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ARTICLE

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# MAGNETICALLY RETRIEVABLE CU CONTAINING NANOPARTICLES FOR MULTICOMPONENT ORGANIC SYNTHESIS

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*The applications of Cu containing magnetically retrievable nanocatalysts to synthesize imperative organic compounds via multicomponent reactions have experienced rapid expansion in recent years. Multicomponent reactions (MCRs) are of high atom economy reactions with low cost, effort and time requirements. Again, magnetic separation of the nanocatalyst offers a method for recycling and reusing the catalyst.This review aims to showcase the advancements made in utilizing Cu containing magnetic nanopartricles to catalyze MCRs for synthesizing diverse organic compounds.*

## Introduction

Organic Synthesis using nanocatalysts have now become an important area of interest among the researchers. Nanocatalysts imitate both the homogeneous (maximum accessible active sites, high activity and selectivity) and the heterogeneous (stable, easy to handle) catalysis systems[1]. But, the major difficulty is the isolation and recovery of the catalyst from the reaction mixture after completion of the reaction. Due to small particle size the nanocatalysts cannot be separated by conventional filtration methods[2]. To conquer this issue the use of magnetically retrievable nanocatalysts has emerged as an effective solution, the insoluble and paramagnetic nature enables easy separation of the catalyst from the reaction mixture by means of an external bar magnet[3]. Among different metal based nanocatalysts, Cu containing magnetically separable nanocatalysts have achieved much attention due to its high abundance, low cost, low toxicity, high malleability, ease of synthesis and easier isolation and recovery. Magnetically retrievable copper nanoparticles (CuNPs) have enormous applications in synthetic organic chemistry for C-C and C-hetero atom bond formation[4]. Among them multicomponent reactions (MCRs) catalyzed by CuNPs have developed in recent time. Multicomponent reactions (MCRs) are those in which more than two molecules combine in a sequential and simultaneous manner to produce highly selective products and ensure the maximum conversion of the reacting substances into the final products[5]. MCRs have arisen as a commanding tool in synthetic organic chemistry for its straight-forward reaction scheme, convergent and high atom economy nature, resulting in substantial decrease of waste or byproducts, time and cost. These advantages of MCRs with easily available cost effective Cu containing nanoparticles allow to develop a wide range of Cu containing magnetically retrievable nanocatalysts for synthesizing enormous organic compounds.

## Multicomponent Reactions Catalyzed by Magnetically Retrievable Copper Nanocatalysts

***Synthesis of Propargylamines:*** Propargylamines are interesting and useful synthons for synthesizing divergent therapeutic drugs and polyfunctional heterocyclic compounds[4, 6]. Zhang *et al.*[7] developed a method for the synthesis of propargylamines by using reusable $Fe_3O_4$@$CuSiO_3$ nanocomposite under solvent-free conditions via decarboxylative $A^3$-coupling of $\alpha$-keto acids, amines and alkynes in good to excellent yields (Scheme 1).

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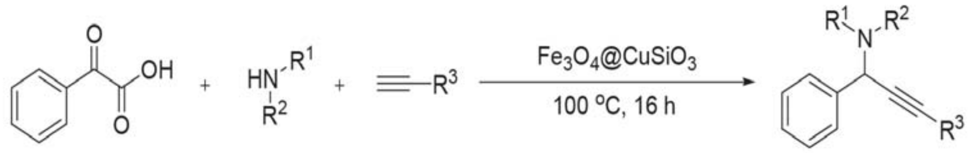
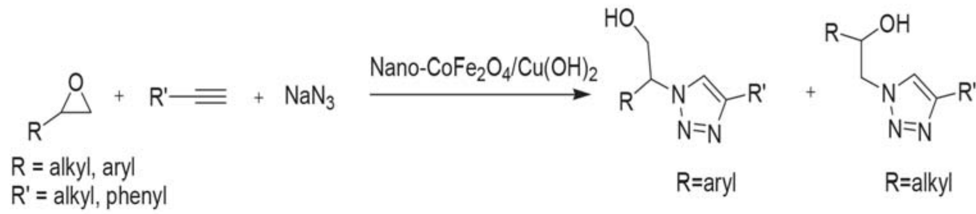
***Synthesis of 1,2,3-triazoles:*** 1,2,3-triazoles are significant intermediates for the synthesis of dyes, agrochemicals, drugs etc. Karimi *et al.*[8] used magnetically separable $CoFe_2O_4/Cu(OH)_2$ nanocomposite for the regioselective synthesis of $\beta$-hydroxy-1,4-disubstituted-1,2,3-triazoles *via* a three component coupling of sodium azide, terminal alkynes and structurally different epoxides in water at 60 $^0$C (Scheme 2).

***Synthesis of imidazoles:*** Imidazoles are the well - recognized heterocyclic entity having biological activities such as antitubercular, antifungal, antibacterial, anticancer, anti-depressant and antileishmanial activity[9]. A magnetically separable copper loaded L-DOPA functionalized magnetite nanoparticles ($Fe_3O_4$-DOPA-CuNPs) was synthesized and employed as a catalyst for synthesizing imidazole derivatives with excellent yields by a group of researchers (Scheme 3)[10].

