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ONE-POT ESTER SYNTHESIS BY COPPER-CATALYZED CARBON? CARBON CROSS-COUPLING BETWEEN ARYLSILANES AND CO2.

AUTHORS

Joelle CHAR / CEA SACLAY, NIMBE,CEA, CNRS, UNIVERSITY PARIS-SACLAY, GIF SUR YVETTE
Xavier FROGNEUX / CEA SACLAY, NIMBE,CEA, CNRS, UNIVERSITY PARIS-SACLAY, GIF SUR YVETTE
Thibault CANTAT / CEA SACLAY, NIMBE,CEA, CNRS, UNIVERSITY PARIS-SACLAY, GIF SUR YVETTE

PURPOSE OF THE ABSTRACT

Lots of efforts in fundamental and industrial research are focused on the use of carbon dioxide
as an abundant, environmentally friendly, non-toxic, cheap and renewable carbon feedstock for the synthesis of value-added products [1]. Since non-polar Carbon?Carbon bonds and especially esters are ubiquitous in organic chemistry and in the chemical industry (e.g. pharmaceuticals, cosmetics, packaging), their formation from CO2 is an interesting alternative to petrochemistry-based methodologies. Currently, the conversion of CO2 to esters usually involves two-pots two-steps and transition-metal-based stoichiometric or catalytic systems. First, a nucleophile reacts with CO2 to form the correspondent carboxylate, then a second step where the latter is trapped with a strong electrophile such as diazomethane, trimethylsilyldiazomethane or alkyl iodides is requiered [2]. However, several one-pot ester synthesis have been reported. Indeed, lactones can be obtained by the coupling of CO2 with various unsaturated derivatives such as alkynes, functionalized alkenes or bifunctional molecules. Some aliphatic esters are also obtained, by coupling terminal alkynes, CO2 and alkyl bromides, or by using organostannanes for a carboxylative Stille coupling. Finally, picolinate esters were successfully obtained in our group from pyridylsilanes, organic halides and CO2. It was the first one-step conversion of CO2 to hetero-aromatic esters under metal-free conditions where the aromatic moiety comes from an arylsilane [3].
However, no system is so far capable of forming, in a one-pot process, simple phenyl esters from CO2, a nucleophile and an electrophile. Among all the available nucleophiles reagents, organosilanes are stable, easy to prepare and to handle. Their use might require activation by fluoride or alkoxide salts.
Therefore, we targeted the development of a new catalyzed one-pot C?C cross-coupling reaction
leading to phenyl esters from simple phenyl silanes, an alkyl iodide and CO2. A NHC based coppercatalyst, (IPr)CuF, already known for some similar reactions [4], was found to be a suitable catalyst forthis new transformation.

FIGURES

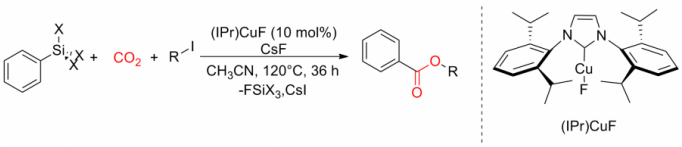

FIGURE 1

Scheme 1

One-pot C?C coupling reaction leading to phenyl esters from simple phenyl silanes, an alkyl iodide and CO2

FIGURE 2

KEYWORDS

CO2 valorisation | fluoride activation | copper catalyst

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