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Sujet de Thèse ADR Ecole Doctorale de Chimie 2019

Title: Development of new catalytic cross-coupling reactions of ethers, esters, or amides using combined transition metal and visible light activation strategies.

Titre: Développement de méthodes catalytiques de couplage d'éthers, esters ou amides basées sur des stratégies d'activation combinant les métaux de transition et l'irradiation par la lumière visible.

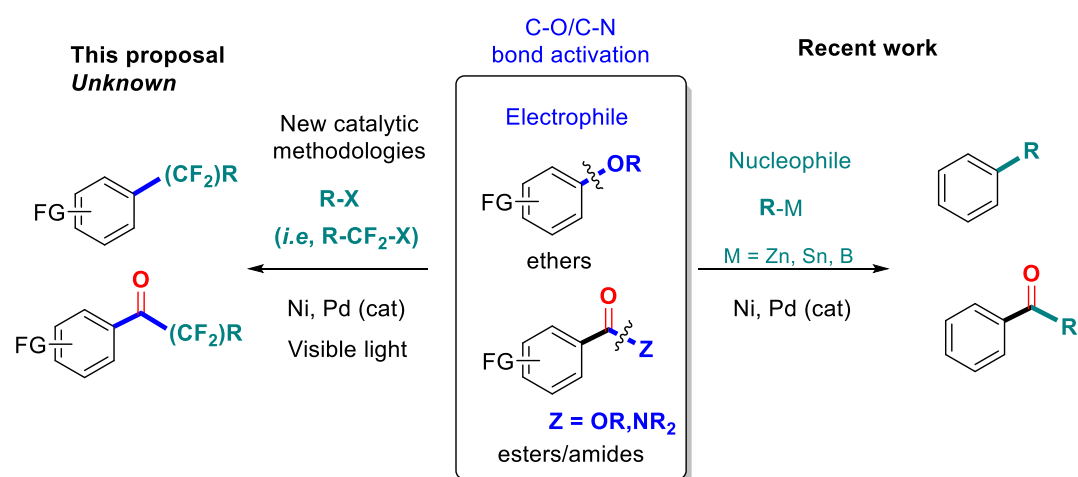
Cross-coupling reactions catalyzed by transition metals represent one of the most powerful methodology because they can couple organic electrophiles and a wide range of nucleophiles to form a vast array of carbon-carbon and carbon-heteroatom bonds. The classical approach relies on the coupling of aryl and vinyl halides, triflates or sulfonates as electrophiles which raises some concerns in terms of toxicity, cost and waste. Extension of these catalytic developments to the coupling of greener and more naturally abundant electrophiles is highly desirable. To this end, aryl ether, ester and amide electrophiles are good candidates not only because their coupling avoids the formation of toxic wastes such as halide salts but also because they are widely found in a broad range of organic molecules, including pharmaceuticals, agrochemicals and organic materials. In this context, the selective functionalization of C-O and C-N bonds recently attracted huge interest in the development of more sustainable synthetic methodologies to high value-added compounds.¹ While important progress have been achieved over the last few years using nickel- and palladium-based catalysts, major challenges remain to be addressed. Among important synthetic targets, considerable efforts are being devoted to the development of efficient methods allowing the incorporation of fluorine substituents into organic molecules.² Fluorinated molecules are high value chemicals in the pharmaceutical and agrochemical industries.³

¹ Reviews: For ethers, see M. Tobisu, N. Chatani, *Acc. Chem. Res.* **2015**, 1717; for esters and amides, see R. Takise, K. Muto, J. Yamaguchi, *Chem. Soc. Rev.* **2017**, 5864.

² For recent reviews of metal-catalyzed trifluoromethylation processes, see T. Furuya, A.S. Kamlet, T. Ritter, *Nature* **2011**, 473, 470; O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **2011**, 111, 4475; T. Besset, C. Schneider, D. Cahard, *Angew. Chem., Int. Ed.* **2012**, 51, 5048; for difluoromethylation processes, see M.-C. Belhomme, T. Besset, T. Poisson, X. Pannecoucke, *Chem.-Eur. J.* **2015**, 21, 12836; D. E. Yerien, S. Barata-Vallejo, A. Postigo, *Chem. Eur. J.* **2017**, 23, 14676; Z. Feng, Y.-L. Xiao, X. Zhang, *Acc. Chem. Res.* **2018**, 51, 2264.

³ K. Müller, C. Faeh, F. Diederich, *Science* **2007**, 317, 1881; S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, 37, 320; Y. Zhou *et al.* *Chem. Rev.* **2016**, 116, 422.

In the framework of a new research program dedicated to the exploration of selective activation and functionalization of challenging C-N and C-O bonds, we propose to investigate new transition metal catalyzed processes, including visible light induced transformations (photoredox catalysis⁴ and direct photoexcitation⁵). As a prototype example of synthetic application, we will explore these strategies for the catalytic fluoroalkylation of ethers, esters or amides via C-O or C-N bond cleavage.⁶



This project will be considered through an interdisciplinary approach that gathers, *organic synthesis, homogeneous catalysis, preparative organometallic chemistry and mechanistic studies*. The candidate should have good knowledge in organic synthesis and organometallic chemistry. An experience in catalysis and / or in molecular chemistry will be appreciated. The candidate should be very enthusiastic and autonomous, and should appreciate to work closely with a team.

⁴ See for examples: Z. Zuo, D. T. Ahneman, L. Chu, J. A. Terrett, A. G. Doyle, D. W. MacMillan *Science* **2014**, 345, 437; L. Chu, J. M. Lipshultz, D. W. C. MacMillan *Angew. Chem., Int. Ed.* **2015**, 54, 7929; C. L. Joe, A. G. Doyle *Angew. Chem., Int. Ed.* **2016**, 55, 4040; J. Amani, G. A. Molander *J. Org. Chem.* **2017**, 82, 1856.

⁵ For a recent review, see: M. Parasram, V. Gevorgyan *Chem. Soc. Rev.* **2017**, 46, 6227.

⁶ For previous work from our laboratory, see: A. Prieto, R. Melot, D. Bouyssi, N. Monteiro, *Angew. Chem., Int. Ed.* **2016**, 55, 1885; A. Prieto, R. Melot, D. Bouyssi, N. Monteiro, *ACS Catal.* **2016**, 6, 1093; A. Prieto, D. Bouyssi, N. Monteiro, *J. Org. Chem.* **2017**, 82, 3311.