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Two different facile and efficient approaches for the synthesis of various *N*-arylacetamides via *N*-acetylation of arylamines and straightforward one-pot reductive acetylation of nitroarenes promoted by recyclable $CuFe_2O_4$ nanoparticles in water

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Abstract: Two simple, efficient, and environmentally benign protocols for the synthesis of various *N*-arylacetamides via *N*-acetylation of arylamines and straightforward one-pot reductive acetylation of aromatic nitro compounds promoted by $CuFe_2O_4$ nanoparticles in water at reflux have been developed. The prepared $CuFe_2O_4$ MNPs are well known and fully characterized by various techniques. Furthermore, the $CuFe_2O_4$ NPs easily separated from the reaction environment using an external magnetic field and can be reused for several times without significant loss of its activity for both mentioned reactions.

Keywords: *N*-arylacetamide; *N*-acetylation of arylamine; reductive acetylation of nitroarene; $CuFe_2O_4$; green chemistry

1 Introduction

Performing organic reactions into the green solvents especially water is very favorable for academic researchers and industrial chemical companies due to its many desirable features such as low-cost, non-toxicity, safety, abundantly and also environmentally friendless compared with organic solvents [1-10].

In recent years, construction of amide linkages is one of the valuable reactions in organic synthesis because of their extensive applications in various area such as peptide synthesis, agrochemicals, polymers, functional materials, dyes, fragrances and also existence in pharmaceuticals (Figure 1) and natural products (Figure 2) [11-25]. Due to the importance of amide compounds, developing simple, practical, environmentally benign, cost- and time-effective manners for their synthesis is very valuable and necessary. Undoubtedly, acetylation of arylamines is a very simple approach for the preparation of amides which is widely used in chemistry labs and chemical industry [26]. Therefore, the development of this mentioned method is justifiable. It is worthwhile to note that aromatic nitro compounds are much cheaper than arylamines in terms of price and one of the most important substrates for the preparation of arylamines via reduction process. So, designing new protocols for the synthesis of amides via straightforward one-pot reductive acetylation of aromatic nitro compounds without isolation of the arylamine intermediates is very interesting. In this regard, it should be noted that one-pot multicomponent reactions (MCRs) are remarkable instruments for versatile preparation of a wide diversity of organic compounds especially biologic active molecules which have advantages such as high atom economy, escape of time-consuming protection-deprotection steps, and environmentally friendliness, making them absolutely better than classical multistep synthetic pathways [27-37].

Notably, in recent years, spinel ferrite nanoparticles with the general formula MFe_2O_4, where M(II) is a d-block transition metal (such as Mn, Co, Ni, Cu, Zn) have been in the vanguard of nanoscience and nanotechnology due to their unique specifications like nanometer size, high saturation magnetization, large surface area to volume ratio, high electric resistivity, low eddy current loss, very good optical properties in the visible region and also their extensive applications in sensors, memory storage devices, magnetically controlled drug delivery,

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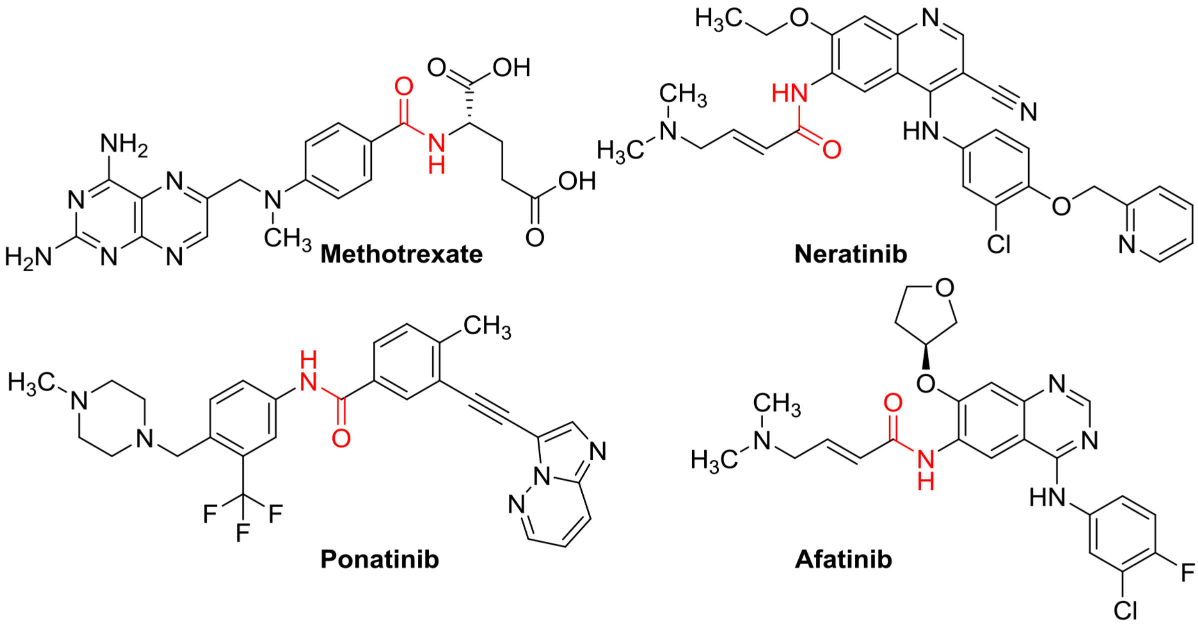


