

Sujet de Thèse

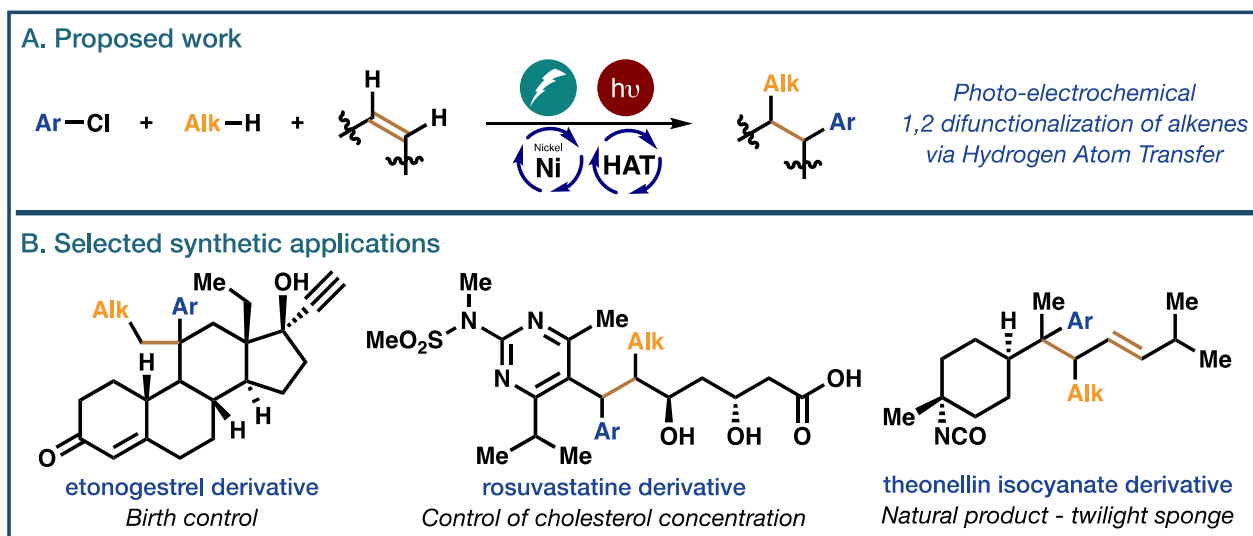
ADR École Doctorale de Chimie 2021

Title: Alkenes Difunctionalization Enabled by Photo-Electrochemical Nickel-Catalyzed C(sp³)-H Functionalization of Alkanes.

Titre: Fonctionnalisation C(sp³)-H d'Alcanes par Catalyse Photo-Électrochimique au Nickel permettant la difonctionnalisation d'Oléfines.

Keywords: *organic chemistry – electrochemistry – photoredox catalysis – transition metal catalysis.*

This project aims to develop an unprecedented method based on the combination of transition metal catalysis and hydrogen atom transfer (HAT) catalysis to synergistically achieve challenging C-C bond formation reactions *e.g.* (i) the direct C-C bond formation from alkanes, and (ii) the difunctionalization of alkenes with alkanes and aryl halides (**Scheme 1**). To reach this goal, we propose to explore a new approach that will combine photocatalysis and electrochemistry.



Scheme 1: Alkenes Difunctionalization Enabled by Photo-Electrochemical Nickel-Catalyzed C(sp³)-H Functionalization of Alkanes.

The direct functionalization of C(sp³)-H bonds represents an atom- and step-economical alternative to more traditional synthetic methods based on functional group transformation, which often require multi-step sequences.¹ Among recently developed methods for the functionalization of alkanes, the HAT approach has emerged as a very powerful technique to achieve selective C(sp³)-H bond activation.² The generated alkyl radical then affords a versatile intermediate able to undergo numerous of transformations such as the addition onto alkene moieties. Similarly, difunctionalization of alkenes via C-C bond formation enables the streamlined construction of complex aliphatic structures and have thus

¹ R. H. Crabtree, A. Lei. *Chem. Rev.* **2017**, *117*, 8481–8482.

² L. Capaldo, D. Ravelli. *Eur. J. Org. Chem.* **2017**, 2056–2071.

been the subject of intense research efforts especially using transition metal-based methods.³ A combination of these two transformations is therefore highly attractive and should allow for the synthesis of valuable building blocks and the late-stage functionalization of complex molecules.

In this project, an innovative technology combining both photocatalysis and electrochemistry will be investigated (**Scheme 1A**).⁴ The development of this catalytic protocol will provide direct access to important synthetic targets (**Scheme 1B**).

This project will be carried out in the framework of a collaborative work between specialists in synthetic electro- and photo-catalytic transformations (*SMITH team*, **J. C. Vantourout** and **M. Médebielle**)⁵ and in dual transition metal/photoredox catalysis (*CASYEN 1*, **A. Amgoune**).⁶ This project will combine several chemistry topics including organic synthesis, electrochemistry, photoredox catalysis and organometallic chemistry.

The candidate should have good organic synthesis and organometallic chemistry knowledge. An experience in catalysis and/or in molecular chemistry will be valued. The candidate should also be very enthusiastic, autonomous, and appreciate to work closely with a team. Further information may be obtained from Julien Vantourout (julien.vantourout@univ-lyon1.fr), Maurice Médebielle (maurice.medebielle@univ-lyon1.fr) and/or Abderrahmane Amgoune (abderrahmane.amgoune@univ-lyon1.fr).

³ R. K. Dhungana, S. KC, P. Basnet, R. Giri. *Chem. Rec.* **2018**, *18*, 1314–1340.

⁴ For a recent review on application of photo-electrochemistry in organic synthesis, see: J. P. barham, B. König, *Angew. Chem., Int. Ed.* **2020**, *59*, 11732.

⁵ (a) C. Li, Y. Kawamata, H. Nakamura, **J. C. Vantourout**, Z. Liu, Q. Hou, D. Bao, J. T. Starr, J. Chen, M. Yan, and P. S. Baran.. *Angew. Chem. Int. Ed.* **2017**, *42*, 13088–13093.; (b) Y. Kawamata, **J. C. Vantourout**, D. P. Hickey, P. Bai, L. Chen, Q. Hou, W. Qiao, K. Barman, M. A. Edwards, A. F. Garrido-Castro, J. N. deGruyter, H. Nakamura, K. Knouse, C. Qin, K. J. Clay, D. Bao, C. Li, J. T. Starr, C. Garcia-Irizarry, N. Sach, H. S. White, M. Neurock, S. D. Minter and P. S. Baran. *J. Am. Chem. Soc.* **2019**, *141*, 6392–6402.; (c) C. Adouama, R. Keyrouz, G. Pilet, C. Monnereau, D. Gueyrard, T. Noël, **M. Médebielle**. *Chem. Commun.* **2017**, *53*, 5653–5656; (d) J. B. I. Sap, N. J. W. Straathof, T. Knauber, C. F. Meyer, **M. Médebielle**, L. Buglioni, C. Genicot, A. A. Trabanco, T. Noël, C. W. am Ende and V. Gouverneur. *J. Am. Chem. Soc.* **2020**, *142*, 9181-9187.

⁶ (a) T. Kerackian, A. Reina, T. Krachko, H. Boddaert, D. Bouyssi, N. Monteiro, **A. Amgoune**, *Synlett*, **2020**, DOI: 10.1055/s-0040-1707301, invited contribution (modern nickel catalysis); (b) T. Kerackian, A. Reina, D. Bouyssi, N. Monteiro, **A. Amgoune**, *Org. Lett.*, **2020**, *22*, 2240.