

**CELLEX-ICIQ POST-DOCTORAL PROGRAMME ON HIGH THROUGHPUT EXPERIMENTATION
FOR THE DISCOVERY AND OPTIMIZATION OF CATALYTIC PROCESSES**

The Institute of Chemical Research of Catalonia (ICIQ), with the sponsorship of CELLEX Foundation, is now launching the CELLEX-ICIQ post-doctoral programme on High Throughput Experimentation (HTE) for the discovery and optimization of catalytic processes. The programme involves nine one-year positions, renewable for a second year upon agreement. Eight of the positions will be to work at ICIQ Research Groups, and one will be to work at the CSOL laboratory. In all cases, the goal of these positions will be to develop and boost the use of High Throughput Experimentation (HTE) methods and techniques at ICIQ.

The titles of the different research projects and the names of the scientists in charge are listed below. A more detailed description can be found in the annex below.

1. Discovery of Unprecedented Photo-Organocatalytic Asymmetric Processes by means of High-Throughput Screening (Prof. Paolo Melchiorre)
2. Metal-Catalyzed Reductive Cleavage of Electrophilic Coupling Partners (Prof. Ruben Martin)
3. Discovery of New Catalysts for the Synthesis of Bio-Renewable Polymers and Heterocyclic Structures Incorporating CO₂ as a Synthon (Prof. Arjan W. Kleij)
4. HTE Methodologies for the Development of Catalytic Asymmetric Flow Processes with Supported Systems (Prof. Miquel A. Pericàs)
5. Development of an Enantioselective Palladium(II/IV) Catalysis for the Asymmetric Diamination of Alkenes (Prof. Kilian Muñiz)
6. Discovery of Group 10 Metal-Catalyzed Reactions by High-Throughput Experimentation (Prof. Antonio M. Echavarren)
7. Towards Valuable Optically Pure Compounds by Hydrogenative Desymmetrization of Achiral or meso-Compounds using High-Throughput Catalyst Screening Techniques (Prof. Anton Vidal)
8. Reaction Discovery and Optimization through Rapid Evolution of Aminophosphine Ligand Scaffolds (Dr. Alexandr Shafir)
9. Development of HTE Techniques for the Fast Optimization of Industrially Relevant Processes Developed at ICIQ (Dr. Fernando Bravo, CSOL)

Applicants should submit an application letter indicating four of the proposed projects arranged by decreasing preference, a detailed cv, and the names and contact addresses of three references to: pdp@iciq.es, indicating "CELLEX-ICIQ PDP" as the subject of your message. Only applications received until April 30, 2014 will be considered. No mobility restrictions will apply to this call.

The ICIQ HTE laboratory and the CELLEX-ICIQ post-doctoral programme are funded by the CELLEX Foundation.

ANNEX TO THE CELLEX-ICIQ POST-DOCTORAL PROGRAMME ON HIGH THROUGHPUT EXPERIMENTATION FOR THE DISCOVERY AND OPTIMIZATION OF CATALYTIC PROCESSES

1. Discovery of Unprecedented Photo-Organocatalytic Asymmetric Processes by means of High-Throughput Screening (Prof. Paolo Melchiorre)

High-throughput, automated workflow can be transformative of the overall methodology development process, both in the discovery and optimization phase. We want to apply this approach for discovering and developing unprecedented photochemical organocatalytic asymmetric transformations. We have recently found a bridge, the electron donor-acceptor (EDA) interaction, to connect two powerful fields of molecule activation: asymmetric organocatalysis and photochemistry, challenging the current perception that photochemistry is too unselective to parallel the levels of efficiency reached by the asymmetric catalysis of thermal reactions (*Nature Chem.* 2013, 5, 570).

With the present research endeavor, we want to further consolidate the idea that the photochemistry of EDA complexes, formed upon aggregation of organic substrates, may provide a general reactivity framework for the design of unprecedented photo-organocatalytic transformations, expanding the way chemists think about making chiral molecules.

2. Metal-Catalyzed Reductive Cleavage of Electrophilic Coupling Partners (Prof. Ruben Martin)

This project aims at unraveling the prospective impact of metal-catalyzed reductive cleavage of electrophilic coupling partners such as organic halides or pseudohalides with carbonyl-type compounds. Unlike the classical catalytic cross-coupling events, reductive approaches avoid the unnecessary prefunctionalization of the substrates, do not require the use of preformed organometallic species and are typically operationally-simple, thus constituting a straightforward alternative in the cross-coupling arena. This project will deal with such challenge by providing new vistas in a relatively unknown area of expertise by using a high-throughput experimentation platform.

