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BOOK OF ABSTRACT

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Synthesis of Oxazines by Palladium Catalyzed Reductive Cyclization of Nitroarenes and Dienes Using Phenyl Formate as CO Surrogate

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The synthesis of hetero-Diels-Alder adducts derived from nitrosoarenes as dienophiles (oxazines) has been the focus of much attention in recent years, since these products have pharmacological activity themselves or can be easily transformed into other products.[1] However, their usual synthesis requires problematic intermediate isolation of nitroso compounds. We have previously reported a method for oxazines synthesis in up to 91% yields in one pot by the reaction of unfunctionalized dienes with nitroarenes and carbon monoxide.[2] Despite the high efficiency of this synthetic procedure, it has not become of widespread use by the chemical community. This is mostly because it involves the use of pressurized CO, requiring safety measures that are not available in most synthetic organic laboratories. To overcome this limitation, we started investigating the use of molecules capable of releasing CO in situ, thus avoiding the need for high-pressure equipment and CO lines. Recently, we have reported[3] an efficient, convenient and general synthetic procedure to produce nitrogen heterocycles from nitro compounds in presence of a Pd catalyst employing phenyl formate as the CO releasing agent. In this study, we take advantage of this general procedure in the synthesis of oxazines from dienes and nitroarenes (Figure 1). First, due to its high cost, the amount of the diene was optimized down to 1:4 nitroarene to diene ratio. The reaction works well for nitroarenes bearing either electron-donating or electron-withdrawing substituents, a moderate steric hindrance on the nitroarene is well tolerated and yields up to 99% in one pot were reached. In addition, variation in the diene were also investigated using 2,3-dimethoxy-1,3-butadiene, isoprene and myrcene affording the corresponding oxazines in good yields.

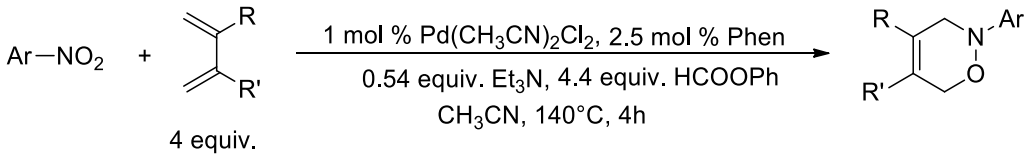

Figure 1. Oxazines synthesis from nitroarenes, dienes and a CO source.

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