

Transition Metal-Catalyzed $C_{\text{vinyl}}-C_{\text{vinyl}}$ Bond Formation via Double $C_{\text{vinyl}}-H$ Bond Activation

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Reporter: LAN Xia

Date: 2013.11.18

Seminal work



R¹=aryl, vinyl
X=I, Br, Cl, OTf

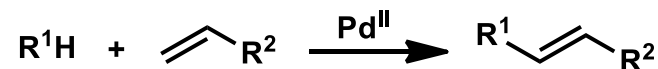
Mizoroki-Heck Reaction



2010 Nobel Prize

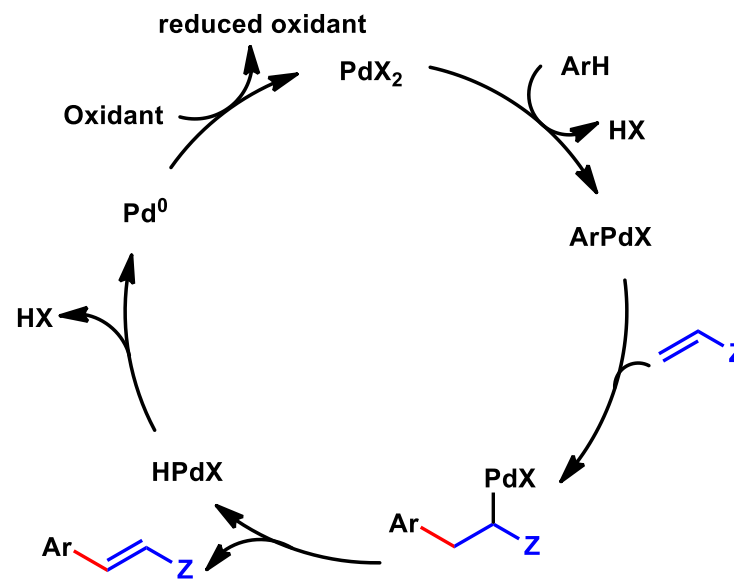


Richard F. Heck



R¹=aryl, vinyl

Fujiwara-Moritani Reaction



J. L. Bras, J. Muzart, *Chem. Rev.* **2011**, *111*, 1170

Outline of This Talk

- Palladium-catalyzed

- Oxidative cross-coupling of linear alkenes with terminal alkenes

- Oxidative cross-coupling of cyclic alkenes with terminal alkenes

- Rhodium-catalyzed

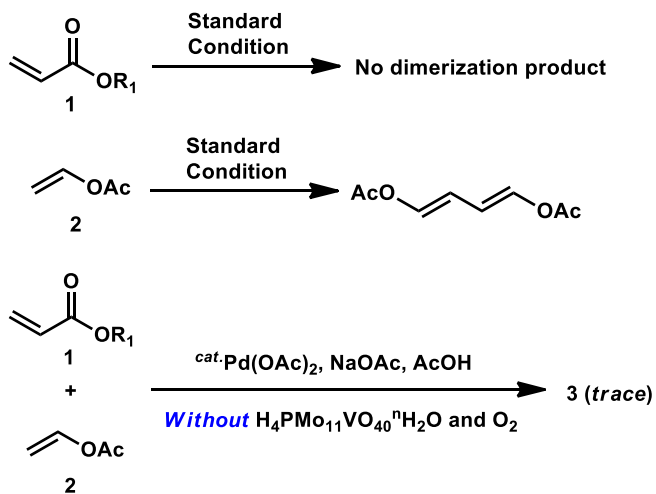
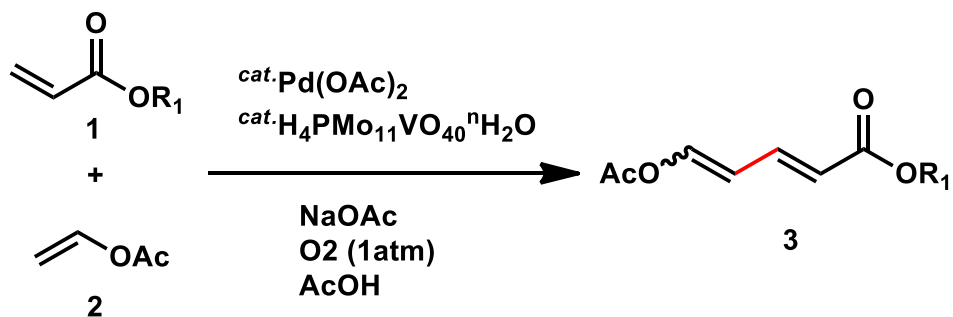
- Enamides directed

