

RCC : HECK TYPE REACTION

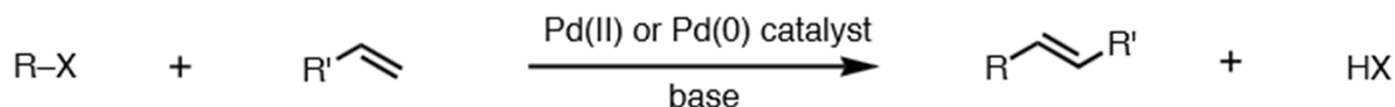
Rhodium-Catalyzed Oxidative Olefination of C-H Bonds in Acetophenones and Benzamides

Frederic W. Patureau, Tatiana Besset, and Frank Glorius *Angew. Chem. Int. Ed.* **2011**, *50*, 1064 –1067



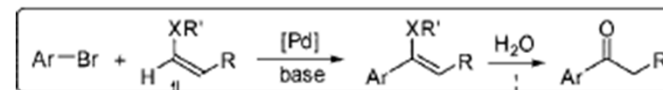
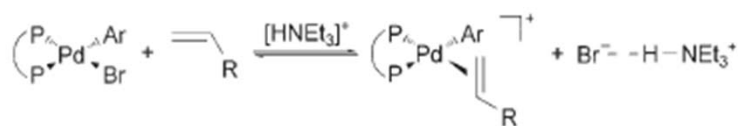
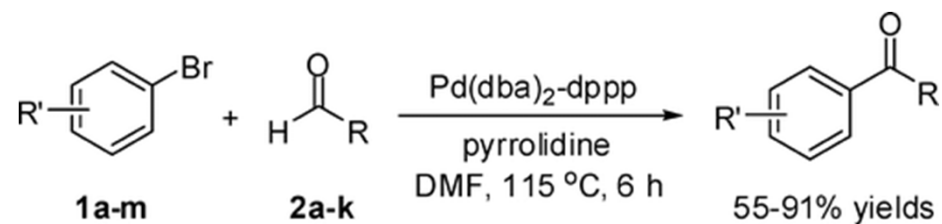
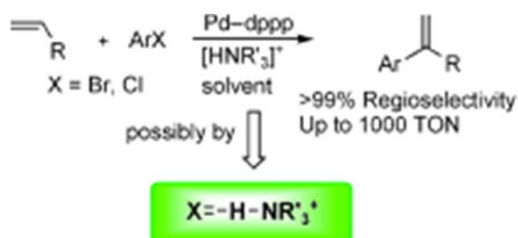
THE HECK REACTION

The palladium-catalyzed C-C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base is referred as the "**Heck Reaction**"



R = alkenyl, aryl, allyl, alkynyl, benzyl X = halide, triflate R' = alkyl, alkenyl, aryl, CO₂R, OR, SiR₃

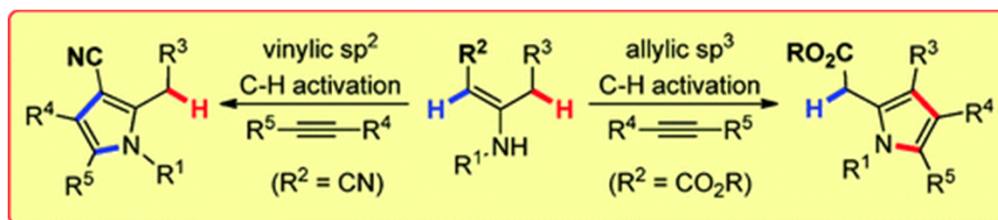
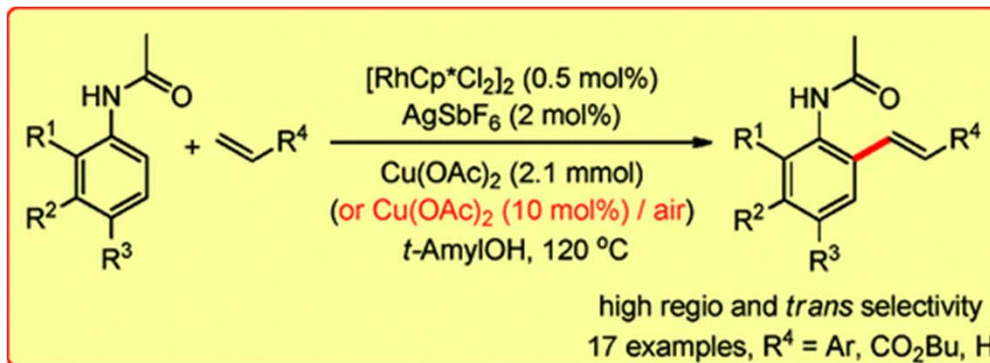
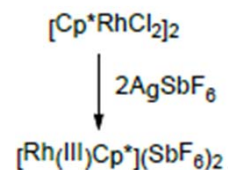
"first reported in 1971"



