*Title:* **Development of new bipyridine ligands for the self-assembly of asymmetric catalysts**

*Student:* Sabela Vega Ces

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*Supervisor/s:* Dra. Laura Rodríguez Raurell

Departament de Química Inorgànica i Orgànica

Dr. Ciril Jimeno Mollet

Institut de Química Avançada de Catalunya (IQAC-CSIC)

In order to develop new asymmetric catalysts with self-assembly properties, two of the four proposed bipyridine-derived ligands have been synthesized (**L1** = $N^5$,$N^{5'}$-dihydroxy[2,2'-bipyridine]-5,5'-dicarboxamide and **L2** = $N^5$,$N^{5'}$-di(pyrrolidin-3-yl)-[2,2'-bipyridine]-5,5'-dicarboxamide).

**L1** is able to perform HOMO activation by forming an enamine with the nucleophilic ketone, and **L2** has the ability to form hydrogen bonds with the electrophile in order to direct the nucleophilic attack to one of its enantiotopic faces. The capacity of the catalyst to form enantiomerically enriched products has been tested in an aldol and a Michael reaction by adding a mixture of these ligands (**L1** and **L2**) and a Zn (II) salt (zinc trifluoroacetate).

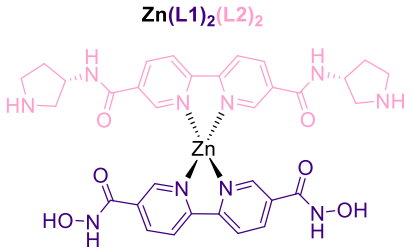
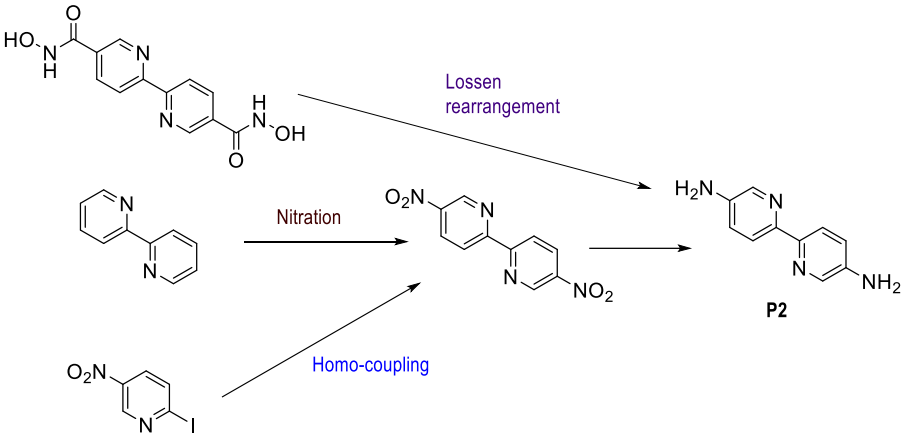



**Figure 1.** Envisioned self-assembled catalytic structure for the combination of ligands (**L1** and **L2**) with zinc trifluoroacetate.

The catalysed Michael reaction has come to no product. However, the aldol reaction, despite of its low conversion, has shown a change in the diastereoselectivity of the obtained products.

The remaining two ligands (**L3** = 1,1'-([2,2'-bipyridine]-5,5'-diyl)bis(3-phenylthiourea) and **L4** = N,N'-([2,2'-bipyridine]-5,5'-diyl)bis(pyrrolidine-3-carboxamide)) have not been synthesized but their precursor (**P2** = [2,2'-bipyridine] -5,5'-diamine) has been succesfully obtained. The synthesis of this compound is considered the decisive step of the work, three different synthetic pathways

have been studied in order to achieve it (Lossen rearrangement, nitration of bipyridines and metal-catalysed homo-coupling reactions).




**Scheme 1.** Studied synthetic pathways for the obtention of [2,2'-bipyridine] -5,5'-diamine (**P2**).

**Keywords**: Asymmetric catalysts, self-assembly, bipyridines, aldol reaction, stereoselectivity, synthetic pathways.