- Acrylamides directed

- Acrylic acids directed

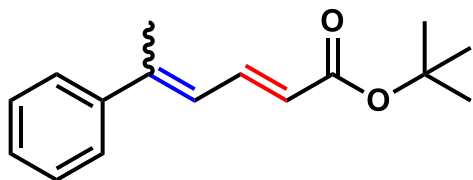
- Potential developing directions

Oxidative cross-coupling of linear alkenes with terminal alkenes



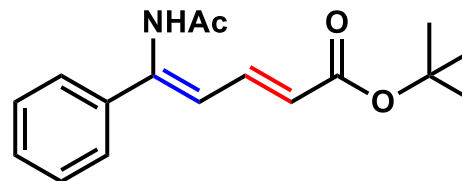
- The first catalyzed cross-coupling of two different linear alkenes by using O_2 as the critical oxidant
- NaOAc prevents the deposition of $\text{Pd}(0)$ generated in the course of the reaction
- **2**, not **1**, reacts with Pd(II) species in the first step
- O_2 and $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (phosphomolybdic acid) are essential components that serve as oxidants

Oxidative cross-coupling of linear alkenes with terminal alkenes



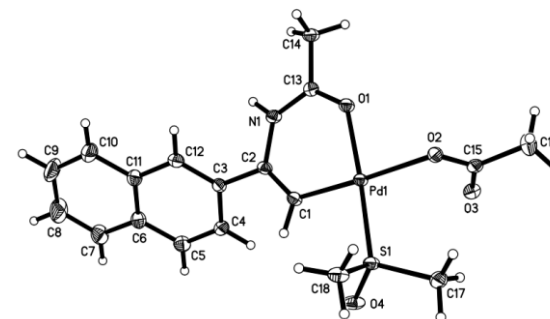
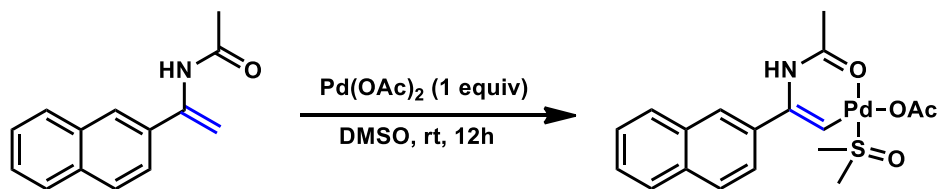
T-P Loh *JACS* 2009

- The first example of oxidative coupling of simple styrene derivatives with acrylates
- Only 2-substituted olefins can be tolerated



