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Pd(II) Catalyzed C-H nitration of N-aryl-7- azaindoles

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Aromatic nitro compounds have been recognized as valuable synthetic intermediates for the preparation of pharmaceuticals, dyes, and explosive materials. A common approach for the construction of nitroarenes relies on the electrophilic aromatic substitution by certain nitrating agents. However, this process suffers from some

limitations with respect to poor regioselectivity, functional group tolerance, and harsh reaction conditions using strong acidic systems. To overcome these issues, the transition-metal-catalyzed site-selective nitrations of aryl halides, aryl boronic acids, and other pre-functionalized arenes have been developed. However, these precedented methods also present intrinsic drawbacks, namely, the employment of expensive nitro-sources such as AgNO_2 and AgNO_3 and the additional stoichiometric oxidants such as peroxides, hypervalent iodine oxidants, and toxic metal salts. Therefore,

it is still attractive to develop a more efficient methodology for synthesizing nitroarenes with less expensive nitrating reagents and an environmentally benign oxidant such as molecular oxygen. Azaindole motif is one of the most privileged frameworks found in a large number of pharmaceutical molecules and a drug candidate. we herein report the site-selective Pd(II)-catalyzed C-H nitration of 7-azaindoles with t-butyl nitrite (tBuNO_2) in the presence of molecular oxygen as an ideal oxidant to afford ortho-nitrated azaindoles.

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