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Digest paper

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Recent advances in the field of nucleophilic aromatic substitution of hydrogen

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ABSTRACT

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Recent advances in the field of direct C–H functionalization of aromatics and heteroaromatics through nucleophilic displacement of hydrogen in an aromatic ring are discussed.

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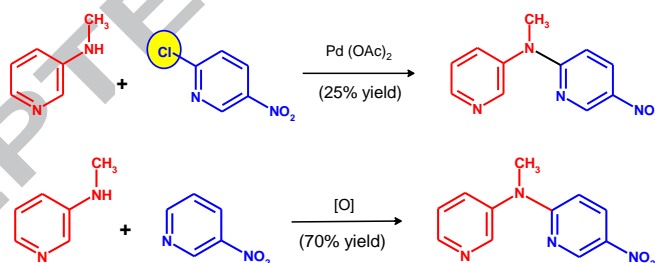
Oxidative and eliminative departure of hydrogen;

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1. Introduction

One of the highlight topics of current organic chemistry is direct C–H functionalization of aromatics without the incorporation of halogen or other functionalities, and thus corresponding to the principles of green chemistry.¹ A large number of methods for structural modification of aromatic and heteroaromatic compounds, including the wide-spread palladium-catalyzed cross-coupling reactions,^{2–4} are based on the use of halogenated starting materials, although at times direct C–H functionalization can give better results. For instance, palladium-catalyzed amination of 2-chloro-5-nitropyridine results in the target amino compound in 25% yield, while the direct metal-free oxidative amination reaction of 3-nitropyridine provides a much better yield of the same compound (Scheme 1).⁵



Scheme 1. Metal-catalyzed cross-coupling and metal free amination of nitropyridines

It is worth noting that the first approach requires incorporation of a chlorine atom into the pyridine ring, only to displace it later, and this certainly does not correspond to the principle of atom economy. On the other hand, it is well known that C–H carbons in electron-deficient aromatics are more vulnerable to nucleophilic attack than those of C–X bonds of compounds bearing a substituent X (Scheme 2).^{6–12} Therefore, the σ^H -adducts, rather than the Meisenheimer complexes are expected to be formed, although appropriate conditions for elimination of hydrogen atom with pair of electrons have to be found (Scheme 2).^{6–14} There are a large number of examples, where substitution of hydrogen proved to occur with retention of a leaving group X, even located in an activated position in nitroarenes or heteroaromatic compounds.^{10–14}

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