T-P Loh *Chem. Sci.* 2011

↑
t-butyl acrylate (1equiv)
NaOAc (1equiv)
DMSO, 80°C, 16h, air
53% yield

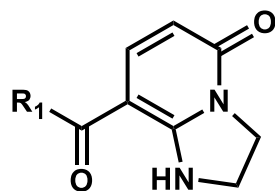
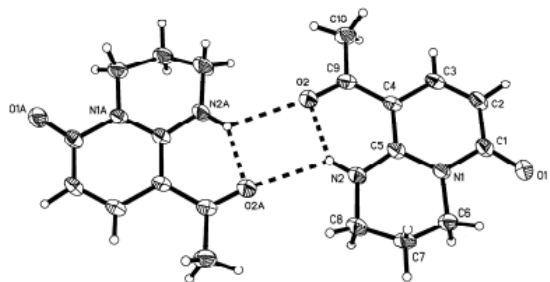
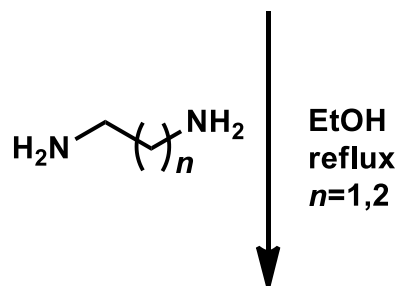
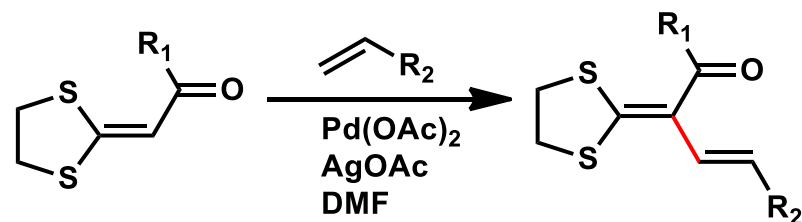


Cyclic Vinylpalladium Complex

Y.-H. Xu, J. Lu, T.-P. Loh, *J. Am. Chem. Soc.*, **2009**, *131*, 1372

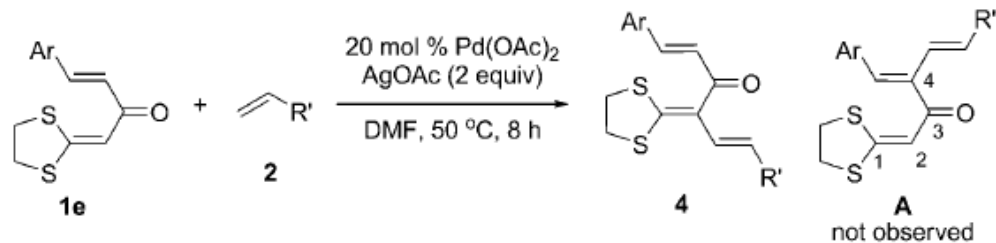
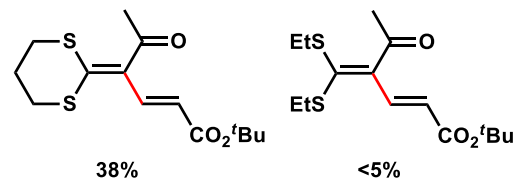
Y.-H. Xu, Y.K. Chok, T.-P. Loh, *Chem. Sci.*, **2011**, *2*, 1822

Oxidative cross-coupling of linear alkenes with terminal alkenes

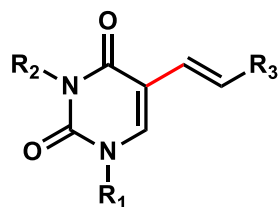


- The first example of oxidative coupling of an internal alkene with a terminal alkene
- 1,2-dithiane group is important
- C(4)-H bond is much less reactive than the C(2)-H bond

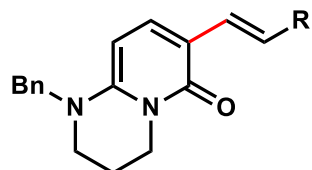
The polarization flows from the two electron-donating sulfur atoms to the electron-withdrawing carbonyl group and makes C(2) more nucleophilic



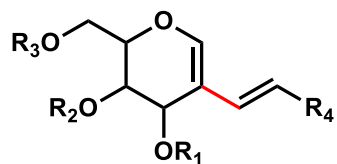
Oxidative cross-coupling of cyclic alkenes with terminal alkenes



