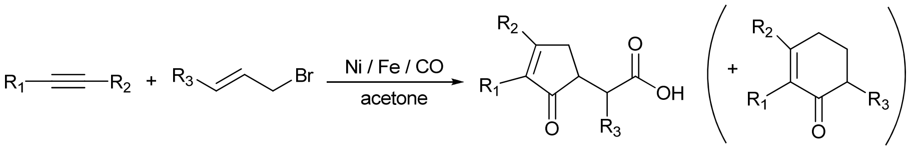
# OUT-STANDING TUNING OF CHEMOSECTIVITY IN CATALYTIC CYCLOCARBONILATIONS PERFORMED IN CO$_2$-EXPANDED SOLVENTS

D. del Moral[2], A. Banet Osuna[1,2], A. Cordoba[1], J.M. Moretó[2], S. Ricart[2],
N. Ventosa[1], J. Veciana[1]

[1] *Dep. Molecular Nanoscience and Organic Materials, ICMAB-CSIC-CIBER-BBN*
*Campus de la UAB, 08193-Barcelona, Spain*
[2] *Homogeneous Catalysis Group, ICMAB-CSIC, Campus de la UAB, 08193-Barcelona, Spain*

Among the most important reactions in organic synthesis are those performing multiple C-C bond formation, in special under catalytic conditions. However, its application has been limited to laboratory scale mainly due to: low yields in organic solvents and difficult product separation.[1] In this context, the catalytic carbonylative cycloaddition of allyl halides and alkynes, mediated by nickel, developed by Moretó et al., can be considered a very efficient reaction, since it creates, at least, three C-C bonds in a single step in order to generate a cyclopentanone derivative.[2] The cyclopentane structure is present in numerous natural products, many of them bioactive. In some cases, the reaction gives cyclohexanones as by-products, but it has not been possible, in the standard conditions, to enhance the chemoselectivity towards this monocarbonilation product. Recently, this procedure has been also applied to strained olefins, resulting always in a mixture of two products corresponding to a single and a double carbonylation.[2]



**Scheme 1.** Catalytic carbonylative cycloaddition of alkynes and allyl halides in conventional solvents.

Here, we report the out-standing improvement of the chemoselectivity of this Ni-catalyzed cyclocarbonilation reaction, when working with CO$_2$-expanded acetone, instead of liquid acetone. Indeed, in CO$_2$-expanded liquids, in contrast with conventional liquid solvents, it is possible to tune the CO content in the solvent media by changing the operational conditions (*P,T,z*), and selectively enhance the direction of the reaction towards the mono or the double carbonylation.

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