Figure 1: Representative examples of amide-containing drugs.

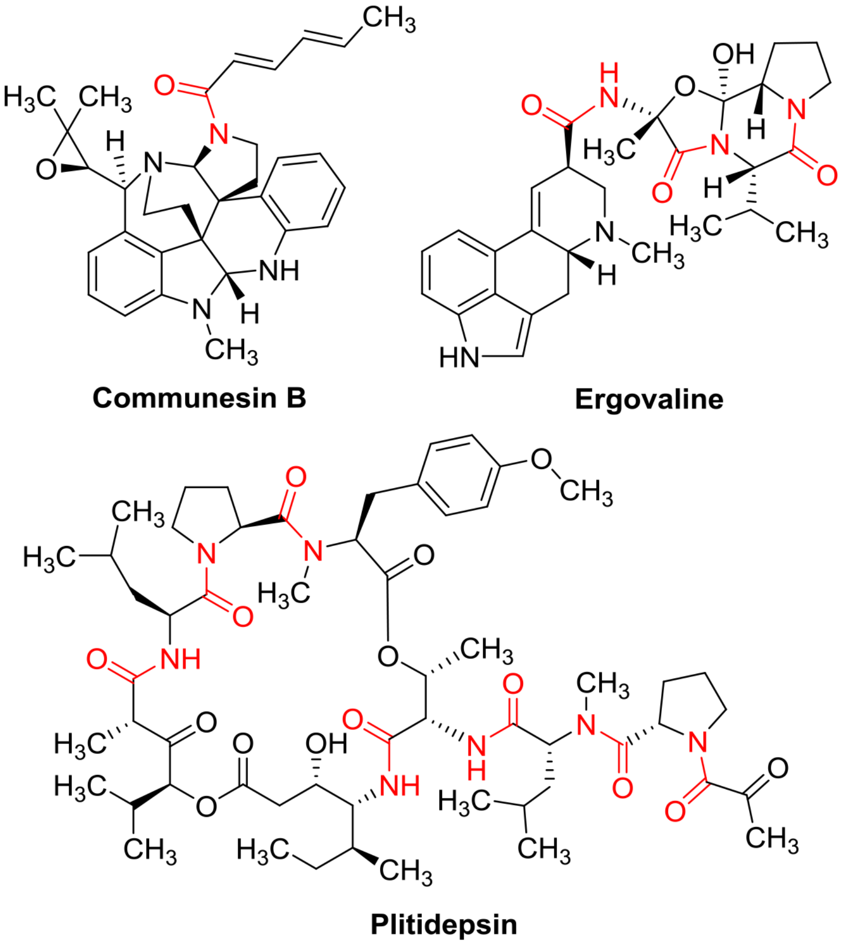
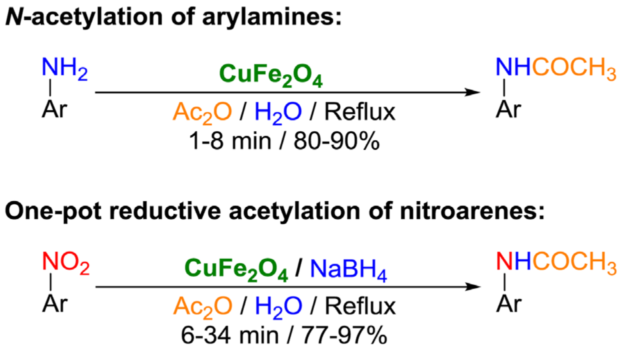


Figure 2: Examples of amide-containing natural products.