3. Discovery of New Catalysts for the Synthesis of Bio-Renewable Polymers and Heterocyclic Structures Incorporating CO₂ as a Synthon (Prof. Arjan W. Kleij)

In this project the development of new and powerful catalysts based on poly-phenolate ligands is combined with their use as effective mediators of CO₂ conversion reactions. The principal aim is to discover suitable metal or organo-catalysts that have strong activation potential in the formation of bio-renewable polymers based on simple, accessible and cheap reagents, and the preparation of oxazolidinones. High-throughput experimentation techniques will be required to quickly screen a series of process parameters (defining parameter space) to identify in a screening phase the best conditions and catalyst scaffolds for further process optimization. Finally, after full optimization the selected process conditions will be used to translate the chemistry to bench-scale proportions.

4. HTE Methodologies for the Development of Catalytic Asymmetric Flow Processes with Supported Systems (Prof. Miquel A. Pericàs)

This project will be centered on the identification of organocatalytic species mediating the enantioselective formation of C-C and C-X bonds, suitable for immobilization onto solid matrices, with the ultimate goal of developing continuous flow processes catalyzed by these supported species. Projects within this research programme will normally involve four stages, two of which involving extensive use of the HTE facility: i) Identification of homogeneous catalysts with optimal characteristics for the targeted reactivity (HTE lab), ii) Design of a chemically modified version of the catalyst identified in stage one suitable for immobilization, and immobilization of this species onto different supports (Research lab), iii) Parallel testing and elucidation of optimal reaction conditions for high catalytic activity and enantioselectivity (HTE lab), and iv) Implementation of a continuous flow process based on the results optimized in stage iii

5. Development of an Enantioselective Palladium(II/IV) Catalysis for the Asymmetric Diamination of Alkenes (Prof. Kilian Muñiz)

The project aims to develop an enantioselective palladium catalysed diamination of alkenes. This reaction should make use of the concept of palladium high oxidation state catalysis and will use previous results from our group as the starting point. We have developed a series of oxidative vicinal diamination reactions of alkenes under strictly intermolecular reaction control. Recent unpublished work from our group suggested a mechanism that is based on unprecedented phthalimidato complexes of palladium. These catalysts do not tolerate the presence of any common mono- or bidentate ligands and, as a consequence, an enantioselective process has yet to be developed. Based on theoretical and experimental evaluation, the transition state of the initial aminopalladation appears to offer the chance to interfere with chiral non-racemic acids in order to generate enantioinduction. We thus aim to employ high-throughput experimentation for the identification of efficient acid promoters.

6. Discovery of Group 10 Metal-Catalyzed Reactions by High-Throughput Experimentation (Prof. Antonio M. Echavarren)

The goal of this project is to discover new copper-, silver-, or gold-catalyzed reactions by high-throughput experimentation using a series of readily available group 10 metal precatalysts and ligands. A major objective is to promote copper to the level of gold as the catalyst of choice for the activation of alkynes. We will focus our work on the development of new intermolecular reactions of alkynes, enantioselective cascade cyclizations, and cross-coupling reactions. We will also study new methods for the generation of electrophilic metal carbenes.

7. Towards Valuable Optically Pure Compounds by Hydrogenative Desymmetrization of Achiral or meso-Compounds using High-Throughput Catalyst Screening Techniques (Prof. Anton Vidal)

Our past and current aims encompass the design and development of efficient catalytic methodologies for transformations of interest and their application to the preparation of targets of biological, pharmacological and agrochemical interest. This project is aimed to develop efficient and reliable catalytic systems for the hydrogenative desymmetrizations of achiral or *meso* compounds (mainly epoxides, 1,2-dihalocompounds, thioanhydrides and unconjugated dienes). Catalyst design and/or optimization based on the analysis of the diastereomeric transitions states of the corresponding processes, a modular design of the catalytic system and the use high throughput methods for catalyst preparation and screening should hopefully boost the discovery and development of efficient catalytic systems for the preparation of valuable intermediates *via* the aforementioned transformations.

8. Reaction Discovery and Optimization through Rapid Evolution of Aminophosphine Ligand Scaffolds (Dr. Alexandr Shafir)

A great number of catalytic processes rely on the use of chelating phosphines. However, modifications in a diphosphine structure are work-intensive, which may hamper reaction optimization and process discovery. Alternatively, bis-aminophosphines could be envisaged as “surrogates” of the chelating diphosphines; structurally diverse set of ligands could then be generated through a wide variety of amines (and chlorophosphines) available.

This project is based on a rapid approach to a condensative aminophosphine synthesis recently developed in our laboratory. The postdoctoral fellow will now apply the High Throughput Experimentation to identify catalysts for hitherto inefficient (or non-existent) H₂-autotransfer reactions, including, the direct conversion of adiponitrile to nylon 6,6.

9. Development of HTE Techniques for the Fast Optimization of Industrially Relevant Processes Developed at ICIQ (Dr. Fernando Bravo, CSOL)

Given the nature of the research to be developed, no summary of this project is available.