PROPOSITION DE SUJET DE THESE
Campagne 2019/2020

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ECOLE DOCTORALE : Ecole Doctorale de Chimie de Lyon (ED206)

TITLE OF RESEARCH SUBJECT /TITRE DU SUJET DE RECHERCHE :

Synthesis and applications of a structurally unprecedented highly preorganised bi-functionalised chiral platform

Research team/Equipe de recherche : Laboratoire de chimie – Supramolecular chemistry and Chemical biology
http://www.ens-lyon.fr/CHIMIE/recherche/Teams/Chimie_Organique_et_Materiaux_Nanostructures

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Lab Language/ Langue de travail: English (mainly) and French

Abstract/Présentation du sujet and references: see next pages

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Direction des Affaires internationales : international.strategy@ens-lyon.fr

Synthesis and applications of a structurally unprecedented highly preorganised bifunctionalised chiral platform

Under the supervision of Philippe Maurin
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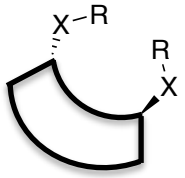
keywords : diols, axial chirality, hélicoidal compounds, chiral ligands, asymmetric catalysis

***Summary**: Synthesis / characterisation of a new class of highly preorganised chiral compounds with chelating properties supported by a rigid planar base with various potential applications. The project will include development / evaluation of the performances of derivatives with applications in domains such as*

- *New chiral catalysts*
- *« chiral building blocks » with axial chirality*
- *Access to helicoidal compounds with control of the helicity*



X = heteroatoms such as O or N

Project:

This subject constitutes a new subject of research that has been recently initiated in the team. It will consist in the continuation of very promising results obtained in the laboratory at ENS de Lyon with the obtention of a first family of enantiomerically pure chiral compounds based on the planar rigid base.

Our project consists in taking profit of the very strong preorganisation (elbow shaped) of the planar rigid base with two chiral centers bearing heteroatoms pointing in two different half-spaces. Those building blocks will be used as precursors for the conception of compounds with

constraint geometry with potential interesting applications in domains such as asymetric catalysis or chiral helicoidal compounds.

Workplan:

1- A first part of the PhD will be dedicated to the validation and development of the access route to the enantiomerically pure family of precursors that has already been explored. It will allow the PhD student to become familiar with the specific chemistry involved in the project. It will also widen the range of precursors by introducing various functional groups or substituents to enlarge the scope of applications. It will also be possible, if needed, to functionalise the planar rigid base for more specific goals.

2- The developed molecular platforms being unprecedented, they will be potentially of high interest for a wide range of applications. The second part of the PhD will thus be dedicated to performance evaluations in domains such as (non restrictive and not exhaustive list) :

- Chiral recognition / separation
- Asymmetric catalysis / synthesis
- Non-linear optics
- Chelating properties[1], chiral bidentate ligands
- Helicoidal compounds
- foldamers
- material chemistry

It will be of particular interest to compare the properties of this unprecetended structure with Binol based compounds[2] or chiral cyclohexyldiamines, and for different kind of applications such as supramolecualr aggregates auto-assembling or catalytic properties of chiral complexes issued from our platform[3]

We are exploring the opportunities to collaborate or to co-supervise the PhD student with a chinese partner for the design / characterisation parts of the project concerning chiral complexes and evaluation of their performances.

[1] Bunzen, J.; Bruhn, T.; Bringmann, G.; Lüthzen, A. *J. Am. Chem. Soc.* **2009**, 131, *10*, 3621-3630

[2] Brunel, J.M. *Chem. Rev.* **2005**, 105, *3*, 857-898 ; Yu-Lut Leung, S.; Lam, W.H.; and Wing-Wah, V. PNAS, **2013**, *110*, 20, 7986-7991

[3] a) Balsells, J.; Davis, T.J.; Carroll, P.; Walsh, P.J. *J. Am. Chem. Soc*. **2002**, *124*, 10337. b) Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979** , *101*, 3129– 3131. c) Guo, C.; Qiu, J.; Zhang, X.; Verdugo, D.; Larter, M.L.; Christie, R.; Kenney, P.; Walsh, P.J. *Tetrahedron*, **1997**, *53*, 4145. d) Van Rijn, J.A.; Siegler, M.A.; Spek, A.L.; Bouwman,E.; Drent, E. *Organometallics*, **2009**, *351*, 1637