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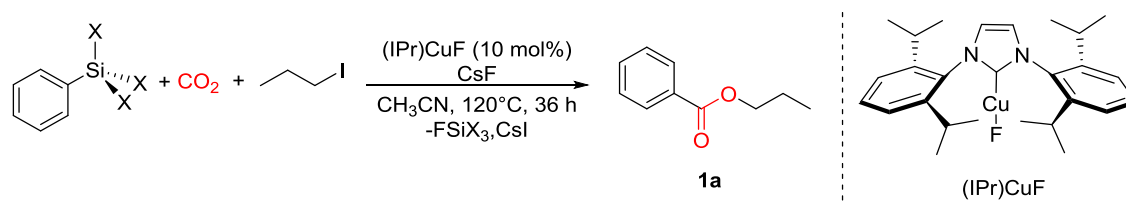
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ONE-POT ESTER SYNTHESIS BY COPPER-CATALYZED CARBON–CARBON CROSS-COUPLING BETWEEN ARYLSILANES AND CO₂.

Joelle Char, Xavier Frogneux, Guillaume Lefèvre and Thibault Cantat*
Laboratoire de Chimie Moléculaire et Catalyse pour L'Energie (LCMCE)
CEA Saclay, UMR 3685 CEA/CNRS, 91191 Gif-sur-Yvette
thibault.cantat@cea.fr

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 required.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 arylsilane³.

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 copper catalyst, (IPr)CuF, already known for some similar reactions⁴, was found to be a suitable catalyst for this new transformation.



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