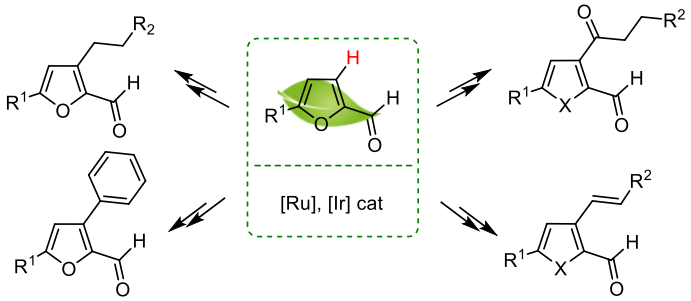
Subject M2 2022-2023

Catalytic conversion of furfural to dimers for the synthesis of biobased-polymers

Period. From February to mi-July in Sorbonne University (IPCM, ROCS team G. Poli, J. Oble)

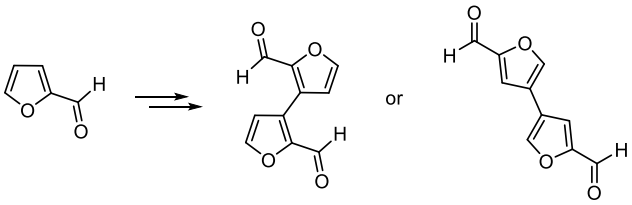
Context. In order to develop an ever more eco-compatible synthetic chemistry, it is nowadays essential to synthesize intermediates and value-added chemical compounds starting from biomass derivatives rather than from fossil resources.[1] Furfural and 5-hydroxymethylfurfural (HMF) are versatile bio-based platform molecules derived from renewable lignocellulose. These simple aromatic heterocycles are of great importance to prepare bio-fuels, monomers for material science, as well as to reach more value-added chemicals in the frame of crop, fragrance, and medicinal chemistry.[2]

Within a broad project directed towards the sustainable C–H functionalizations of furfural derivatives, the selective formation of new bonds through the direct transition metal (TM) catalyzed C–H activation process[3] without modification of the redox state of the aldehyde function, has become one of our (J. Oble and G. Poli) main areas of research. In the last years, we have developed a number of directed Ru(0)-catalyzed C3 functionalizations of furfurylimines, such as the alkylation, arylation, alkenylation and acylation, as well as a directed Ir-catalyzed C3–H silylation.[4]



Global plastic pollution has pushed the scientific community to create new solutions to increase the implementation of dynamics in these materials. Dynamism is conferred to materials in the presence of labile non-covalent bonds or dynamic covalent bonds capable of reversibly forming and breaking, thus conferring to materials a dynamic reversible.[5] Thus, bifurfurals, composed of a bifuryl unit with two formyl groups, can be recognized as an alternative to the petroleum analogs. Specifically, 5,5-diformyl-2,2-difuran is a popular monomer used in the synthesis of versatile 2D and 3D covalent organic frameworks in the form of biosourced polyimines.[6]

Objectives. In order to extend further the synthetic utility of our processes based on metal (TM) catalyzed C–H activation, we now plan to develop strategies for the transformation furfural into versatile bifunctionalized monomers for polymer syntheses. In particular, during this internship, the synthesis of the 3,3- and 4,4-diformyl-2,2-difurans will be tackled.



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4 For our publications, see: a) *Chem. – Eur. J.* **2017**, *23*, 8385–8389; b) *Eur. J. Org. Chem.* **2018**, *2018*, 6101–6106; *ChemSusChem* **2019**, *12*, 4629–4635; *Adv. Synth. Catal.* **2020**, *362*, 2486–2493; *Asian J. Org. Chem.* **2022**, e202200199; *Eur.J. Org.Chem.* **2022**, *e202200.*
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