hyperthermia in the treatment of cancer diseases, medical diagnostics, magnetic resonance image (MRI) enhancement, telecommunication, pigments, and catalysis [38-45]. Furthermore, compared with iron oxides, spinel ferrites provide flexibility to control both crystal structures and magnetic properties by choosing different non-iron metals in spinel ferrite backbone and controlling their molar concentrations. Among various type of spinel ferrite magnetic nanoparticles (MNPs), $CuFe_2O_4$ nanocomposite, in addition to numerous applications, has shown satisfactory performance as the recyclable catalyst in various organic transformations such as synthesis of heterocyclic compounds [46-52], Ullmann C-O coupling reaction [53], direct synthesis of chemical structures containing both phenol ester and benzothiazole moieties via dehydrogenative coupling reactions [54], reduction of *p*-nitrophenol [55], one-pot odorless carbon-sulfur bond formation reactions [56], directed phenol/formamide coupling [57], synthesis of diaryl/aryl alkyl sulfides via cross-coupling process [58], S-arylation of thioureas by aryl halides [59], one-pot four-component Dakin-West reaction (synthesis of *β*-acetamido ketones) [60], Friedel-Crafts acylation [61], *N*-arylation of heterocycles [62], direct C-H amination of benzothiazoles [63], oxidative hydroxylation of arylboronic acids [64], palm oil methanolysis [65], oxidation of benzyl alcohol [66], synthesis of unnatural arundines [67], *N*-arylation of indole and imidazole with aryl halide [68], and so on.

In continuation of our research programs on various type of organic reactions [67-71], especially on the simple methodologies for the preparation of *N*-arylacetamides [72-75], we wish to report two different facile and efficient approaches for the synthesis of divers *N*-arylacetamides via *N*-acetylation of arylamines and straightforward one-pot reductive acetylation of nitroarenes promoted by recyclable $CuFe_2O_4$ MNPs in water at reflux (Scheme 1).



Scheme 1: Two different facile and efficient approaches for the synthesis of various *N*-arylacetamides promoted by $CuFe_2O_4$ MNPs.

2 Results and discussion

2.1 Preparation and characterization of the $CuFe_2O_4$ magnetically nanocomposite

First of all, $CuFe_2O_4$ magnetically nanoparticles (MNPs) prepared through the simple procedure which was reported by Jia and co-workers [76]. Notably, the obtained $CuFe_2O_4$ nanocomposite fully characterized by various techniques including Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectroscopy, inductively coupled plasma-optical emission spectrometry (ICP-OES), vibrating sample magnetometer (VSM) and also BET-BJH analyses.

In the FT-IR spectrum of the prepared $CuFe_2O_4$ (Figure 3), the absorption band at 586.8 cm^{-1} is ascribed to the stretching vibration frequency of octahedral site, and the absorption band at 405.8 cm^{-1} is related to the tetrahedral site.

As can be seen from Figure 4, the XRD pattern of the mentioned $CuFe_2O_4$ nanocomposite reveals that all the peaks matched with the standard XRD pattern of $CuFe_2O_4$ (JCPDS card no. 34-0425). Furthermore, the sharp peaks which existed in the XRD pattern of the synthesized copper ferrite MNPs prove the crystalline nature of the mentioned nanocomposite.

According to the SEM (Figure 5) and TEM (Figure 6) images, the particles of the synthesized $CuFe_2O_4$ nanocomposite are in the nanometric range along with irregular morphology.

The EDX spectrum of the $CuFe_2O_4$ shows that Cu, Fe, and O are present in the structure of the prepared nanocomposite (Figure 7). Also, the ICP-OES analysis showed that the amounts of Cu, Fe, and O in the $CuFe_2O_4$ nanocomposite were 22.52%, 46.71%, and 30.77%, respectively.

The obtained saturation magnetization value ($Ms = 38\ emu \cdot g^{-1}$) and the shape of the illustrated pattern show that the prepared nanocatalyst has a ferromagnetic characteristic for a convenient magnetic separation (Figure 8).

The nitrogen adsorption-desorption isotherm of the $CuFe_2O_4$ NPs was measured (Figure 9). As shown in Figure 9, the prepared nanocomposite exhibited type III isotherm, indicating micro-pore nature of the $CuFe_2O_4$. Also, according to the BET equation, the specific surface area (SSA) and pore volume value (PVV) of the mentioned nanocomposite calculated ($SSA = 5.46\ m^2 \cdot g^{-1}$ and $PVV = 0.0077\ cm^3 \cdot g^{-1}$).

