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TOPIC(s) : Homogenous, heterogenous and biocatalysis

Ru-bipyridine entrapped in the supercages of EMC-1 Faujasite as catalyst for the trifluoromethylation of arenes.

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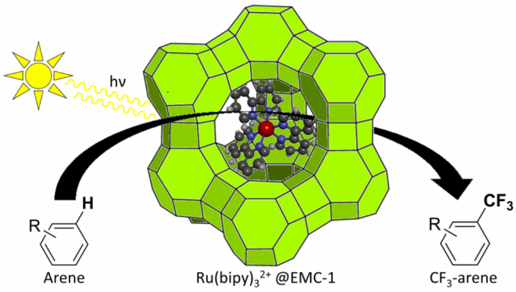
PURPOSE OF THE ABSTRACT

Trifluoromethyl (CF3) groups are versatile structural motifs, since this entity is abundantly present in pharmaceuticals, agrochemicals and organic functional materials [1,2,3]. More recently, a remarkable increase in FDA-approved drug molecules containing a CF3 group is noticed, because it significantly enhances molecular properties such as binding selectivity, liphophilicity and metabolic/chemical stability [4,5]. Nowadays, this CF3 moiety is typically installed on arenes via cross-coupling reactions requiring expensive trifluoromethylating agents and stoichiometric amounts of homogeneous organometallic complexes/metal oxidants at elevated temperatures.[6] Recently, homogeneous photoredox catalysis using Ru(bipy)3Cl2 as photocatalyst, has emerged as a promising alternative, since it is a mild and efficient approach for creating electrophilic °CF3 radicals [6]. Nevertheless, the high cost and the laborious post synthetic separation of the homogeneous photoactive catalyst hamper their further application in large-scale processes and heterogeneous materials should be considered. Therefore, faujasite-type zeolite Y materials are of great interest due to its ability to entrap organometallic complexes in their supercages via ?a-ship-in-a-bottle' strategy [7]. In this work, Ru(bipy)32+, is synthesized within the supercages of the faujasite type zeolite Y via a ?ship-in-a-bottle' method to produce a single-site heterogeneous catalyst for the trifluoromethylation of arenes using CF3SO2Cl as trifluoromethylating agent at room temperature (Figure 1).

The support material was carefully selected to provide; (1) suitable cage dimensions and (2) the optimal Si/Al ratio to withstand the reaction conditions. The incorporation of the Ru(bipy)32+ into the supercages of the faujasite was confirmed by FTIR, UV-Vis and N2-physisorption experiments. Furthermore, the oxidation state and the local environment of the Ru-center was thoroughly studied by XAS experiments. The performance of this single-site heterogeneous catalyst was tested for the trifluoromethylation of different arenes resulting in high yields (>70%) (Figure 2). Moreover, the substrate scope was expanded towards pharmaceutically relevant substrates, such as uracil analogues and drug precursors. Ultimately, the heterogeneity of the catalyst was confirmed via recycling tests and metal analysis of the reaction mixture indicated that leaching of the Ru-complex was very limited.

FIGURES



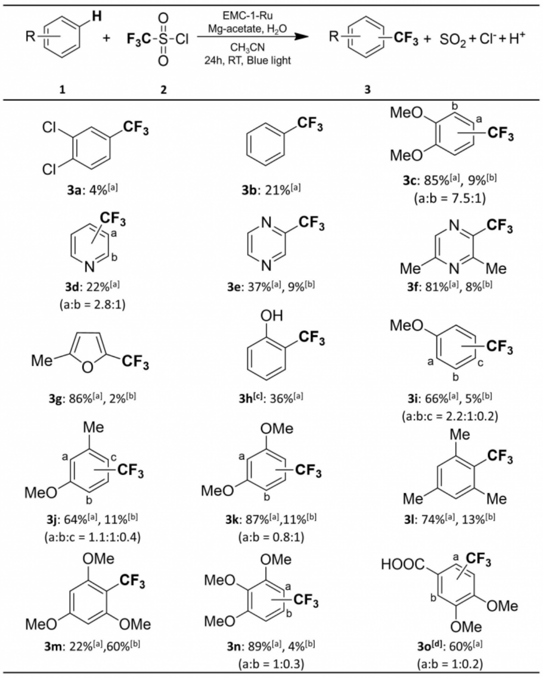


FIGURE 1

Graphical abstract

Graphical demonstration of the trifluoromethylation reaction using the Ru(bipy)32+ catalyst entrapped in EMC-1.

FIGURE 2

Substrate scope

Substrate scope of different (hetero)arenes.

KEYWORDS

Trifluoromethylation | Photocatalysis | Heterogeneous catalysis | Faujasite

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