

**Sujet de stage de Master 2**

**Laboratoire : Département de Chimie Moléculaire**

**Directeur : Didier Boturyn**

**Intitulé de l'équipe : SeRCO**

**Responsable : Jean-François Poisson**

**Nom et Qualité du Responsable du Stage : Sébastien Carret (MCF)**

**HDR non**

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**Parcours de Master 2 : Organic Synthesis (SOIPA)**

**Titre du sujet : THIOIMIDATES AND DERIVATIVES : ASYMMETRIC SYNTHESIS OF CHIRAL DIAMINES**

**Objectifs visés du stage :**

Development of an asymmetric catalytic sequence to access chiral vicinal diamines.

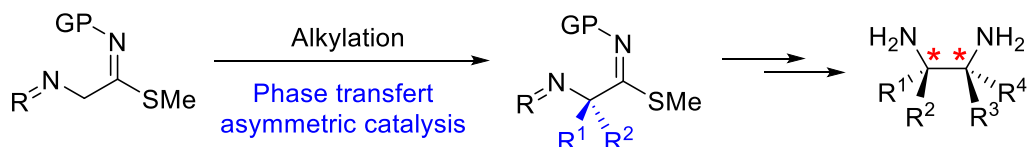
**Intérêts pédagogiques et compétences visées :**

Reactions under anhydrous conditions. Multisteps synthesis. Purification and characterization/analytical techniques. Bibliographic research.

**Résumé :**

The recent development of a new efficient and flexible synthesis pathway for alkaloids from the Lycorine family and more precisely the first total synthesis of Kirkine, has led us to explore the reactivity of a new key intermediate: a sulfinylthioimide. Laboratory work has shown that these novel compounds can be alkylated in a completely diastereoselective way, reduced to imine which can then undergo a totally diastereoselective 1,2-addition, making possible to generate two stereogenic centers entirely controlled by the chiral auxiliary, tertbutanesulfinamide (Ellmann's chiral auxiliary). Direct coupling of the sulfinylthioimide followed by a reduction reaction makes it possible to obtain the other diastereoisomer with excellent diastereoselectivity and very good yields.

The objective of this internship is to develop an asymmetric catalytic version of this reaction sequence in order to prepare chiral vicinal diamines which prove to be of great importance for their biological activities but also for their usefulness as ligands or chiral auxiliaries in asymmetric synthesis. Preparation and the exploration of the reactivity of derivatives of thiooxime or thiohydrazone will also be studied.



**Approches & matériels utilisés:**

The student will use most of the techniques in organic synthesis (inert atmosphere, low temperature, small quantity reaction), as well as numerous analytical methods to determine the structures of the compounds obtained (NMR, supercritical CO<sub>2</sub> HPLC, UHPLC-MS, Mass). The student will develop flow reaction conditions.

**Domaines de compétences souhaitées du candidat:**

Good level in organic chemistry, experience in separation techniques and analysis methods; use of bibliographic databases.

**Dates du stage : January – June 2022**