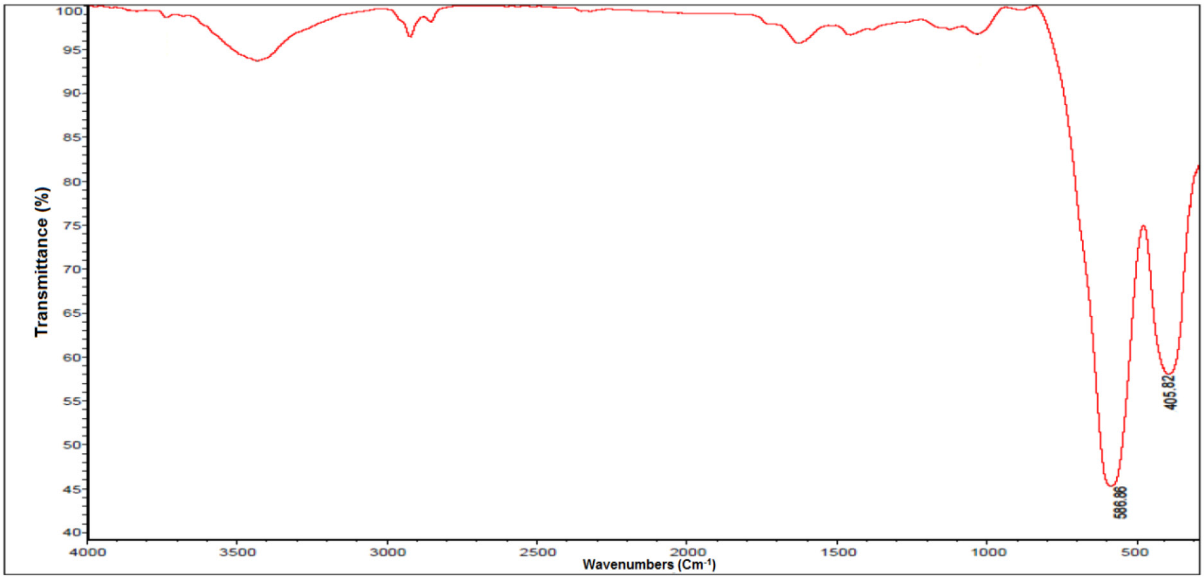


Figure 3: FT-IR spectrum of the $CuFe_2O_4$ MNPs.

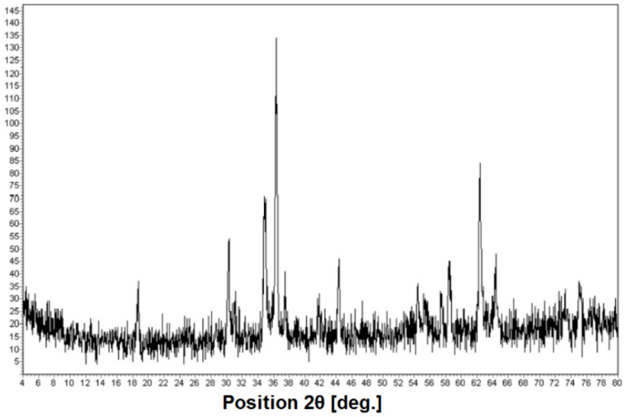


Figure 4: XRD spectrum of the $CuFe_2O_4$ MNPs.

Besides, the distribution of pore size is 1.88 nm based on the Barrett-Joyner-Halenda (BJH) analysis.

2.2 *N*-acetylation of arylamimes promoted by $CuFe_2O_4$ MNPs

Indisputable, amine acetylation is one of the most extensively used reactions in organic chemistry and is often used in the preparation of amide compounds and also protection of –NH functional group. *N*-acetylation of amine is generally accomplished using acetic anhydride or acetyl chloride as acetyl donors in the presence of an acidic or basic catalyst in the organic medium. Up to now,