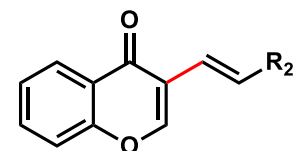
Hirota, *Synthesis*, 1987



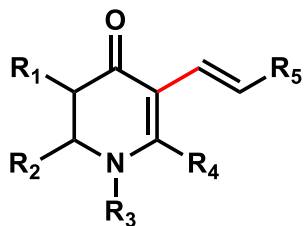
Gallagher, *Org. Lett.*, 2009



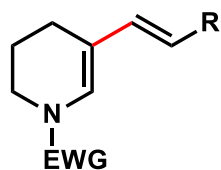
Liu, *Org. Lett.*, 2011



Hong, *Org. Lett.*, 2011



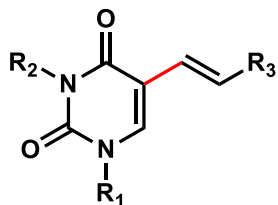
Georg, *Org. Lett.*, 2011



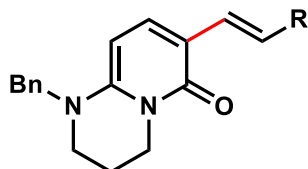
Gillaizeau, *Org. Lett.*, 2012

- The first example of oxidative coupling of a cyclic alkene with a terminal alkene

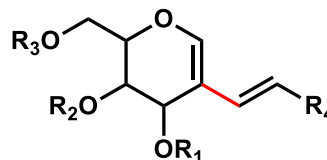
Oxidative cross-coupling of cyclic alkenes with terminal alkenes



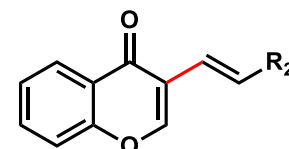
Hirota, *Synthesis*, 1987



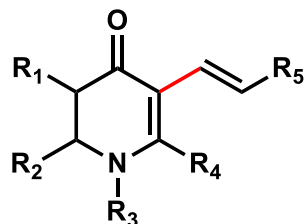
Gallagher, *Org. Lett.*, 2009



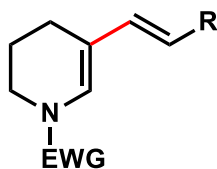
Liu, *Org. Lett.*, 2011



Hong, *Org. Lett.*, 2011



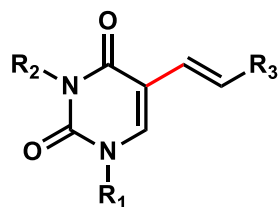
Georg, *Org. Lett.*, 2011



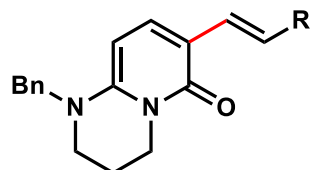
Gillaizeau, *Org. Lett.*, 2012

- A series of C(7)-olefinated bicyclic pyridine scaffolds were regioselectively isolated
- 2-cyclohexylethene could tolerate in this system
- The δ -C(7)-Pd species had been characterized by ¹H NMR in this work

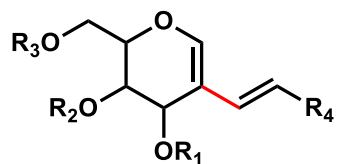
Oxidative cross-coupling of cyclic alkenes with terminal alkenes



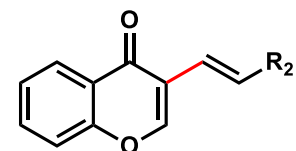
Hirota, *Synthesis*, 1987



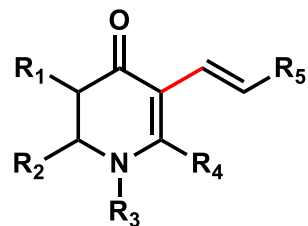
Gallagher, *Org. Lett.*, 2009



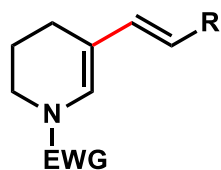
Liu, *Org. Lett.*, 2011



Hong, *Org. Lett.*, 2011



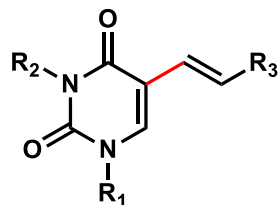
Georg, *Org. Lett.*, 2011



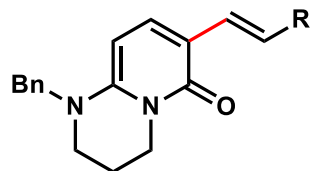
Gillaizeau, *Org. Lett.*, 2012

- Pyran derivatives were obtained with pure E selectivity.

