

XIV International School of Organometallic Chemistry

Camerino, Italy

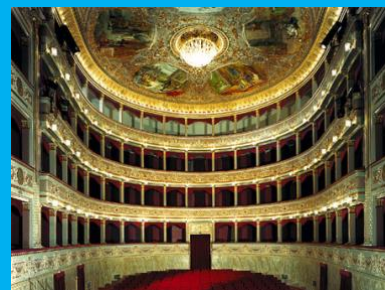
7-11 September 2023

<http://d7.unicam.it/isoc/>



University of Camerino

School of Pharmacy and School of Science and Technology



Organometallic Chemistry beyond the future

Interdivisional Group of Organometallic Chemistry

Poster 30

Formic Acid as Carbon Monoxide Source: A two-steps Synthesis of 2,5-unsubstituted *N*-Arylpyrroles from Nitroarenes and Dienes

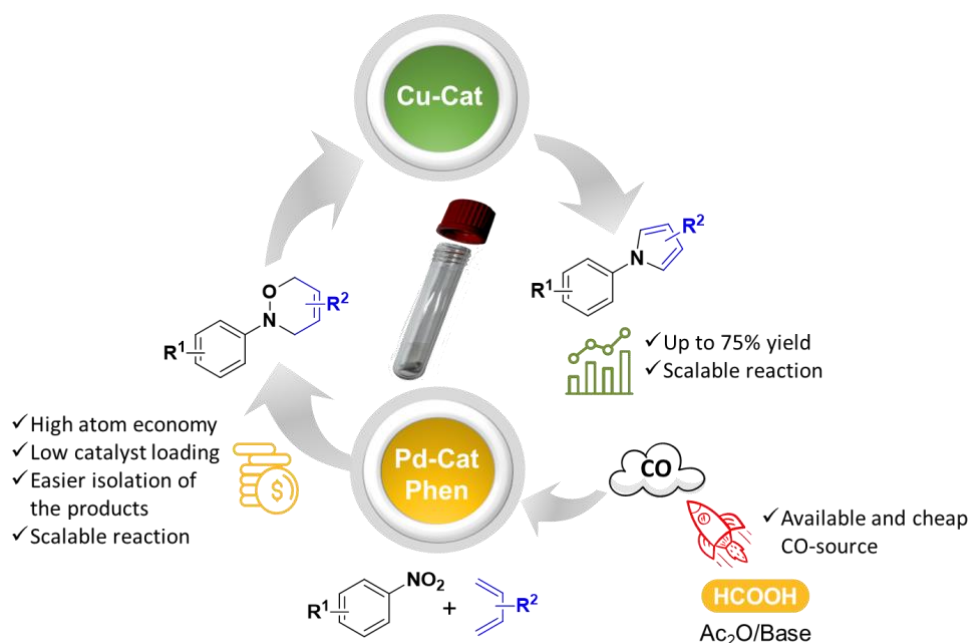
Manar Ahmed Fouad,^{a,b} Simone Galie,^{a*} Francesco Ferretti,^a and Fabio Ragaini^a

^a Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milano, Italy.

^b Chemistry Department, Faculty of Science, Alexandria University, P.O. Box 426, Alexandria 21321, Egypt

simone.galie@unimi.it

Working with pressurized CO requires high-pressure equipment and safety measures, thus the development of alternative methods exploiting the role of the so-called “CO surrogates” is a noteworthy issue in the field of reactions involving carbon monoxide. In this perspective, we recently reported that phenyl formate performs as an excellent CO source in the reductive cyclization of various nitro compounds.^{1,2} An improvement of this strategy has been achieved by employing an equimolar mixture of formic acid, acetic anhydride and a base:³ in this way we are able to prevent the formation of phenol from the decomposition of phenyl formate, which may be annoying in the isolation step. This methodology has been applied in this work for the reduction, by carbon monoxide, of nitroarenes to nitrosoarenes, which are quickly trapped by conjugated dienes in an hetero-Dies-Alder reaction to give 3,6-dihydro-2*H*-[1,2]-oxazines. The initial reduction requires only a low loading of a palladium/phenanthroline complex as a homogeneous catalyst, while the hetero-cyclization takes place “off-metal”. In the second step, oxazines conversion to 2,5-unsubstituted *N*-arylpyrroles is achieved with yields up to 75% employing CuCl as the catalyst.



[1] D. Formenti, F. Ferretti, F. Ragaini, *ChemCatChem* **2018**, *10*, 148.

[2] F. Ragaini, F. Ferretti, M. A. Fouad, *Catalysts*, **2023**, *13*, 224.

[3] M. A. Fouad, F. Ferretti, F. Ragaini, *J. Org. Chem.* **2023**, *88*, 5108.