



HAL
open science

One-pot ester synthesis by Copper-catalyzed carbon? Carbon cross-coupling between arylsilanes and CO₂

Joëlle Char, Xavier Frogneux, Thibault Cantat

► **To cite this version:**

Joëlle Char, Xavier Frogneux, Thibault Cantat. One-pot ester synthesis by Copper-catalyzed carbon? Carbon cross-coupling between arylsilanes and CO₂. ISGC2017, May 2017, La Rochelle, France. cea-02341599

HAL Id: cea-02341599

<https://cea.hal.science/cea-02341599>

Submitted on 31 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

N°819 / FC

TOPIC(s) : Renewable carbon / Catalytic systems

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 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 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 for this new transformation.

FIGURES

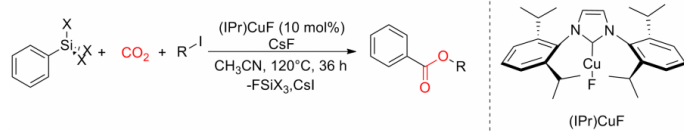


FIGURE 1

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

BIBLIOGRAPHY

- [1] in Carbon Dioxide as Chemical Feedstock, Wiley-VCH Verlag GmbH & Co. KGaA, 2010.
- [2] Y. Tsuji, T. Fujihara, Chem. Commun. 2012, 48, 9956-9964.
- [3] X. Frogneux, N. von Wolff, P. Thuéry, G. Lefèvre, T. Cantat, Chemistry ? A European Journal 2016, 22, 2930-2934.
- [4] J. R. Herron, Z. T. Ball, Journal of the American Chemical Society 2008, 130, 16486-16487; T. Ohishi, M. Nishiura, Z. Hou, Angewandte Chemie International Edition 2008, 47, 5792-5795.