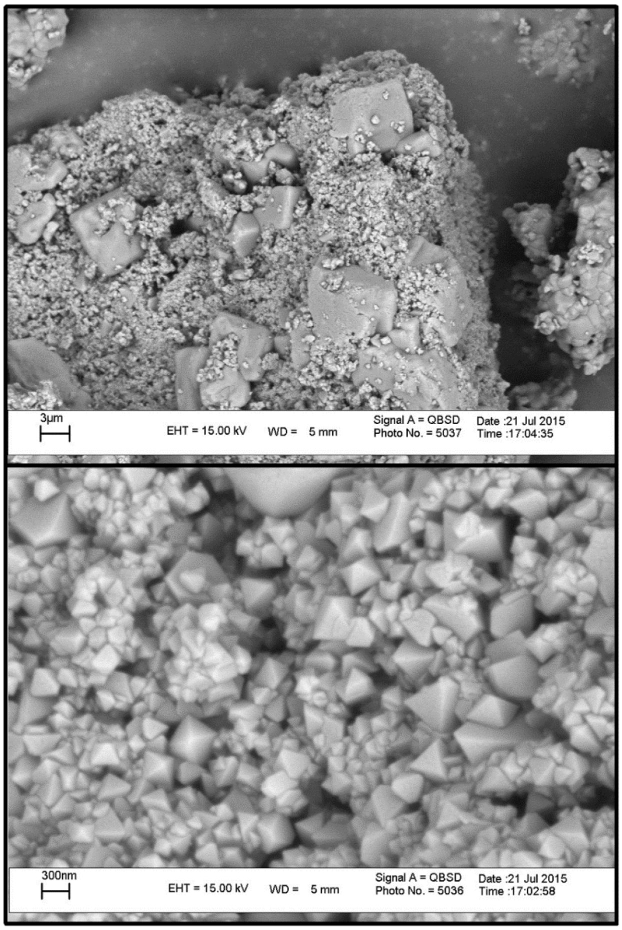


Figure 5: SEM images of the $CuFe_2O_4$ MNPs.

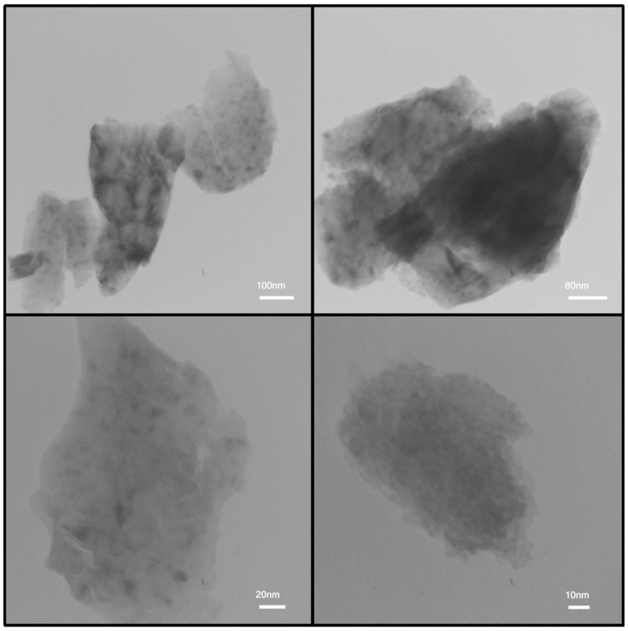


Figure 6: TEM images of the $CuFe_2O_4$ MNPs.

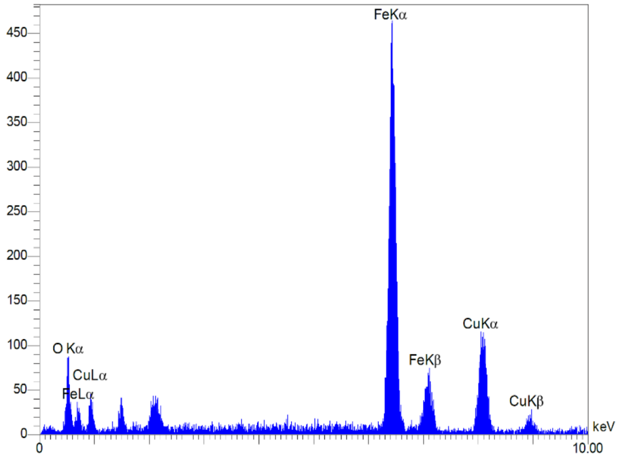


Figure 7: EDX spectrum of the $CuFe_2O_4$ MNPs.

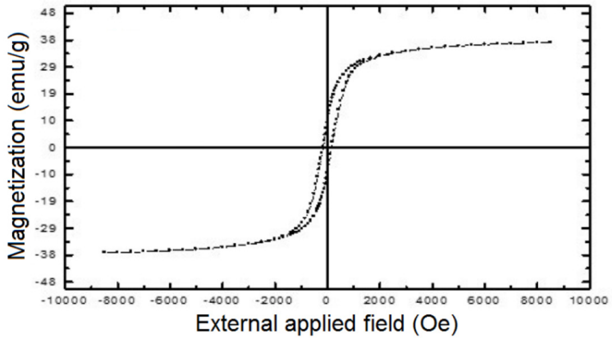


Figure 8: VSM spectrum of the $CuFe_2O_4$ MNPs.

