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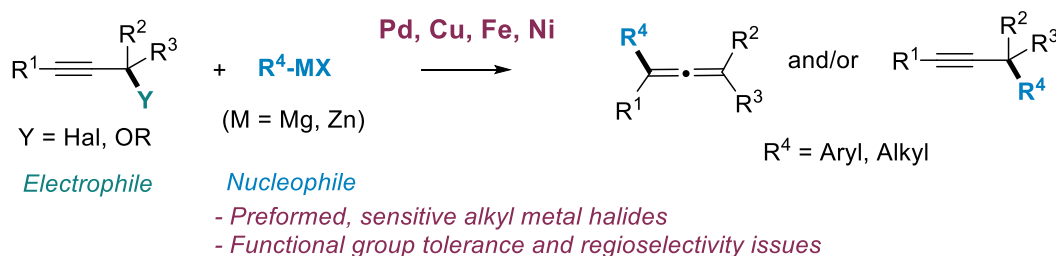
Sujet de Thèse ADR Ecole Doctorale de Chimie 2024

Title: Development of dual metallo-photoredox-catalyzed methods for allene synthesis.

Titre: Développement de méthodes de catalyse duale métal-photo-rédox pour la synthèse des allènes

Allenes are key intermediates in organic synthesis due to their high and diverse chemical reactivity. They are important structural motifs found in natural products and pharmaceuticals, and used to design advanced functional materials as well, making them interesting target molecules.¹ Nowadays, S_N2' -type nucleophilic substitution reactions of propargyl electrophiles still stand among the most attractive strategies for constructing allene motifs. However, these methods rely on nucleophilic additions of highly reactive organometallic reagents that need to be prepared/handled under inert conditions and allow limited functional group tolerance.²

Transition metal-catalyzed nucleophilic aryl/alkylation with organometal halides

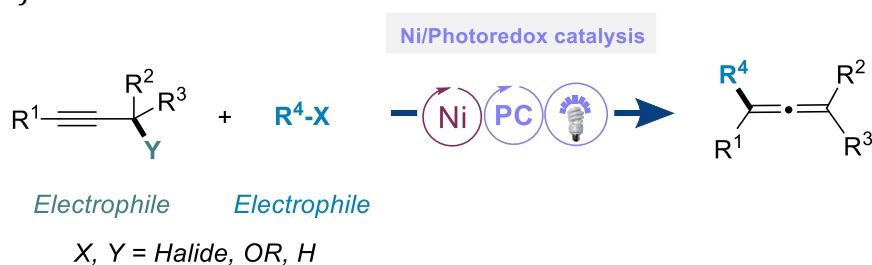


Therefore, the development of alternative new processes avoiding the use of such reagents is highly desirable.

Recently, dual metallophotoredox catalysis has emerged as a powerful strategy that allows the cross-coupling of two readily available, bench-stable electrophilic species. These processes that combine transition metal catalysis (Ni, Cu, Co...) and photocatalysis operate under mild and eco-compatible conditions by converting light energy to chemical energy with the help of a photocatalyst (PC).³

The aim of the project will consist in exploring new nickel/photoredox-catalyzed strategies, notably those based on hydrogen atom transfer (HAT) and halogen atom transfer (XAT) processes, for constructing allene motifs featuring otherwise difficult-to-access substitution patterns and functionalities. As alternative/complementary cross-coupling strategies, processes combining Nickel catalysis and electrochemistry will also be envisioned.⁴

This Project:



This project will be considered through an interdisciplinary approach that gathers, *organic synthesis, homogeneous catalysis, preparative organometallic chemistry and mechanistic studies*.⁵ 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, autonomous, and should appreciate to work closely with a team.

- 1 *Allenic natural products and pharmaceuticals*: A. Hoffmann-Röder, N. Krause, *Angew. Chem., Int. Ed.* **2004**, 43, 1196. *Allenic materials*: P. Rivera-Fuentes, F. Diederich, *Angew. Chem., Int. Ed.* **2012**, 51, 2818.
- 2 *How easy are the syntheses of allenes?* S. Yua, S. Ma, *Chem. Commun.* **2011**, 47, 5384.
- 3 *Metallaphotoredox catalysis*: (a) J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan, *Nature Reviews Chemistry* **2017**, 1(7), 0052. (b) J. A. Milligan, J. P. Phelan, S. O. Badir, G. A. Molander, *Angew. Chem., Int. Ed.* **2019**, 58, 6152.
- 4 *For existing Nickel-catalyzed reactions of propargyl electrophiles*: X. Liu, C. Jiao, S. Cui, Q. Liu, X. Zhang, G. Zhang, *ChemCatChem* **2023**, 10.1002/cctc.202300601.
- 5 *For recent contributions from this lab to photo- and electrochemical cross-coupling processes, see*: (a) T. Kerackian, D. Bouyssi, G. Pilet, M. Médebielle, N. Monteiro, J. C. Vantourout, A. Amgoune, *ACS Catal.*, **2022**, 12, 12315. (b) T. Hu, M. Jaber, G. Tran, D. Bouyssi, N. Monteiro, A. Amgoune, *Chem.-Eur. J.*, **2023**, e202301636.