N°59 / OC

TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Direct functionalization of biomass-derived 2-formyl heteroaromatic compounds

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PURPOSE OF THE ABSTRACT

Furfurals are important building blocks derived from cyclodehydration of lignocellulosic biomass.[1] Since their large-scale production from agricultural residues is developed worldwide, these synthons constitute sought-after raw materials for the sustainable production of value-added compounds.[2] Within a broad project directed towards the sustainable functionalizations of furfurals, the selective formation of new bonds through direct transition metal (TM) catalyzed C-H activation process,[3] without prior modification of the redox state of the aldehyde function, has become one of our emerging areas of research.

Herein, we will describe our recent developments on Ru(0)-catalyzed C3 functionalization of furfurylimines, such as alkylation,[4] arylation,[5] acylation[6] and alkenylation[7] that involved the directed C-H activation of the furan ring. The acylation process was also extended to pyrrole 2-carboxaldehydes,[6,7] which can also be considered as a biomass-derived building block, given its accessibility from furfurals in one step. In addition, we also performed a directed Ir-catalyzed C3-H silylation of furfuryl imines with various silanes, given access even more versatile platform.[8] Discovery of these reactivity, as well as optimizations and scopes of these methods will be described. Mechanisms are proposed on the basis of experimental results as well as Density Functional Theory (DFT) calculations.

FIGURES

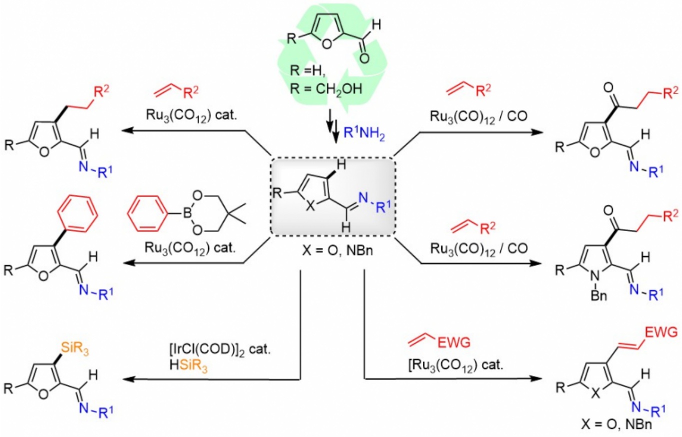

FIGURE 1

Directed Ru- or Ir-catalyzed C3 functionalizations of furfurylimines

Directed Ru- or Ir-catalyzed C3 functionalizations of furfurylimines

FIGURE 2

KEYWORDS

Furfural | Biomass | C-H activation | Homogeneous catalysis

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