New Versatile Chiral Platforms for Enantioselective Catalysis

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The need to create new chiral materials is constantly increasing to meet the major issues of our society that are health care and the environment. In this context the importance of designing new low-cost chiral tools with the most straightforward and atom-economical approaches is crucial. This will lead to the preparation of new organic/organometallic chiral pockets which would be capable of having a high specificity for their substrates.

Surprisingly, although chiral N-heterocyclic carbene (NHCs) are well established as enantioselective organocatalysts,[1] their use as chiral ligands for transition metals is still marginal compared to well establish enantiopure phosphines.[2] Nonetheless, chiral NHCs are still attractive ligands considering their high synthetic modularity and the exceptional stability exhibited by the metal-NHC bond, and bidentate one in particular.[3] On the other hand, the robustness of NHCs-metal complexes makes them very attractive to stabilize very reactive species which allows a better control of the selectivity. One of the most exciting and necessary challenge remains the replacement of expensive noble metals (Ir, Pd, Pt or Rh) by either earth abundant and less toxic metals or by organocatalysts to diminish the impact on both economic and environmental factors.

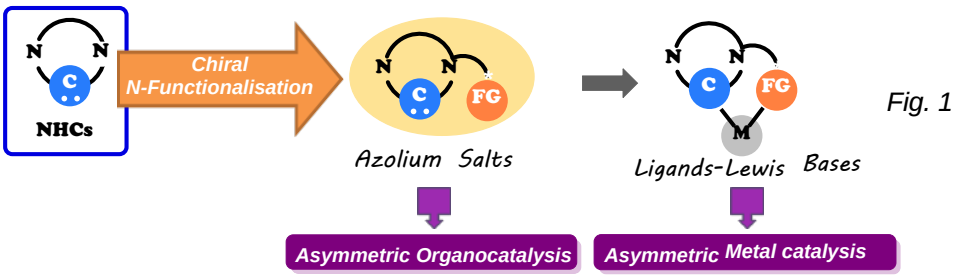

Fig. 1

In this project, we plan to use a singular family of chiral NHC bidentate ligands with an ancillary arm with a chiral atom. First the chiral azolium salts will be evaluated in organocatalytic transformation with challenging substrate and secondly they will be attached to transition metals such as ruthenium and less toxic and eco-friendly iron. NHCs-metal complexes, and especially very challenging NHCs-Fe, will be evaluated in asymmetric catalysis and particularly in the “borrowing and acceptorless hydrogen strategy”(BH).[4] This research project is based on synthetic innovation and meets the criterion of economy of steps to access molecular diversity.

To summarize, our goal for this project is to synthesize new chiral objects based on NHC moities that will serve as a platform for *asymmetric catalysis*. During this PhD, the student will learn to conduct chiral organic syntheses, to prepare organometallic complexes and to perform several types of catalyzed reactions.

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[2] (a) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485.; (b) D. Janssen-Muller, C. Schlepphorst, F. Glorius, *Chem. Soc. Rev.* **2017**, *46*, 4845.
[3] C. Fliedel, A. Labande, E. Manoury, R. Poli, *Coord. Chem. Rev.* **2019**, *394*, 65.
[4] (a) T. Achard, J. Egly, M. Sigrist, A. Maisse-François, S. Bellemin-Laponnaz, *Chem. Eur. J.* **2019**, *25*, 13271-13274. (b) W. Chen, J. Egly, A. Poblador-Bahamonde, A. Maisse-François, S. Bellemin-Laponnaz, T. Achard, *Dalton Trans.* **2020**, *49*, 3243.