

Directed Catalytic C-H Functionalization of Heteroaromatic Compounds

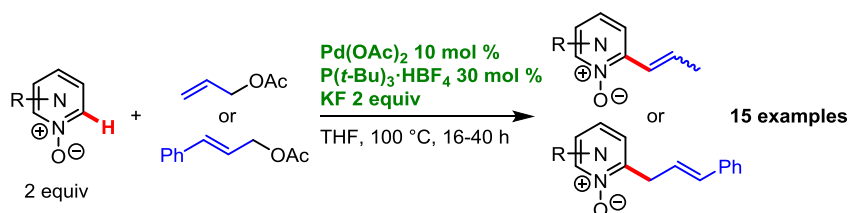
Julie Oble

Sorbonne Université, Faculté des Sciences et Ingénierie, CNRS, Institut Parisien de Chimie Moléculaire (IPCM), 4 place Jussieu 75252 Paris Cedex 05 France

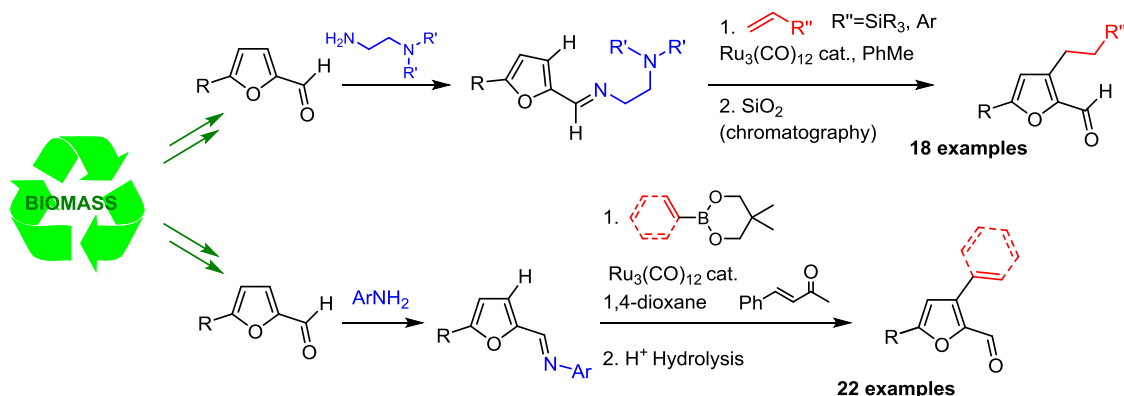
Julie.oble@sorbonne-universite.fr

The direct and selective functionalization of a non-acidic C-H bond - the “unfunctional” group by definition - enables the direct use of the simplest and cheapest starting materials for the construction of complex organic molecules by adding the C-H bond to the catalog of the classical functionalizable groups such as halides, alcohols, carbonyls, etc. This research field, often considered the “Holy Grail” of synthetic chemistry because of its difficulty and importance, is becoming increasingly vast and attracts the interest of experts in both theoretical and organic chemistry, as well as in organometallic catalysis.¹ This presentation talk will focus on two of our recent endeavors in the field of C-H activation for the functionalization of heteroaromatic derivatives.

First, the Pd-catalyzed regioselective allylation and alkenylation of various azine *N*-oxides using allylic acetate and cinnamyl acetate, respectively, will be presented.² The discovery, optimization and scope of this new C-H activation based transformation will be disclosed. A mechanism is also proposed, on the basis of experimental studies and DFT calculations.



Then, the implementation of catalytic C-H transformations on renewable feedstock obtained from biomass, namely furfural derivatives will be presented. We reported a directed Ru(0)-catalyzed hydrofurylation of olefins, involving a directed C-H activation at C3 position of the furan ring.³ A thorough experimentation, including DFT calculations, revealed that only a bidentate imine transient-directing group was able to promote efficiently the desired hydroarylation. We also demonstrated that the analogous Ru(0)-catalyzed arylation of furfuryl imines with arylboronates at the C3 position was feasible in the presence of a sacrificial hydride acceptor.⁴



¹ For a tutorial review see: Roudesly, F.; Oble, J.; Poli, G. *J. Mol. Cat. A. Chem.* **2017**, *426*, 275-296.

² Roudesly, F.; Veiros, L. F.; Oble, J.; Poli, G. *Org. Lett.* **2018**, *20*, 2346.

³ Pezzetta, C.; Veiros, L. F.; Oble, J.; Poli, G. *Chem. Eur J.*, **2017**, *23*, 8385.

⁴ Siopa, F.; Ramis Cladera, V-A.; Afonso, C. A. M.; Oble, J.; Poli, G. *Eur. J. Org. Chem.* **2018**, doi:10.1002/ejoc.201800767.