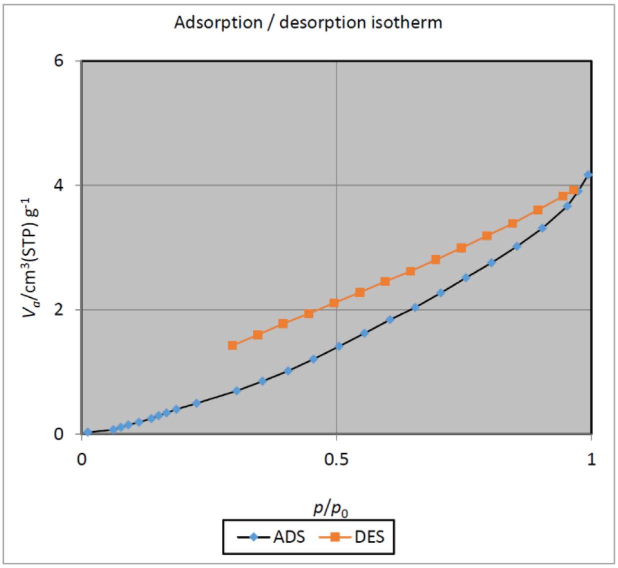
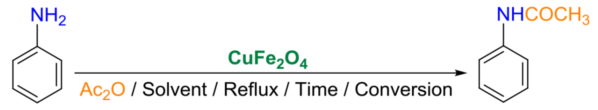


Figure 9: N_2 adsorption-desorption isotherm for the $CuFe_2O_4$ MNPs.

several methods have been reported for the mentioned reaction. Nevertheless, some of these methods along with some merits have one or more drawbacks such as the use of expensive and harmful reagents, solvents or catalysts, harsh reaction conditions, low yield of products and (or) lengthy reaction times and so on [77-96]. In this regard, we decided to introduce a simple, efficient, green, cost- and time-effective protocol for the *N*-acetylation of arylamines.

At the outset of experimental work, the reaction of aniline with acetic anhydride (Ac_2O) as an acetylating agent was chosen as a model reaction to confirm the feasibility of our strategy and optimize the reaction conditions (Table 1). At first, we evaluated the effect of various solvents such as MeOH, EtOH, THF, CH_3CN, and EtOAc, on the model reaction utilizing a different molar ratio of $CuFe_2O_4$ MNPs. As shown in entry 9 of Table 1, the best condition for this mentioned reaction was the use of 1 mmol Ac_2O and also 0.3 mmol of $CuFe_2O_4$ MNPs in water at reflux. Furthermore, to examine the reaction scope, various arylamines possessing electron-withdrawing (EWD) and electron-donating groups (EDG) were reacted with Ac_2O under the optimized reaction conditions to give the corresponding *N*-arylacetamides. Based on the data shown in Table 2, all the desired products were prepared in good to excellent yields. It is worth noting the chemoselectivity observed for the arylamines containing benzylic alcohol group (Table 2, entry 13 and 14).

Table 1: Optimization experiments for the *N*-acetylation of aniline to acetanilide.



Entry	$CuFe_2O_4$ (mmol)	Ac_2O (mmol)	Solvent	Time	Conv. (%)
1	1	3	MeOH	2 h	N.R.
2	1	3	EtOH	2 h	N.R.
3	1	3	THF	2 h	N.R.
4	1	3	CH_3CN	2 h	N.R.
5	1	-	EtOAc	2 h	N.R.
6	1	3	EtOAc	2 h	40
7	1	1	H_2O	1 min	100
8	0.5	1	H_2O	1 min	100
9	0.3	1	H_2O	1 min	100
10	0.2	1	H_2O	2 min	100

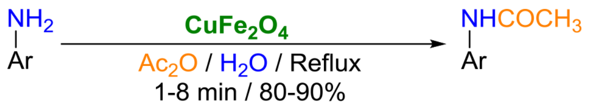
N.R. = No reaction (Conv. = 0)

2.3 One-pot reductive acetylation of aromatic nitro compounds promoted by $CuFe_2O_4$ MNPs

In order to optimize reaction conditions, the transformation of nitrobenzene ($PhNO_2$) as a model compound to acetanilide was studied through a primary reduction of $PhNO_2$ with sodium borohydride ($NaBH_4$) using $CuFe_2O_4$ as recyclable promoter followed by acetylation with Ac_2O in a one-pot procedure without isolation of aniline intermediate under different reaction conditions. The reductive acetylation of $PhNO_2$ under mentioned system in protic and aprotic solvents such as MeOH, EtOH, THF, CH_3CN, and EtOAc (Table 3, entries 1-5) and also under solvent-free condition (Table 3, entry 6) did not take place any more. Interestingly, further investigations demonstrated that H_2O was the best solvent of choice (Table 3, entries 7-11) and using a molar equivalent of 1:1:2:1 for $PhNO_2$, $CuFe_2O_4$, $NaBH_4$ and also Ac_2O, respectively, was an optimum for the complete mentioned one-pot reaction (Table 3, entry 7). More examinations also exhibited that completion of the model reaction with other amounts of the $CuFe_2O_4$ (0.7, 0.5, 0.3, and 0.2 mmol) was also accessible (Table 3, entries 8, 9, 10, and 11). However, prolonging the reaction time impeded using them as the optimum amount.

