NEW METHODS OF DIRECT CATALYTIC ALKENATION OF HETEROCYCLES

Mahmoud Hachem, Jean Baptiste Rouchet, Cedric Schneider, and Christophe Hoarau*

Normandie University, COBRA, UMR 6014 and FR 3038, University Rouen; INSA Rouen; CNRS, IRCOF, 1 Rue Tesnière, 76 821 Mont-Saint-Aignan Cedex, France
mahmoud.hachem1@univ-rouen.fr

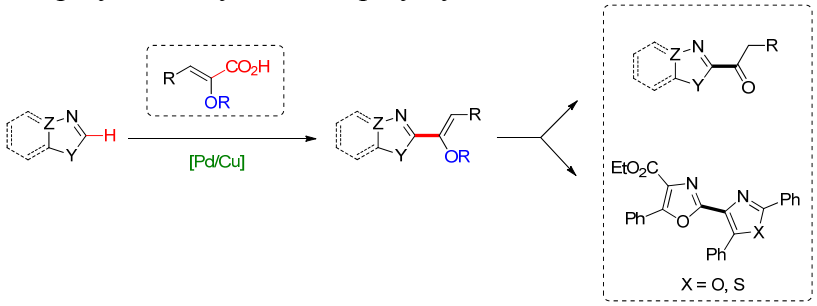
Found in many natural products and biologically active molecules, and employed as masked-ketones and activated alkenes, vinyl ethers are an important building blocks which might be involved in a number of chemical transformations.[1]

Based on the importance of this molecule, the transition-metal-catalyzed heteroarylation of enol ethers has drawn lot of attention. One of this reaction is the Heck reaction with non- prefunctionalized vinyl ethers with halides.[2]

However, this reaction is fraught with difficulties associated with selectivity issues (α/β and Z/E).[3] In this context, straightforward, atom economic, and environmentally benign method for direct hétéroarylation and arylation of vinyl ethers with a full control of the E/Z stereochemistry and α/β regiochemistry are highly demanded.[2] In line with our ongoing interest in direct introduction of heterosubstituted alkenes into the C−H bond of heterocycles and aryles,[3] and knowing that carboxylic acids (potential air-stable and easy to handle) are used as masked catalytic organometallic building blocks by transition-metal-mediated extrusion of CO_2,[4] and as labile and directing group, we turned our attention to the α-alkoxylated acrylic acids as coupling partners for Pd-catalyzed heterosubstituted alkenylation of heterocycles.

Herein, we will present our recent research and development on the use of α-alkoxylated acrylic acids as attractive coupling partners for the direct introduction of enol ethers into C-H bonds of heterocycles by decarboxylative / direct C-H alkenylation of various azoles.

This methodologie offer a rational and step-economical route to attractive regio- and stereocontrolled polyheteroarylated and polyarylated enol ethers.



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