Research Topic for the ParisTech/CSC PhD Program

Field: Chemistry, Physical Chemistry and Chemical Engineering

Subfield: Chemistry

Title: Palladium-catalyzed transformations of oxyallyl cations

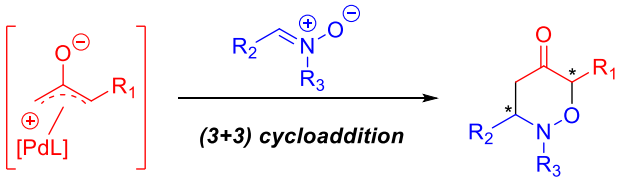
ParisTech School: Ecole Polytechnique

Advisor(s) Name: Alexis Archambeau
Advisor(s) Email: alexis.archambeau@polytechnique.edu
(Lab, website): Laboratoire de Synthèse Organique ; https://portail.polytechnique.edu/lso/en

Short description of possible research topics for a PhD:

In our research group, we focus on the development of original transformations relying on cycloaddition strategies towards the rapid construction of azacycles. In this context, we became interested in the reactivity of oxyallyl cations. In the presence of 1,3-dipoles such as nitrones, we recently showed that a (3+3) cycloaddition can occur to yield functionalized oxazinanones.

This project aims to investigate the reactivity in (3+3) cycloadditions of oxy-π-allylpalladium species. This strategy will allow to control the regio- and diastereoselective outcome of the transformation through a screening of the palladium ligands. Chiral ligands will also be examined to access enantioenriched structures.



The student will 1) find appropriate substrates and conditions to perform this transformation ; 2) develop a diastereoselective version of this transformation relying on modern organometallic catalysis ; 3) survey the potential synthetic applications of these new compounds.

Required background of the student: The applicant must have a strong background in the field of organic chemistry and knowledge of good laboratory practice.

A list of 5(max.) representative publications of the group:

(a) (3+3) Cycloaddition of Oxyallyl Cations with Nitrones: Diastereoselective Access to 1,2-Oxazinanes, Cordier, M.; Archambeau, A. *Org. Lett.*, **2018**, *20*, 2265-2268 *(b) Rhodium(III)-Catalyzed allylic C(sp^3)−H Activation of Alkenyl Sulfonamides: Unexpected Formation of Azabicycles,* Archambeau, A.; Rovis, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 13337-13340. *(c) Highly Efficient Stereoselective Catalytic C(sp^3)−H Insertions with Rhodium Donor Carbenoids Generated from Cyclopropenes*, Archambeau, A.; Miege, F.; Meyer, C.; Cossy, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 11540-11544.