Having established the optimal reaction conditions, we investigated the substrate scope of this one-pot transformation using various aromatic nitro compounds. The obtained results are summarized in Table 4. As seen, all

Table 2: *N*-acetylation of arylamines using Ac_2O promoted by $CuFe_2O_4$ MNPs in water.



$$ArNH_2 \xrightarrow[\text{1-8 min / 80-90\%}]{CuFe_2O_4 \; / \; Ac_2O / H_2O / \text{Reflux}} ArNHCOCH_3$$

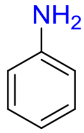
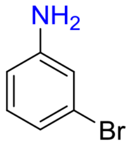
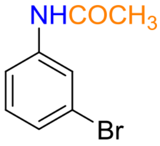
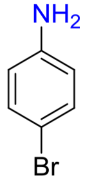
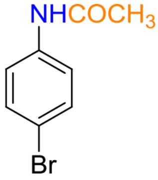
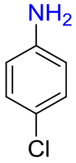
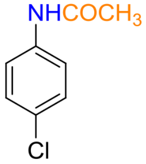
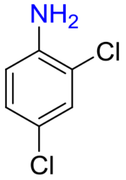
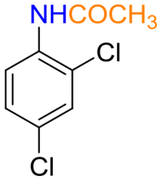
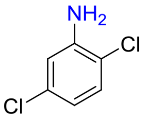
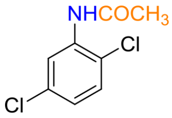
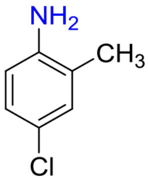
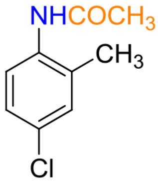
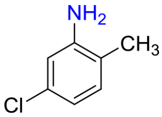
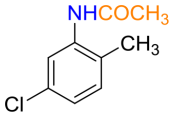
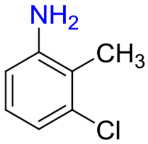
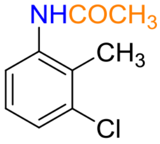
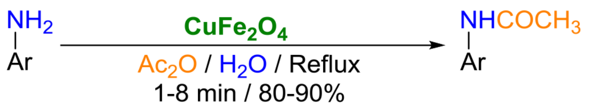
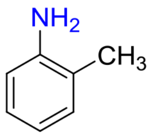
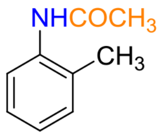
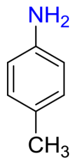
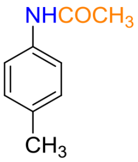
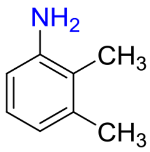
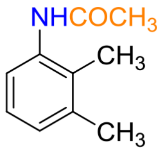
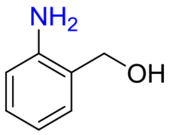
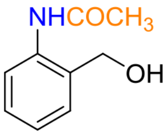
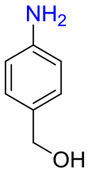
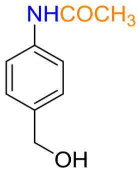
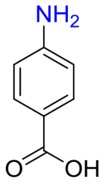
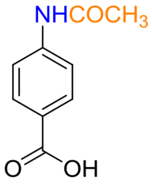
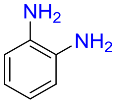
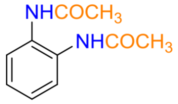
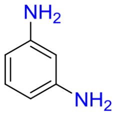
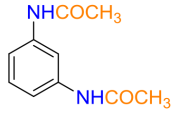
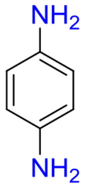
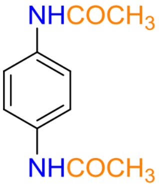
Entry	Substrate	Product	Molar Ratio[a]	Time (min)	Yield[b] (%)
1			1:0.3:1	1	90
2			1:0.3:1	4	85
3			1:0.3:1	4	86
4			1:0.3:1	4	86
5			1:0.3:2	3	89
6			1:0.3:2	3	89
7			1:0.3:1	5	87
8			1:0.3:1.5	5	87
9			1:0.3:1.5	3	85

Table 2: (Continued)

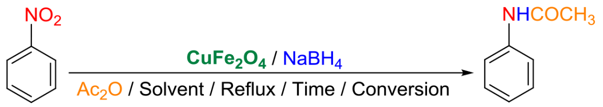


Entry	Substrate	Product	Molar Ratio[a]	Time (min)	Yield[b] (%)
10			1:0.3:1	4	86
11			1:0.3:1	3	88
12			1:0.3:1	3	86
13			1:0:3:1.5	4	80
14			1:0.3:1.5	2	80
15			1:0.3:1.5	8	80
16			1:0.3:2	3	89
17			1:0.3:2	3	87
18			1:0.3:2	3	89

[a] Substrate:$CuFe_2O_4$:Ac_2O.

