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Reductive cyclization of nitroarenes with CO surrogates for the synthesis of six-membered heterocycles

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Transition-metal catalyzed reductive cyclization of nitroarenes represents an efficient and versatile strategy to afford N-heterocyclic compounds in one step. In this regard, carbon monoxide emerges as an optimal reductant, allowing clean reactions and a simplified work-up, with gaseous carbon dioxide as the sole stoichiometric byproduct. Recently, the use of CO-surrogates, molecules capable to release CO during the reaction, has allowed to release the constraints for autoclaves, pressurized lines and safety measures, generally required to handle gaseous carbon monoxide.[1] Our group has recently reported that phenyl formate acts as an excellent CO-source in the palladium/phenanthroline catalyzed synthesis of indoles,[2] carbazoles[3] and oxazines.[4] A further improvement has been achieved by employing formic acid, in the presence of an equimolar amount of acetic anhydride and a base[5,6] as a more atom economical and cheaper CO-surrogate. Among the various possible heterocycles obtainable by intramolecular reductive cyclization reactions, those leading to six-membered rings had proven to be more challenging. Here we report the synthesis of phenazines, an important scaffold present in several natural and synthetic products with biological activity. Despite harsher conditions are required to carry out the cyclization with respect to the five-membered ones, it was possible to employ a catalytic ratio of 4000, uncommon for these kind of reactions.

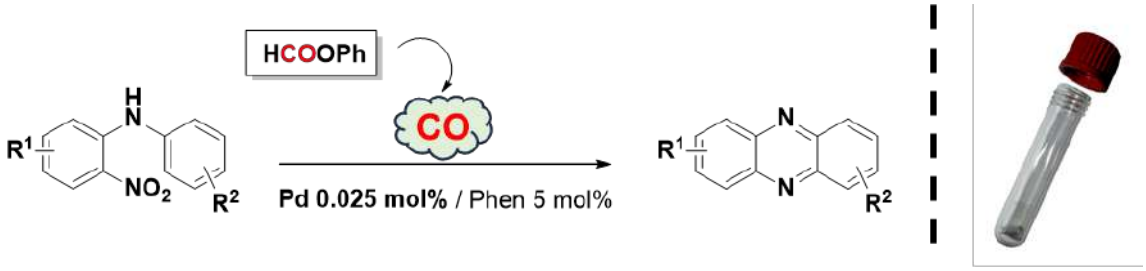

Figure 1: synthesis of phenazine scaffold from o-nitro anilines. Reaction are performed in a thick-walled glass tube

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