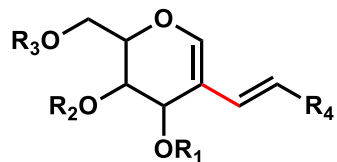
Oxidative cross-coupling of cyclic alkenes with terminal alkenes



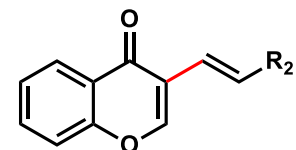
Hirota, *Synthesis*, 1987



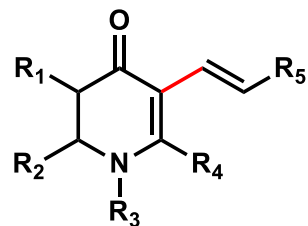
Gallagher, *Org. Lett.*, 2009



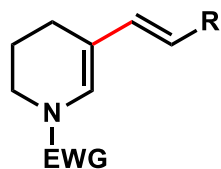
Liu, *Org. Lett.*, 2011



Hong, *Org. Lett.*, 2011



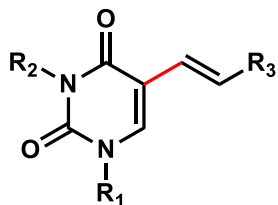
Georg, *Org. Lett.*, 2011



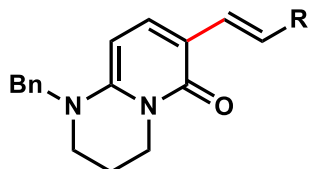
Gillaizeau, *Org. Lett.*, 2012

- A series of C(3)-functionalized chromone scaffolds were synthesized

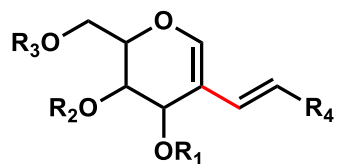
Oxidative cross-coupling of cyclic alkenes with terminal alkenes



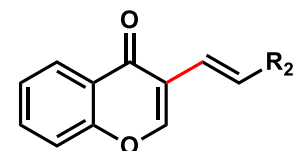
Hirota, *Synthesis*, 1987



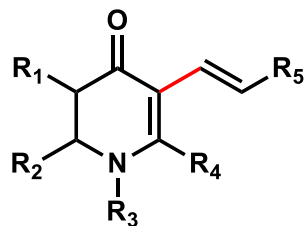
Gallagher, *Org. Lett.*, 2009



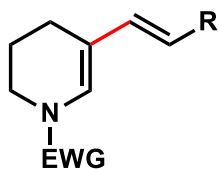
Liu, *Org. Lett.*, 2011



Hong, *Org. Lett.*, 2011



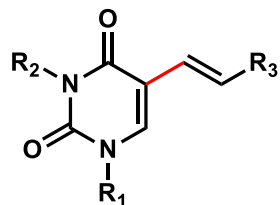
Georg, *Org. Lett.*, 2011



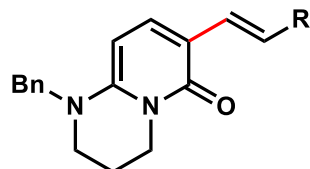
Gillaizeau, *Org. Lett.*, 2012

- A Pd(II)-catalyzed dehydrogenative olefination of cyclic enaminones with activated alkenes
- The migratory insertion is the rate-determining step

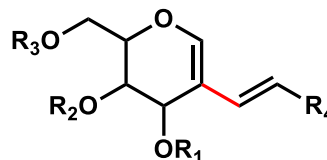
Oxidative cross-coupling of cyclic alkenes with terminal alkenes



