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Original article

Direct synthesis of nitriles by Cu/DMEDA/TEMPO-catalyzed aerobic oxidation of primary amines with air

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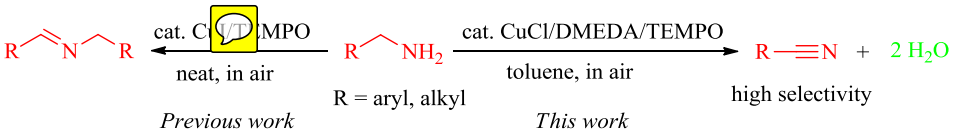
Graphical abstract



A simple and readily available CuCl/DMEDA/TEMPO system-catalyzed aerobic oxidation of primary amines using air as an advantageous oxidant is developed for direct and selective synthesis of the useful nitriles under mild conditions.

ABSTRACT
By screening the copper catalysts, ligands, and the reaction conditions, a simple CuCl/DMEDA/TEMPO catalyst system readily available from commercial sources is developed for a direct and selective synthesis of the useful nitriles by an aerobic oxidation reaction of primary amines using air as an advantageous oxidant under mild conditions.

Keywords: Aerobic oxidation Air Amines Copper catalysis Nitriles

1. Introduction

The nitrile moiety is a significant and abundant building block in dyes and various biologically-, pharmaceutically-, and agrichemically-active compounds as well as in many fine chemicals [1-3]. Nitriles are also important precursors in the synthesis of amides and amide derivatives, carboxylic acid derivatives, as well as numerous heterocycle compounds through multi-component reactions [4-8]. Therefore, nitirle synthesis has been a long term interest among the synthetic chemists and many methods have been reported in the literature. Traditionally, nitriles can be obtained by Sandmeyer reaction of diazonium salt derived from aryl amines [9,10], by Rosenmund–von Braun reaction of aryl halides [11], and by ammoxidation of toluenes [12]. However, the requirement of harsh reaction conditions such as high temperatures (up to 550 °C), the use of highly toxic cyanide salts, and the production of large amounts of wastes greatly limited the potentials of these methods in functional group tolerance and wider applications in synthesis. More recently, dehydration of amides or aldoximes at high temperatures [13,14], transition metal (TM)-catalyzed cross-coupling reactions of CN sources with aryl halides, *pseudo*halides or other aryl sources [15,16], TM-catalyzed anaerobic dehydrogenative or aerobic oxidative coupling of alcohols with ammonia [17], dehydrogenation or oxidation of amines [18-33], as well as other methods