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Gold-catalyzed, direct alkyne hydroarylation in ionic liquids: a powerful tool in organic synthesis

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PURPOSE OF THE ABSTRACT

Among the numerous C-H bond functionalization reactions that have been disclosed and developed in recent years, the direct hydroarylation of alkynes shows great potential for practical applications, since it produces no waste and often exhibits a high, tunable and peculiar chemo-, regio- and stereoselectivity [1,2].
We have recently disclosed that cationic gold(I) complexes in ionic liquids (ILs) as reaction media. display high activities under neutral conditions in direct alkyne hydroarylation reactionsn (Figure 1) [3]. Furthermore, we have demonstrated that in the case of aromatic heterocycles as substrates the reaction chemoselectivity between mono- and bis-hydroarylation products can be controlled, acting in particular on the reactivity of the substrates and on the solubility of reagents and products in the IL. In this contribution, we report on optimization studies involving both the ligand L supporting the gold(I) centre and the characteristics of the employed IL, in particular the nature of the anion. Further to this, we present our latest efforts towards the practical exploitation of this reaction for the sustainable preparation of organic products of technological interest. In particular, we have targeted the one pot synthesis of coumarins from phenols and propiolic acids/esters, in which phenol hydroarylation is followed by a cyclization step (Figure 2). The effect of the substituents at the aromatic ring and at the alkyne are discussed. We demonstrate that the reaction can be performed with a variety of substituted substrates while maintaining a high level of catalytic efficiency. Implications of this reaction for the valorization of waste phenols deriving from lignin depolymerization/decomposition will be presented as well.

FIGURES

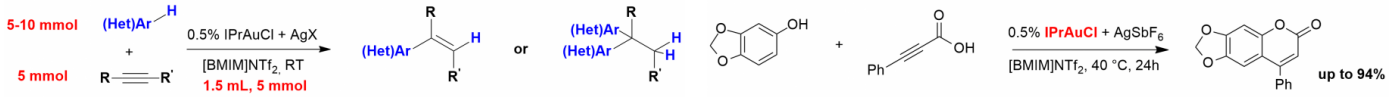

FIGURE 1

Figure 1

General direct alkyne hydroarylation reaction and its possible products

FIGURE 2

Figure 2

Model reaction reaction employed for optimization studies

KEYWORDS

gold | C-H functionalization | coumarins | ionic liquids

BIBLIOGRAPHY

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