Università degli Studi di Salerno
Facoltà di Scienze Matematiche Fisiche e Naturali

Doctor Thesis in Chemistry

Towards the rational design of new catalysts for organic transformations

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The main goal of this PhD thesis has been providing a computational support to the development of new or better performing catalysts, leading to the synthesis of new materials.

In this context, it is worth remembering that catalysis is a topic of primary relevance in the academy as well as in the industry, due to the enormous impact of catalysis in every day life.

In particular, within this PhD project, attention has focused on catalytic systems based on N-heterocyclic carbene (NHC) ligands, which have emerged as useful ligands in the last ten years.

In the first part of this thesis, the development of new molecular descriptors for the quantification of steric and electronic effects in transition metal based catalysts has been pursued.

The final goal of this approach consists in rationalizing the highly disorganized and chaotic catalytic space, to orientate experimental efforts towards possibly well performing catalysts, and away from the ineffective ones. This would allow to pursue a catalysis by design approach, in alternative to the "trial and error" classical approach.

In particular, descriptors based on topographic steric maps have emerged as powerful tools that can be easily used and interpreted by the scientific community.

A user friendly web server has been implemented in order to allow the scientific community to build steric maps for the systems of interest. The web server has already achieved great success with a number of visitors all around the world.

In the second part of the thesis, attention was focused on developing and rationalizing new catalysts in strict collaboration with experimental groups.

The systems investigated represent advanced application of N-heterocyclic carbenes as ligand in Ru-catalyzed olefin metathesis, Pd-catalyzed C-C cross coupling reactions, and as catalysts in the organopolymerization of polar olefins.

The detailed mechanistic studies have offered a comprehensive understanding of the whole mechanisms, an achievement almost impossible to achieve with experimental techniques only.

The studies described in this work demonstrated that computational techniques can be of enormous value to screen novel catalyst architectures more rapidly, and to obtain insights that could help in the design and experimental synthesis of novel and improved catalysts.