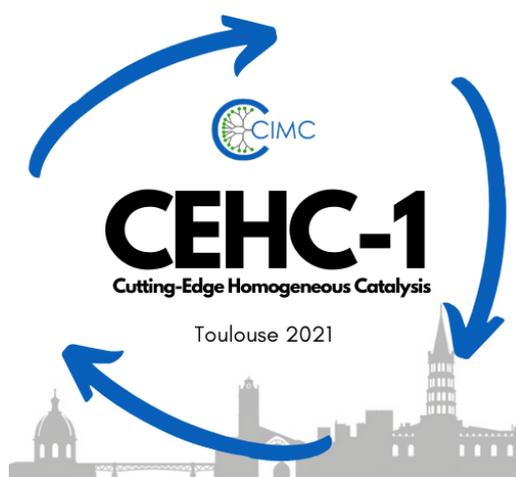




Book of Abstracts

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This workshop will take place in a virtual mode due to COVID-19 restrictions.

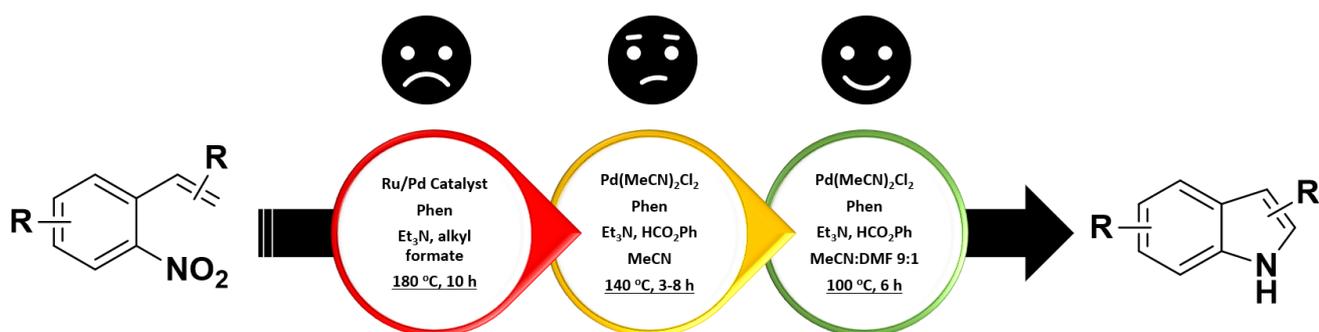
P-9 **Synthesis of Indoles: Use of Formate Esters as CO Surrogates in the Metal Catalyzed Reductive Cyclization of o-Nitrostyrenes (Not Just a Chemistry Soup!)**

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More than three decades ago, Cenini and co-workers reported the first reductive cyclization reaction of o-nitrostyrenes to indoles using carbon monoxide as the reductant, employing different transition metals as catalysts under forcing conditions (220 °C, 80 bar CO).^[1] In spite of the high efficiency and the high atom-economical character of these reactions, they have not become of widespread use. This might be also due to the need to use pressurized CO, requiring safety measures that are not available in most synthetic organic laboratories. Our group presented alkyl and aryl formates as efficient, powerful, low-toxic and cheap *in-situ* CO-releasers, that avoid the direct interaction with pressurized CO and autoclaves, for the metal-catalyzed reductive cyclization reactions of o-nitrostyrenes to indoles. A cheap glass pressure tube can be used as the reaction vessel which turns this kind of reactions into a “General Tool” to the synthetic chemist. Owing to the low cost of alkyl formates, the initial investigation was directed to their use as CO releaser. A bimetallic Ru/Pd-catalytic system was explored in this kind of reactions but satisfying results were achieved only at harsh conditions (180 °C, up to 10 h). On the other hand, when phenyl formate was employed, complete conversions and good selectivities were achieved at a lower temperature (140 °C) and using a Pd/phenantroline complex as the catalyst.^[2] Nevertheless, the temperature is still moderately high, which prompted low selectivity in the cyclization of some substrates. Here we report the results of a further optimization that allowed us to improve both selectivity and yield. Milder reaction temperature and a mixed CH₃CN/DMF solvent system allowed to get improved yield for several substrate including some for which previous conditions failed to afford the indole.



References

- [1] C. Crotti, S. Cenini, B. Rindone, S. Tollari, F. Demartin, *J. Chem. Soc. Chem. Commun.* **1986**, 10, 784.
[2] D. Formenti, F. Ferretti, F. Ragaini, *ChemCatChem* **2018**, 10, 148.