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Oxidation/ MCR domino protocol for direct transformation of methyl benzene, alcohol, and nitro compounds to the corresponding tetrazole using a three-functional redox catalytic system bearing TEMPO/Co (III)-porphyrin/ Ni(II) complex

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ABSTRACT

A redox catalytic system for oxidation-reduction reactions and the domino preparation of tetrazole compounds from nitro and alcohol precursors was designed, prepared and characterized by UV–vis, GPC, TGA, XRD, EDX, XPS, VSM, FE-SEM, TEM, DLS, BET, NMR, and ICP analyses. The catalyst was prepared *via* several successive steps by demetalation of chlorophyll *b*, copolymerization with acrylated TEMPO monomers, complexation with Ni and Co metals (In two different steps), then immobilized on magnetic nanoparticles. The presence of three functional groups including TEMPO, coordinated cobalt, and coordinated nickel in the catalyst, allowed the oxidation of various types of alcohols, alkyl benzenes as well as the reduction of nitro compounds by a single catalyst. All reactions yielded up to 97 % selectivity for oxidation and reduction reactions. Next, the ability of the catalyst to successfully convert alcohol, methyl benzenes and nitro to their corresponding tetrazoles was studied.

Introduction

Oxidation/ reduction reactions have a special place and are widely used in organic chemistry [1,2]. The products of oxidation and reduction reactions are useful and practical precursors in the synthesis of organic compounds, especially multicomponent reactions (MCRs) [3]; one of these reactions is the preparation of tetrazol derivatives.

Aromatic amines are one of the most important and practical raw materials and intermediates in organic synthesis, because they are widely used in the preparation of chemicals required in pharmaceuticals, dyes, agriculture, biological compounds, rubber, photography, synthetic resins, and other industries [4–6]. In addition, in organic synthesis, amines are widely used in the preparation of azo compounds, isocyanates, amides, imines, and diazonium salts [7,8]. Reduction of nitro compounds, as one of the most effective and available precursors, is one of the most common and popular method for the preparation of amines [4]. A variety of catalytic systems, along with various reducing agents, have been reported for reduction of nitro to amine (recent reports): (1) Ni_2BH_2 [1], (2) Ag-rGO/g-C_3N_4/ visible light [9], (3) Fe/TRGO [4], (4) Fe_3O_4-MWCNTs@PEI-Ag [5], (5) Zn powder/ $CuSO_4$ [6], and (6) $CuFe_2O_4$/ $NaBH_4$ [10]. Recently, Gholinejad et al., in an interesting paper used human hair in the presence of $NaBH_4$ for selective reduction of nitro to amine [7]. Very recently, Nasrollahzadeh and his co-workers reviewed the recent methodologies in graphene-based photocatalysts for the nitro reduction [8].

On the other hand, carbonyl compounds are among the most widely used compounds in organic synthesis, preparation of pharmaceutical, agriculture compounds, *etc.*, and its direct preparation through oxidation of alcohols, is the simplest and most cost-effective method [2,11].

The 5-substituted 1*H*-tetrazoles and 1-substituted-1*H*-1,2,3,4-tetrazoles are two main groups of tetrazols, and cyclization between a susceptible compound such as amine or nitrile in the presence of azide ion is the most common method of the preparation of these compounds [4, 12–14]. Mittal and Awasthi studied recent advances in the preparation of 5-substituted 1*H*-teratazoles in a review paper [3]. Tetrazols have a special place in medicine and pharmacy and have properties such as antibacterial, antifungal, antibiotic, anti-HIV, antihypertensive, anticonvulsant agents, anti-inflammatory, *etc.* [15–17]. Sartans are a large

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