

UNDERSTANDING THE ACTIVE ROLE OF THE OXIDANT IN THE OXIDATIVE COUPLING OF BENZOIC ACID AND ALKYNE

Ignacio Funes-Ardoiz,*¹ Feliu Maseras^{1,2}

1- Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avda. Països Catalans, 16, 43007 Tarragona, Catalonia, Spain

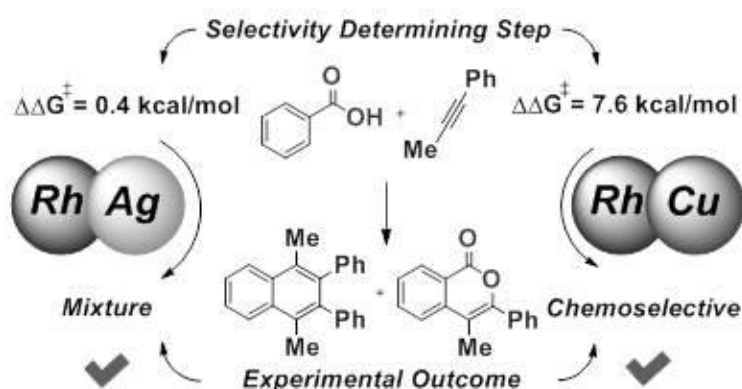
2- Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain

e-mail: ifunes@iciq.es

Oxidative coupling reactions have emerged in the last years as an alternative to the classic cross-coupling reactivity. Although both share similarities, the oxidative version does not require prefunctionalization of the substrate. This fact, in conjunction with the presence of an oxidant to regenerate the catalytic cycle, expands the possibilities of couplings in new synthetic methodologies. However, the mechanistic knowledge of these reactions is still vastly unexplored and it is totally needed to develop new reactions in a rational way.

One of the main questions in oxidative coupling reactivity is the role of the oxidant. For example, in the oxidative coupling of benzoic acid and alkynes reported by Miura and Satoh, they found that the reaction is totally chemoselective when $\text{Cu}(\text{OAc})_2$ is used as the oxidant and the reaction yields mixture when the oxidant is $\text{Ag}(\text{OAc})$.^[1,2]

Herein, we present a comprehensive theoretical study of this reaction, emphasizing the effect of the oxidant along the reaction pathway. We demonstrated that a collaborative model successfully explains the chemoselectivity of the reaction through the cooperative reductive elimination (CRE) pathway.^[3] In addition, we expanded this model to a ruthenium catalyzed oxidative coupling, where kinetic experiments confirms the cooperation in the rate determining step.



References:

- 1) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, 9, 1407
- 2) K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.* **2007**, 72, 5362
- 3) I. Funes-Ardoiz, F. Maseras, *Angew. Chem. Int. Ed.* **2016**, 55, 2764