J. Mo, J. Xiao, *Angew. Chem. Int. Ed.*, **2006**, 45, 4152-4157.

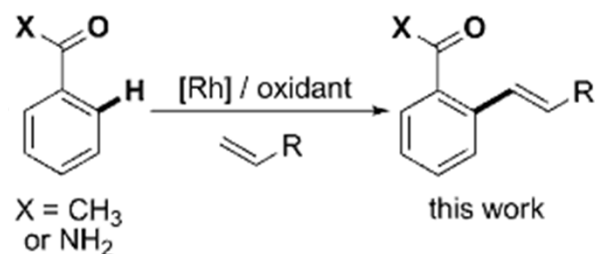
J. Ruan, O. Saidi, J. A. Iggo, J. Xiao, *J. Am. Chem. Soc.*, **2008**, 130, 10510-10511

PREVIOUS WORK



Rich aromatic cycles give best results

electron-poor C-H



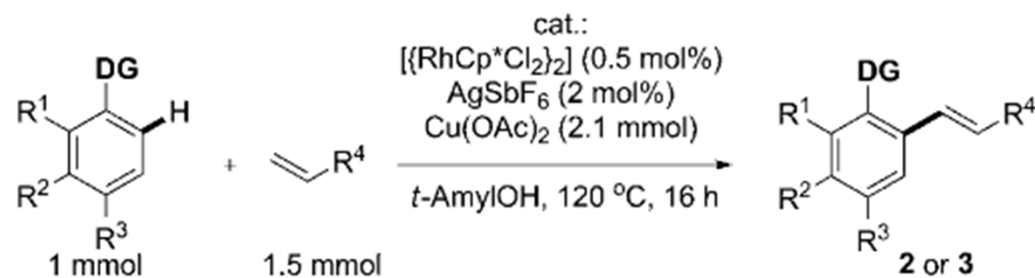
Acetophenones and Benzamides

F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, 132, 9982,

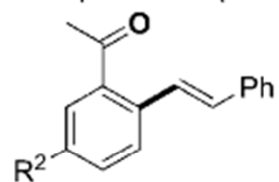
S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, 132, 9585.

S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, 366, 529

CURRENT WORK



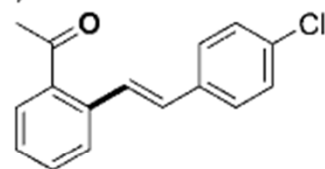
Acetophenones (DG = COMe):



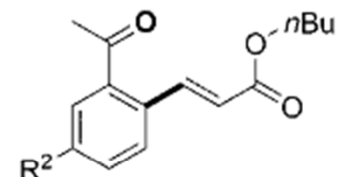
2a: $\text{R}^2 = \text{H}$, 57%^[a,b]

2b: $\text{R}^2 = \text{CH}_3$, 56%^[a,b]

2c: $\text{R}^2 = \text{CF}_3$, 0%^[a]



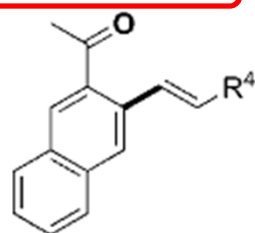
2d: 56%^[a]



2e: $\text{R}^2 = \text{H}$, 76%^[c]

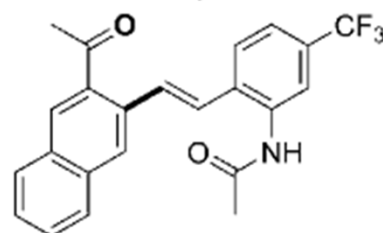
2f: $\text{R}^2 = \text{CH}_3$, 63%

In a second step, from 1a:

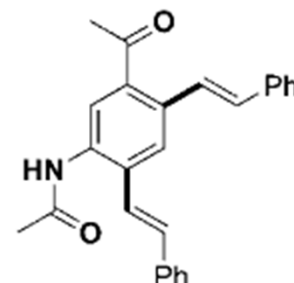


2g: $\text{R}^4 = \text{CO}_2\text{Bu}$, 70%

2h: $\text{R}^4 = \text{Ph}$, 72%



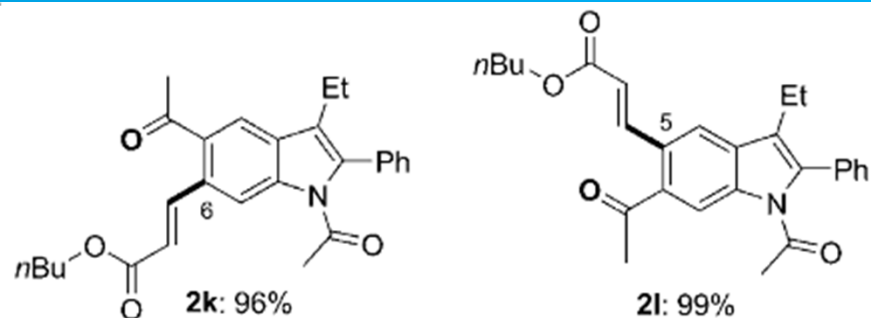
2i: 44%^[a,d]



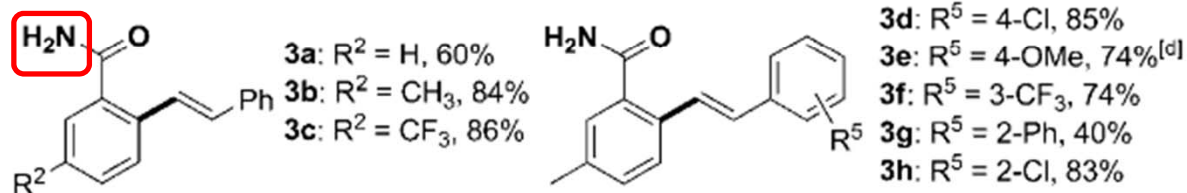
2j: 59%^[e]

CURRENT WORK

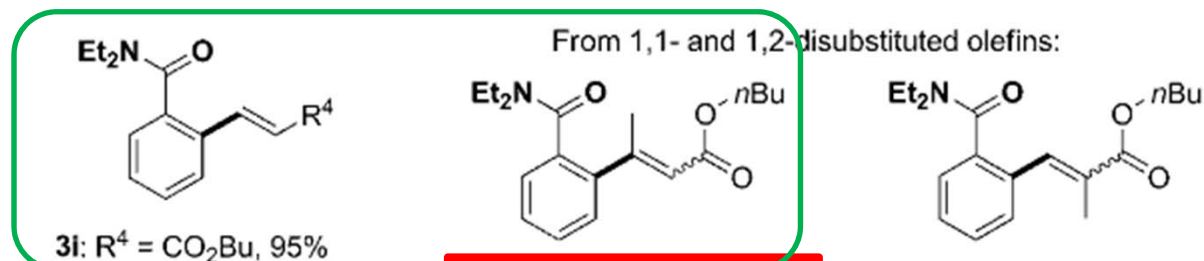
heteroaromatics



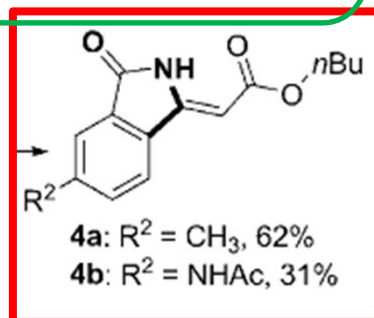
Benzamides (DG = CONH₂): ^[b]



