

PhD position 2022-2025

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New approaches for ethers synthesis catalyzed by nickel complexes

Context and project

The diaryl ether scaffold, present in many natural and synthetic products, is the second most represented unit in active molecules in the medicinal and agrochemical fields.¹ Classically, diaryl ethers are obtained via a coupling reaction between an aryl halide and a phenol derivative in the presence of catalysts based on palladium or copper.²

As part of the NiCatEther research project, funded by the ANR, it is planned to develop original, more economical and more environmentally friendly approaches for the synthesis of diaryl ethers.

Two approaches have been selected and will be studied in partnership with the LCM (Paris): (i) the coupling between two aryls in the presence of an oxygen atom donor and (ii) the intramolecular modification of substrates leading to the



diaryl ether motif. In both cases, nickel-based catalysts supported by extremely tunable diphosphine ligands will be used.³

The progress of the thesis will follow a classic path: development and synthesis of ligands and complexes, evaluation in catalysis and mechanistic studies, in close interaction with the LCM partner (Paris). This will allow the candidate to acquire many skills.

Work context

The Laboratory of Coordination Chemistry (LCC), UPR 8241, in Toulouse is a CNRS research center whose research areas are: Chemistry and catalysis, Chemistry and materials and Chemistry and health. The LCC is associated with the University of Toulouse III – Paul Sabatier.

The PhD student will be recruited within the "Ligands, Complex Architectures and Catalysis" team, which has recognized expertise in the development of original metal complexes and their applications, particularly in the field of catalysis.





The thesis is part of a project funded by the ANR, NiCatEther, in collaboration with the Laboratory of Molecular Chemistry (LCM, Ecole Polytechnique, Paris).

This thesis project will be co-supervised by Christophe FLIEDEL (CNRS Researcher) and Pascal GUILLO (assistant professor at Paul Sabatier University).

Profile of the candidate

The candidate must have a master's degree in chemistry. He/she must demonstrate solid knowledge in organic synthesis, organometallic and coordination chemistry and catalysis. He/she must also have relational skills essential for integration within a research team. The recruited doctoral student will be registered at Paul Sabatier University in Toulouse with mention of the « co-direction ».

Candidature

The candidate must apply via the site <u>https://emploi.cnrs.fr</u> (référence UPR8241-CHRFLI-002).

At the same time, he/she should contact Christophe FLIEDEL (<u>christophe.fliedel@lcc-toulouse.fr</u>) and Pascal GUILLO (<u>pascal.guillo@lcc-toulouse.fr</u>) and send CV, cover letter, Master grades and one or two reference letter(s).

Références

¹ T. Chen, H. Xiong, J.-F. Yang, X.-L. Zhu, R.-Y. Qu, G.-F. Yang, Diaryl Ether: A Privileged Scaffold for Drug and Agrochemical Discovery, *J. Agric. Food. Chem.*, **2020**, *68*, 9839-9877. <u>https://doi.org/10.1021/acs.jafc.0c03369</u>.

² S. Bhunia, G. G. Pawar, S. V. Kumar, Y. Jiang, D. Ma, Selected Copper-Based Reactions for C–N, C–O, C–S, and C–C Bond Formation, *Angew. Chem. Int. Ed.*, **2017**, *56*, 16136-16179. <u>https://doi.org/10.1002/anie.201701690</u>

³ C. Fliedel, A. Ghisolfi, P. Braunstein, Functional Short-Bite Ligands: Synthesis, Coordination Chemistry, and Applications of N-Functionalized Bis(diaryl/dialkylphosphino)amine-type Ligands, *Chem. Rev.* **2016**, *116*, 9237-9304. https://doi.org/10.1021/acs.chemrev.6b00153