

Vidal Research Group



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Abstract

Our past and current objectives encompass **developing efficient and reliable catalytic asymmetric tools** for organic transformations of interest, **and studying their use to prepare relevant products in the industrial sector**. Crucial aspects of this work include the modular design of catalysts; using versatile synthetic procedures (organic transformations, or supramolecular processes); incorporating regulation mechanisms for their active site

geometry and the computational study of their catalytic cycles (through collaborations). Our research interests are also shifting from noble metal-based to earth abundant metal-based catalysts. We are also endeavoring to expand the scope of the catalysts developed to include the enantioselective catalytic synthesis of precursors of bioactive compounds or the valorization of small unsaturated hydrocarbons (*i.e.*, alkenes, alkynes, allenes or dienes) *via* catalytic functionalization transformations.

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Our research project focuses on catalysis, which is an area of chemistry that enables conversion of simple compounds into complex molecules of enormous practical utility. This area has transformed—and will continue to transform—products and processes in diverse sectors (e.g. life sciences and fine chemicals) with significant financial and societal impact.

In response to the objectives of our most recent grants, we have developed extensive methods for the efficient synthesis of highly modular *P-OP* (phosphine-phosphite) ligands. With regard to the application of the ligands designed, we have focused on consolidating new rhodium- and iridium-catalyzed hydrogenation methods as a specialty niche for the group. The group is also

designing and developing supramolecular ligands that resemble a “privileged” structure and include the possibility of offering a range of closely related catalytic sites. The backbone of these ligands is based on a privileged structure in enantioselective catalysis and contains a regulation center. The regulation mechanism is triggered by a regulating agent (RA) that interacts with the ligand (*via* ion-dipole interactions or hydrogen bonding) to create a catalyst that retains the majority of the backbone’s structural features and incorporates subtle changes at its active site that depend on the RA used. By exploiting the interactions between a ligand and a set of structurally diverse RAs, the outcome of the transformation of interest can be maximized by the choice of whether or not to use an RA (and if so, which one).

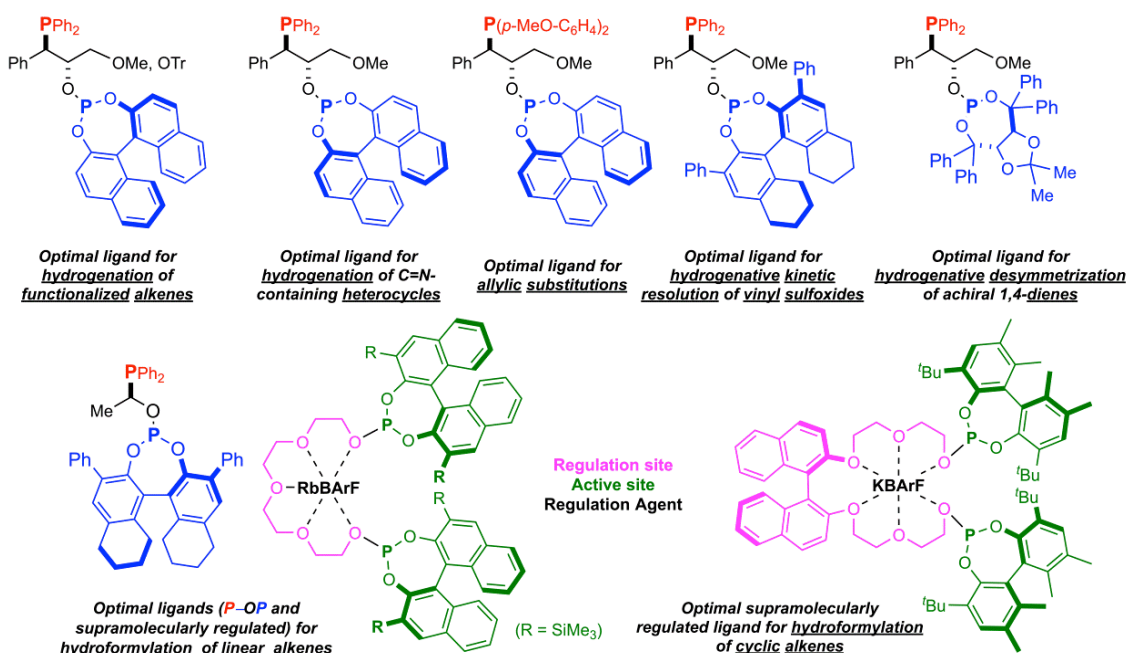


Figure 1. Lead ligands for the asymmetric transformations under study

Ongoing research projects encompass a series of multidisciplinary research activities within the field of chemistry:

Firstly, the group is taking advantage of its expertise in the synthesis of enantiopure ligands to prepare the metal complexes required for catalytic studies. The traditional approach to synthesizing chelating ligands relies on the

covalent connection between the molecular fragments of the ligand and, in many cases, a costly synthetic effort is required. Supramolecular chemistry has emerged as a powerful tool to overcome this limitation, as bidentate ligands can be prepared with unprecedented ease by employing supramolecular interactions. We are pioneering



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the use halogen-bonding interactions for the preparation of supramolecular ligands and metal catalysts containing them.

a) We are also aiming at gaining further insight into new types of hydrogenative transformations such hydrogenative desymmetrizations of *meso*-/achiral compounds and hydrogenative (dynamic) kinetic resolutions.

b) We are endeavoring to expand the use of regulation agents to modify the (stereo)selectivity of organic transformations by supramolecularly modifying the geometry of the active site. We are also working on new catalyst designs that allow steric congestion around the metal center to be supramolecularly regulated.

Further scientific challenges include taking our R&D activities in the direction of applying the group's core expertise to the valorization of petrochemical feedstocks, more concretely to the transformation of small unsaturated hydrocarbons (alkenes, alkynes, dienes and allenes) into higher value-added products *via* catalytic functionalization transformations,

shifting the focus of the research to earth abundant metal-based catalysts when possible.

c) Our group has identified common research interests with the research group led by Dr. Palomares at the Institute of Chemical Research of Catalonia. As a result, the two groups have started to collaborate on designing and developing new small organic molecules as hole transport materials for solar cells.

d) Together with Covestro AG (formerly Bayer MaterialScience), the group is involved in the development of efficient catalysts that mediate the alkoxy carbonylation of anilines with dialkylcarbonates. The catalysts developed can facilitate the longstanding desired phosgene-switch to more benign CO-sources in the polymer industry. Two patents on Zn- and Ce-based catalysts for this transformation have been filed.

Articles

"Syntheses, Characterisation and Solid-state Study of Alkali and Ammonium BARF Salts"
RSC Advances (2017) 7, 32833-32841

L. Carreras, L. Rovira, M. Vaquero, I. Mon, E. Martin, J. Benet-Buchholz, A. Vidal-Ferran

Patents

"Preparation and Catalytic Activity of New and Patentable Zn Based Heterogeneous Catalysts for the Methoxycarbonylation of Aromatic Amines"

EP 17 170 988.4

S. Wershofen, M. Dugal, J. L. Núñez-Rico, A. Vidal-Ferran

"Heterogeneous Catalysts for the Synthesis of Carbamates"

COV171092 EP

S. Wershofen, R. Serra, J. L. Núñez-Rico, A. Vidal-Ferran, J. Pérez-Ramírez, A. Amrute, B. Puértolas