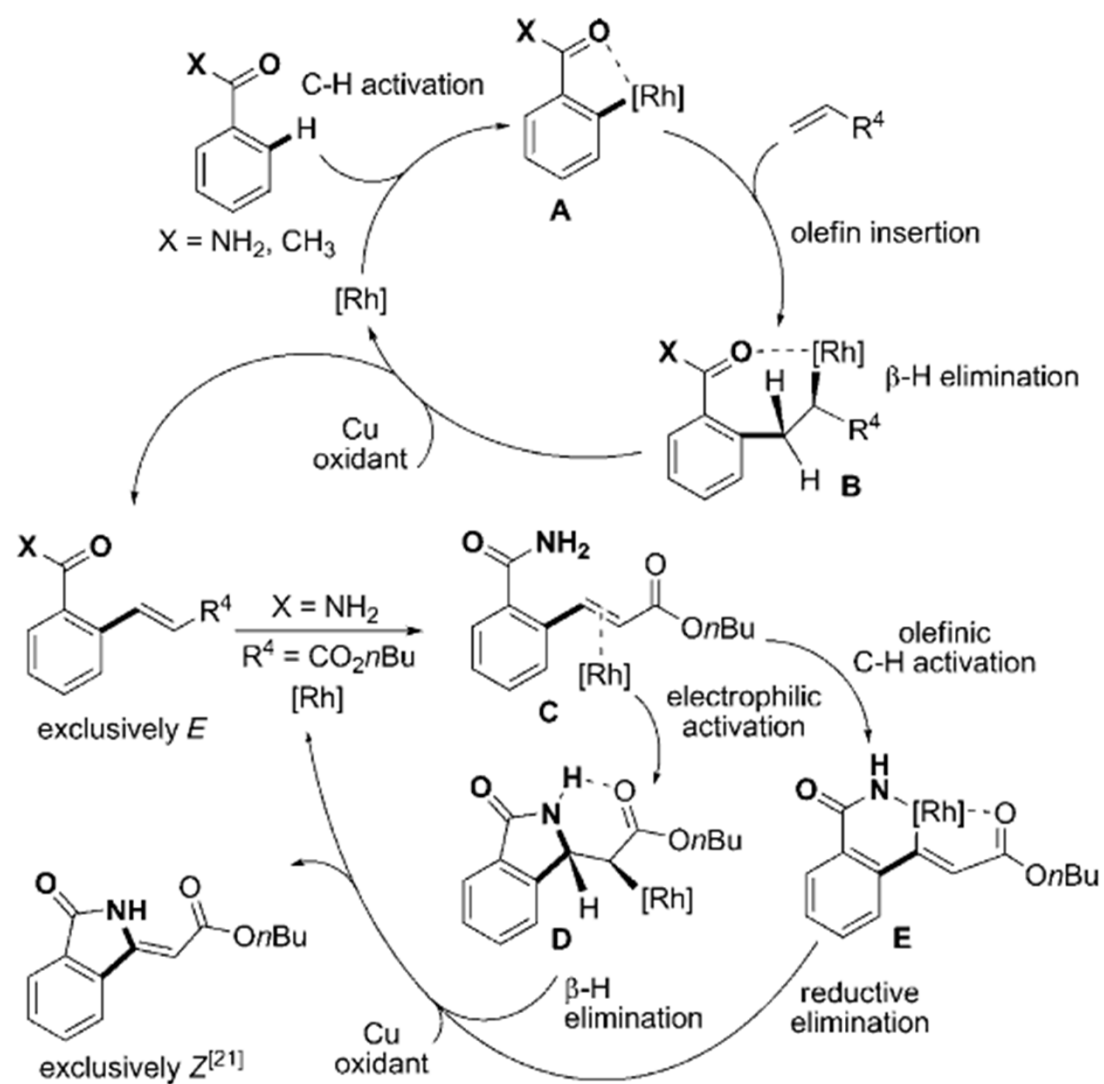
With pd chemistry
Around 20% yield



With butyl acrylate

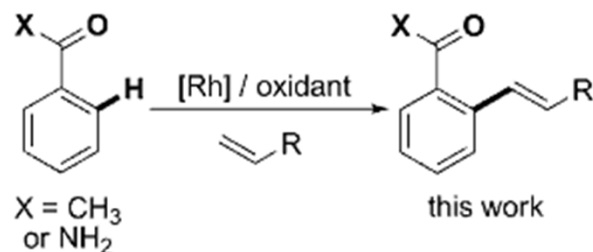


MECHANISTIC APPROACHE



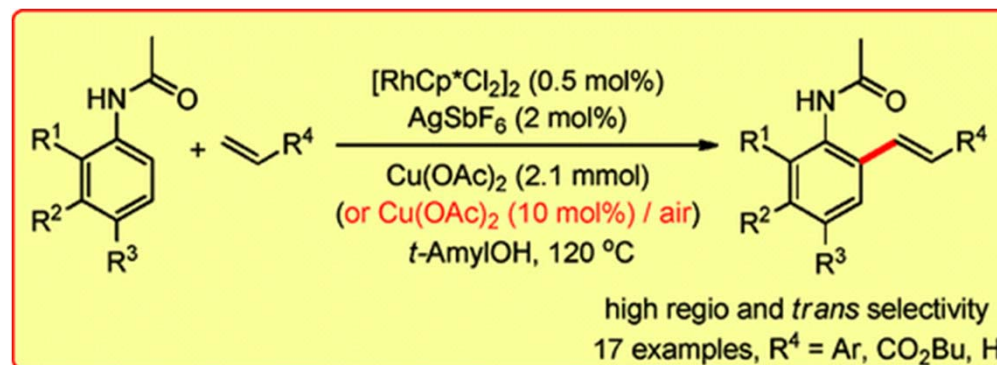
CONCLUSION

electron-poor C-H



Yield up to 95%
with low catalyst loading

Is it a real advance? Probably...



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MERCI DE VOTRE ATTENTION