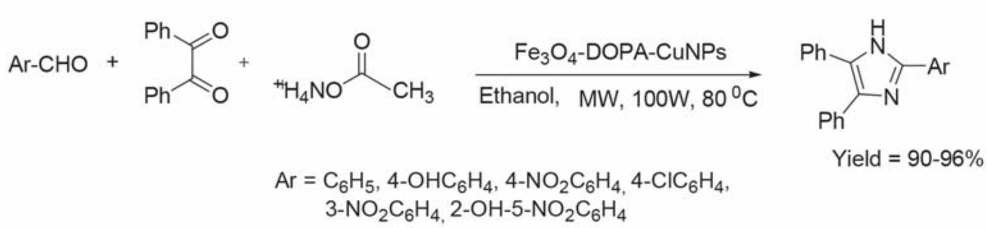
***Synthesis of 1,4-dihydropyridines:*** 1,4-dihydropyridines possesses significant pharmacological and biological activities. Viswanath *et al.*[11] developed a protocol to synthesize 1,4-dihydropyridines *via* a one pot reaction of substituted aldehydes, ethylacetoacetate and ammonium acetate. The reaction was catalyzed by



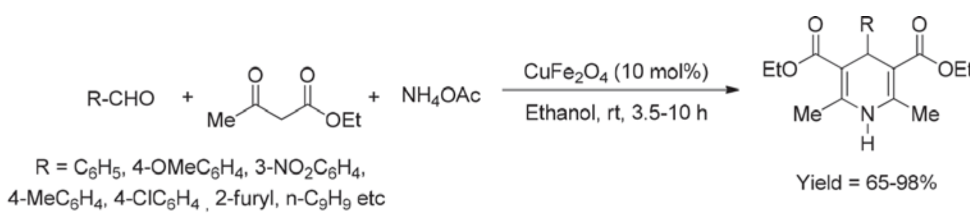

**Scheme 1:** $Fe_3O_4$@$CuSiO_3$ catalyzed synthesis of propargylamines



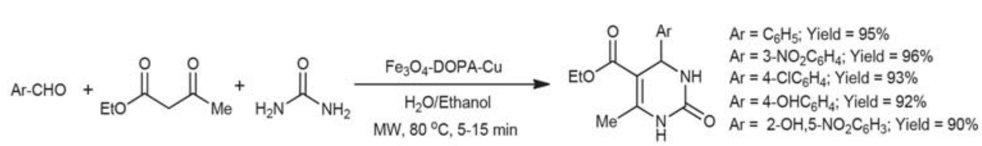

**Scheme 2:** $CoFe_2O_4$/Cu(OH) catalyzed synthesis of triazoles



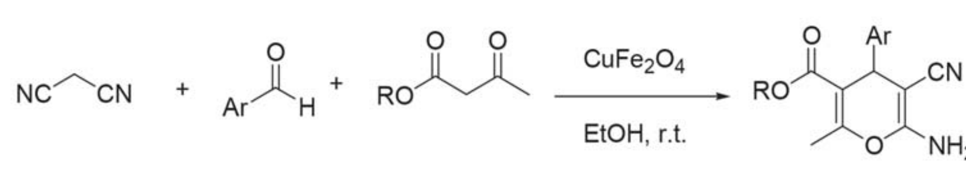

**Scheme 3:** $Fe_3O_4$-DOPA-CuNPs catalyzed synthesis of imidazoles




**Scheme 4:** $CuFe_2O_4$ catalyzed synthesis of 1,4-dihydropyridines




**Scheme 5:** $Fe_3O_4$-DOPA-Cu catalyzedsynthesis of 3,4-dihydropyrimidinones




**Scheme 6:** $CuFe_2O_4$ catalyzed synthesis of 2-amino-3-cyano-4H-pyran

reusable copper ferrite nano powder at room temperature in ethanol medium (Scheme 4).

***Synthesis of 3,4-dihydropyrimidinones:*** 3, 4-dihydropyrimidinone are important heterocyclic nucleus with significant biological properties[12]. Kumari *et al.*[10] developed an effective protocol for the synthesis of dihydropyrimidinone derivatives by using $Fe_3O_4$-DOPA-CuNP as a catalyst under microwave irradiation *via* three component reaction of aldehydes, ethyl acetoacetate and urea (Biginelli reaction) at 80ºC with excellent yields in just 12-18 min reaction times (Scheme 5).

***Synthesis of 4H-pyrans:*** 4H-pyrans have enormous applications in pharmaceutical chemistry[13]. Maleki and coworkers[14] developed an eco friendly synthesis of 4H-pyrans *via* one-pot three-component reactions of aldehyde, malononitrile, and methyl/ethyl acetoacetate in presence of $CuFe_2O_4$ magnetic nanocatalyst under mild reaction conditions in good to excellent yields (Scheme 6).

## Outlook

In this review article, an effort has been made to outline the recent developments towards the utilization of magnetically retrievable Cu containing nanocatalysts in synthesizing a wide variety of organic molecules through one pot multicomponent reactions. The synthetic methodologies using Cu containing magnetically separable nanocatalysts have achieved much attention in the fields of industrial chemistry and pharmaceutical chemistry due to the easy recovery of the catalyst by means of a bar magnet. Again, Cu is an excellent alternative to the novel metals i.e. Au and Ag. Therefore this article will surely contribute to future advancements in Cu containing magnetically separable nanoparticles catalysed multicomponent reactions to synthesize important organic compounds.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