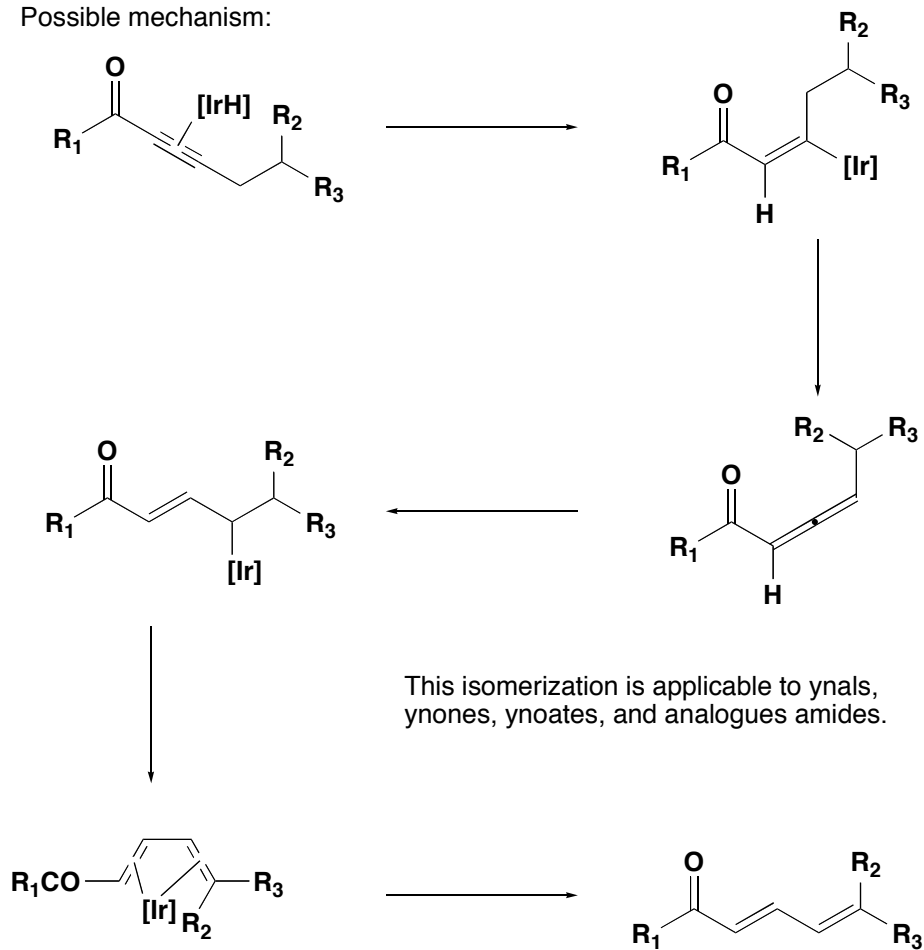
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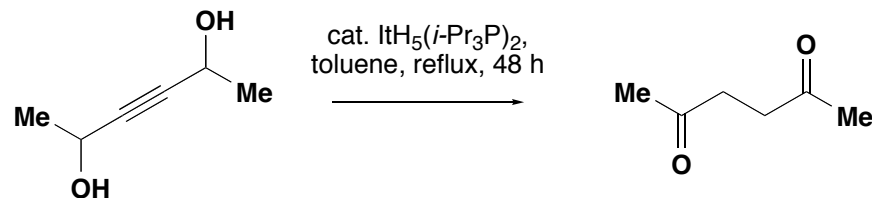
Murahashi, T, 1993, p8805.



Possible mechanism:

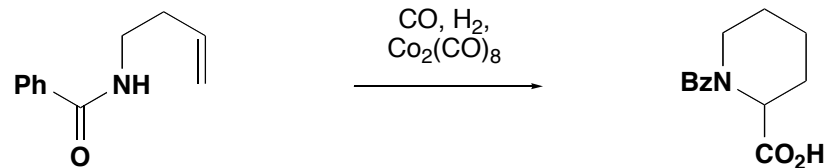
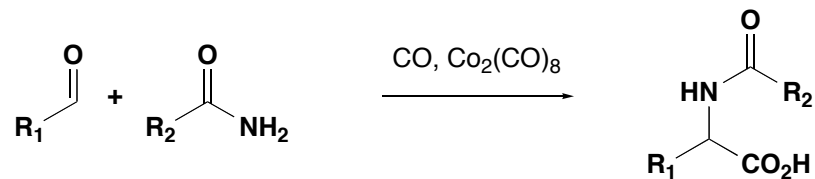


The α,β -unsaturated ketone is also formed as a minor product; propose a mechanism that accounts for both products.



Synthesis of *N*-Acyl Amino-acids by a Carbonylation Reaction

Wakamatsu, JCS, CC, 1971, p. 1540.



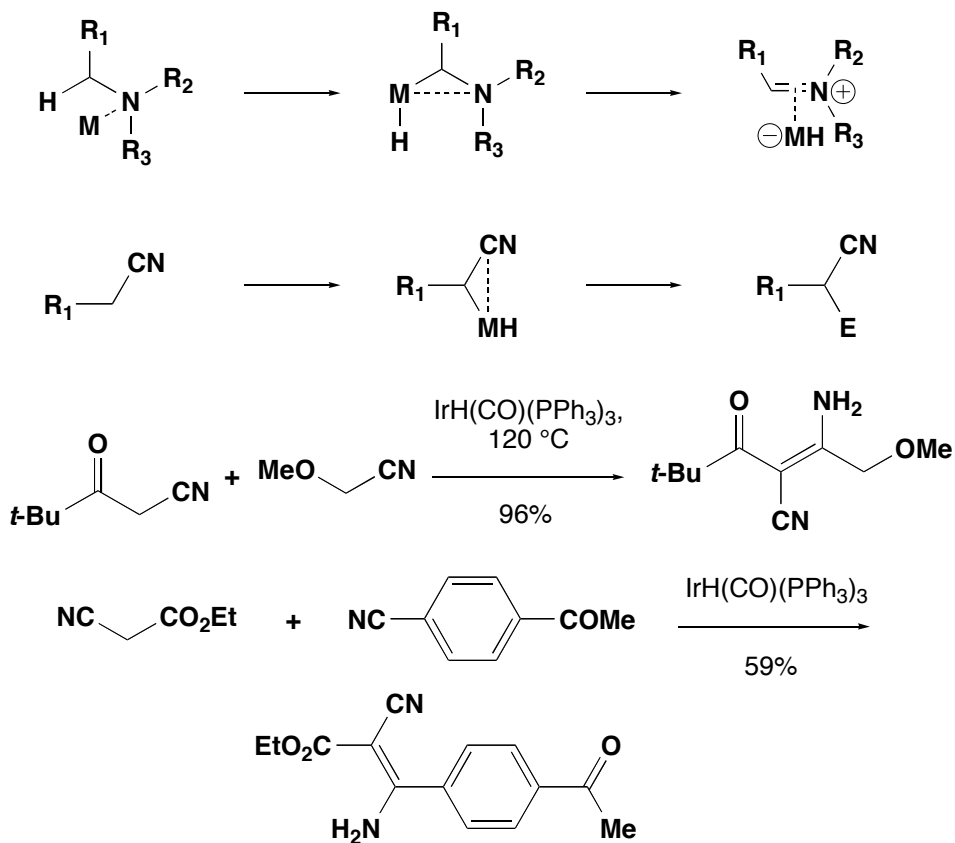
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C–H Activation (i.e. C–H O. A.)

C–H activation of tertiary amines



C–H borylation of arenes

