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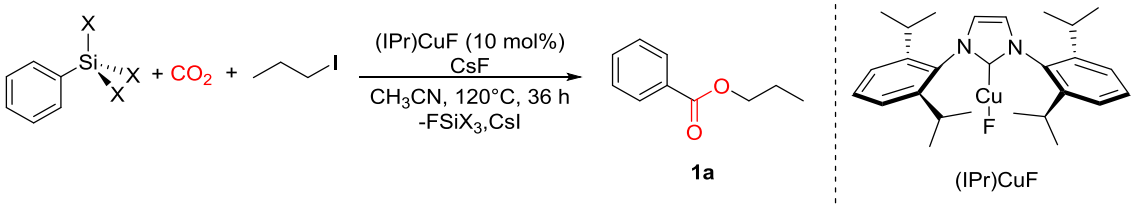
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ONE-POT ESTER SYNTHESIS BY COPPER-CATALYZED CARBON–CARBON CROSS-COUPLING BETWEEN ARYLSILANES AND CO_2.

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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 CO_2 is an interesting alternative to petrochemistry-based methodologies. Currently, the conversion of CO_2 to esters usually involves two-pots two-steps and transition-metal-based stoichiometric or catalytic systems. First, a nucleophile reacts with CO_2 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 CO_2 with various unsaturated derivatives such as alkynes, functionalized alkenes or bifunctional molecules. Some aliphatic esters are also obtained, by coupling terminal alkynes, CO_2 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 CO_2. It was the first one-step conversion of CO_2 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 CO_2, 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 CO_2. A NHC based copper catalyst, (IPr)CuF, already known for some similar reactions[4], was found to be a suitable catalyst for this new transformation.



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