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Amine Synthesis via Iron-catalyzed Reduction of Primary Amides and Nitro Derivatives

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PURPOSE OF THE ABSTRACT

Amines, especially primary amines, are one of the most important motifs in a large number of natural products and biologically active molecules.[1] In the past two decades, huge efforts have been devoted to the development of catalytic methodologies for the synthesis of amines, including the reduction of nitro and amide derivatives via noble metal catalytic systems.[2]

Iron, one of the most abundant and inexpensive metals, has been impressively used as an interesting alternative transition metal in homogeneous catalyzed transformations, more particularly in reduction area.[3] More significantly, several well-defined N-heterocyclic carbene iron complexes have been designed by our group for the efficient reduction of carbonyl and carboxylic derivatives such as the hydrosilylation of esters to aldehydes and the preparation of cyclic amines via reductive amination under hydrosilylation conditions.[4]

In this contribution, the reduction of nitroarenes leading to aniline derivatives is presented under iron-catalyzed system with phenylsilane as reductant. Furthermore, a cascade convenient approach to construct N-substituted cyclic amines starting from nitroarenes and keto-acids has been developed through catalyzed hydrosilylation reactions.[5]

On another hand, tandem iron/zinc or iron/indium-catalyzed reductions of various primary amides to amines under hydrosilylation conditions is also presented. The nature of the co-catalyst (Zn(OTf)2 vs In(OTf)3) played a crucial role for the selective formation of primary amines or symmetrical secondary amines.[6]

FIGURES

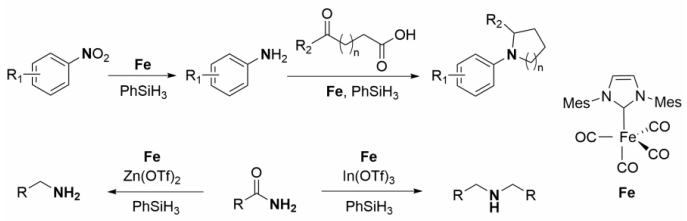

FIGURE 1

Iron-catalyzed Reduction of nitro and primary amide derivatives

The reduction of nitroarenes is presented under iron-catalyzed hydrosilylation conditions. Tandem iron/zinc or iron/indium-catalyzed reductions of primary amides to primary or secondary amines is also presented.

FIGURE 2

KEYWORDS

Iron | Hydrosilylation | Nitroarenes | Primary Amides

BIBLIOGRAPHY