Design of new NHC based microporous polymer as solid macroligand for C-H arylation molecular catalysts

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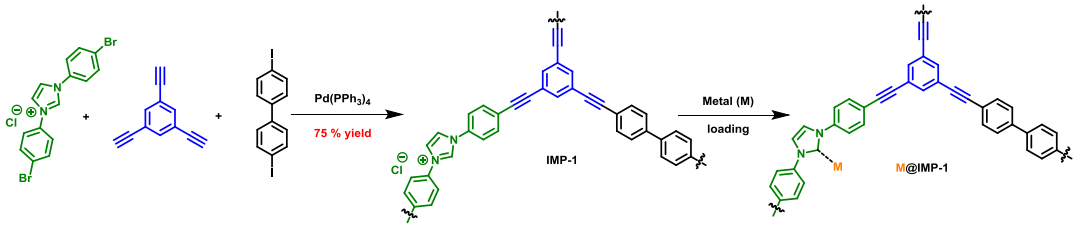
Today, C-H activation processes are largely used to simplify the synthesis of pharmaceuticals, natural products, polymers. Indeed, most of them are based on (hetero)aryl cores, such as indoles, pyrroles, pyrimidines, tetrazoles… .[1] Their synthesis involves at least one catalytic step based on traditional carbon-carbon coupling (Heck, Suzuki…). Usually, homogeneous catalysis with Pd is preferred. However, several issues remain such as the lack of selectivity, the presence of metal residues, ligand stability and, finally, homogeneous catalysts cannot be recovered and/or recycled. Heterogenous catalysts with single site isolated catalytic species might circumvent these issues. In this context, we decided to develop imidazolium based microporous polymer (IMP)



(**Figure 1**) as solid macroligand for the heterogenization of C-H arylation molecular catalysts.

Figure 1: Synthesis of Imidazolium based microporous polymer (IMP-1) and conditions of $Pd(OAc)_2$ loading inside IMP-1

The synthesis of the polymer is achieved with 70 % yield as a yellow powder.[2,3] The polymer was characterized by IR spectroscopy, N_2 adsorption isotherm, solid state NMR spectroscopy. Then metal salt (M) as catalyst precursor is loaded inside the polymer in the presence of KHMDS and toluene. M@IMP-1 is obtained with quantitative yield as a yellow porous solid. Thus IMP can serve as platform by designing them with different NHC and metals to reach several applications in different catalytic processes, and especially in C-H arylation of various heteroarenes as demonstrated here with 100% regioselectivity and yield as high as those reached with molecular analogues (TON up to 100). These novel heterogeneous catalysts will avoid metal leaching, increase catalytic activity and selectivity and will allow for recyclability and implementation in flow processes. This work has been carried out within the H-CCAT project that has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 720996.

(1) Kaushik, N.; Kaushik, N.; Attri, P.; Kumar, N.; Kim, C.; Verma, A.; Choi, E. *Molecules* **2013**, *18* (6), 6620–6662.

(2) Wisser, F. M.; Berruyer, P.; Cardenas, L.; Mohr, Y.; Quadrelli, E. A.; Lesage, A.; Farrusseng, D.; Canivet, J. *ACS Catal.* **2018**, *8* (3), 1653–1661.

(3) Wisser, F. M.; Mohr, Y.; Quadrelli, E. A.; Farrusseng, D.; Canivet, J. *ChemCatChem* **2018**, *10* (8), 1778–1782.