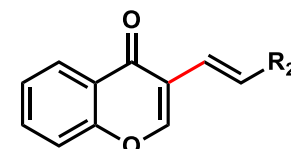
Hirota, *Synthesis*, 1987



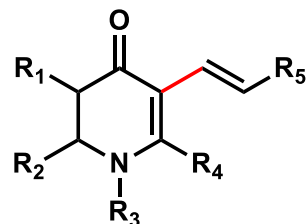
Gallagher, *Org. Lett.*, 2009



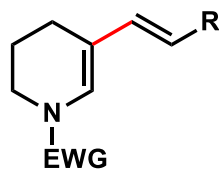
Liu, *Org. Lett.*, 2011



Hong, *Org. Lett.*, 2011



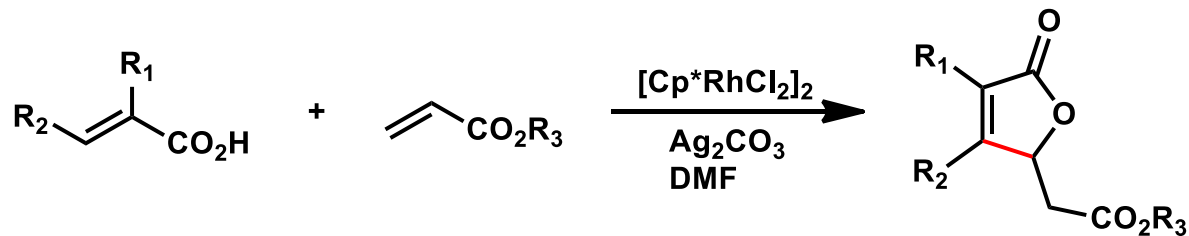
Georg, *Org. Lett.*, 2011



Gillaizeau, *Org. Lett.*, 2012

- A palladium(II)-catalyzed oxidative alkenylation of nonaromatic enamides
- homocoupling of enamide occurred without additional alkenes

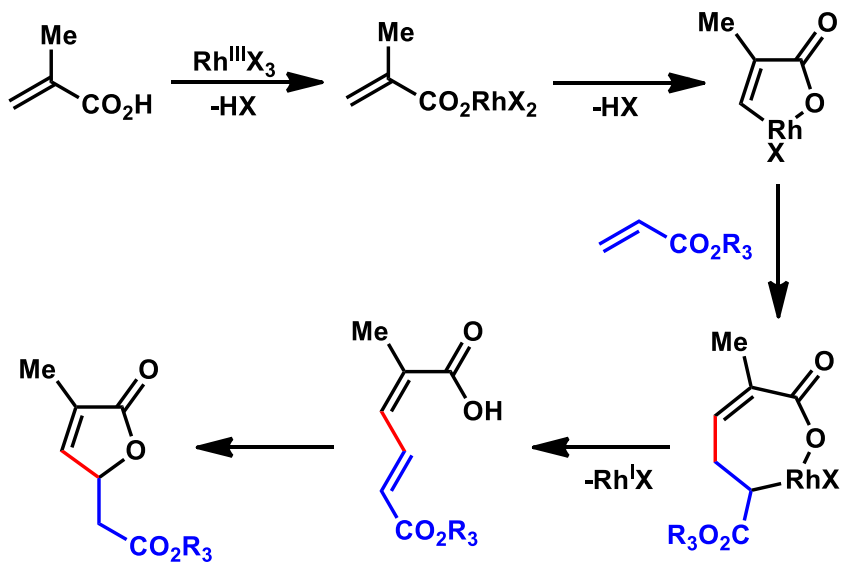
Acrylic acids Directed



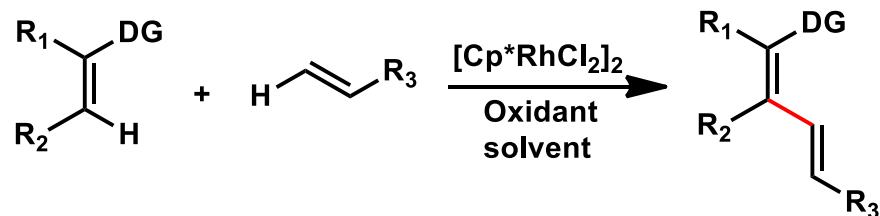
- The initial olefination product was further complicated by in situ Michael cyclization

A typical process of rhodium-catalyzed olefination reaction

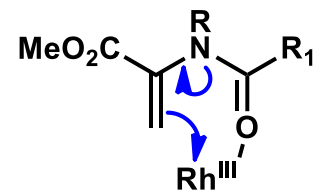
- Cyclorhodation
- Alkene insertion
- β -hydrogen elimination



Enamides Directed

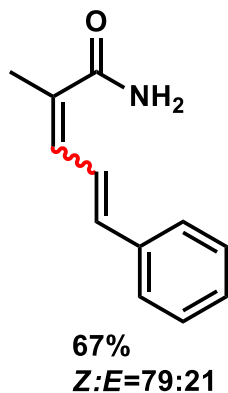
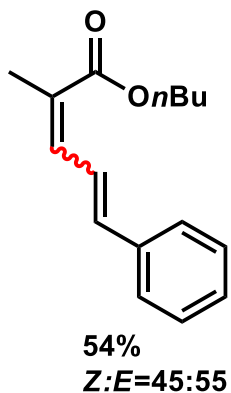


Another plausible mechanism of the first step

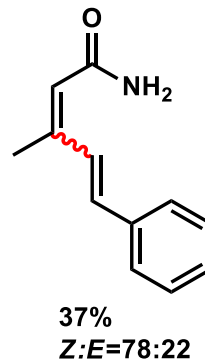
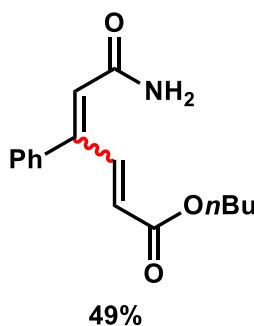


Electrophilic substitution

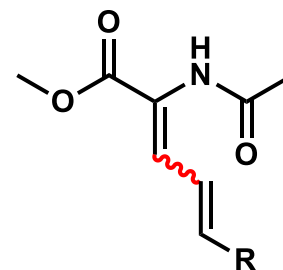
■ 1,1-disubstituted olefins



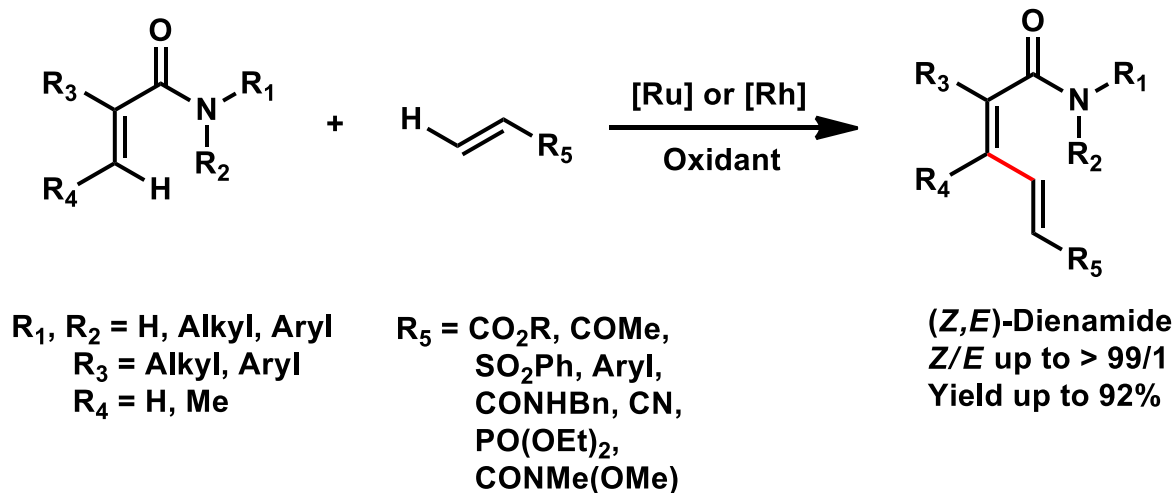
■ 1,2-disubstituted olefins



■ *Application*: Synthesis of $\alpha,\beta,\gamma,\delta$ -unsaturated amino acids



Acrylamides Directed



- The Ru- and Rh-catalyzed direct cross-coupling to produce (Z,E)-dienamides.
- Allowed oxidative olefination of a wide range of alkenes bearing different functional groups.

What's Going on

- Find the application of other metals
- Use the eco-friendly oxidants
- Search for the more effective directing-groups

Thanks for your attention !