[b] Yields refer to isolated pure products.

Table 3: Optimization experiments for the one-pot reductive acetylation of nitrobenzene to acetanilide promoted by $CuFe_2O_4$ MNPs.



Entry	$NaBH_4$ (mmol)	$CuFe_2O_4$ (mmol)	Ac_2O (mmol)	Solvent	Time	Conv. (%)
1	3	1	3	MeOH	2 h	N.R.
2	3	1	3	EtOH	2 h	N.R.
3	3	1	3	THF	2 h	N.R.
4	3	1	3	CH_3CN	2 h	N.R.
5	3	1	-	EtOAc	2 h	N.R.
6	3	1	3	-	2 h	N.R.
7	2	1	1	H_2O	11 min	100
8	2	0.7	1	H_2O	24 min	100
9	2	0.5	1	H_2O	46 min	100
10	2	0.3	1	H_2O	49 min	100
11	2	0.2	1	H_2O	52 min	100
12	2	1	0.5	H_2O	45 min	50

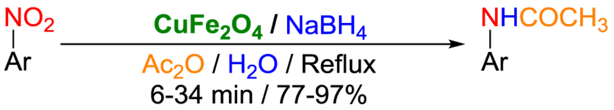
N.R. = No reaction (Conv. = 0)

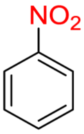
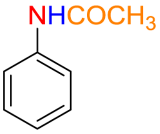
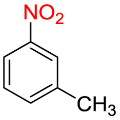
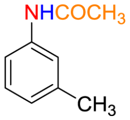
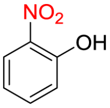
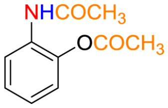
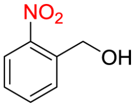
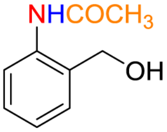
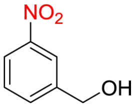
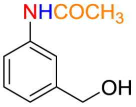
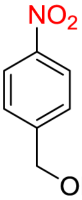
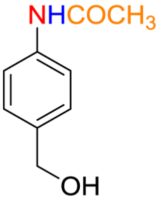
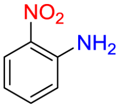
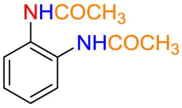
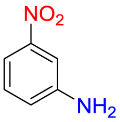
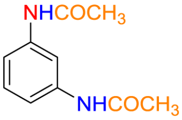
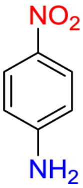
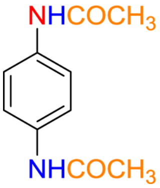
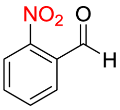
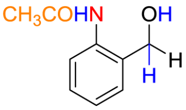
reactions were carried out successfully in H_2O within 6-34 min, and the corresponding *N*-arylacetamides were obtained in good to excellent yields.

More examinations showed that the chemoselective reductive acetylation of nitro group versus alcohol was successfully accessible. For example, reductive acetylation of 4-nitroabenzylalcohol to 4-acetamidobenzyl alcohol was carried out in 88% yield (Table 4, entry 6). In the case of nitrobenzaldehydes and nitroacetophenones, the same behavior was observable. In which, the nitro group was reduced and acetylated to acetamide, however, the carbonyl moieties were reduced to alcoholic function without acetylation (Table 4, entries 10-14). Molecules with the complexity of nitro and phenolic groups did not show any selectivity, and both of the functional groups were acetylated with the same reactivity. This fact was shown with reductive acetylation of *o*-nitrophenol to the corresponding 2-acetamidophenyl acetate (Table 4, entry 3). Table 4, entry 16 represents this protocol was also efficient for reductive acetylation of dinitro compounds using 1:3:2 molar equivalents of the $CuFe_2O_4$, $NaBH_4$, and Ac_2O respectively, in H_2O at reflux.

Notably, the exact mechanism for the one-pot reductive acetylation reaction of nitroarenes in the presence of $CuFe_2O_4$ as a simple and efficient promoter is not known. But, based on our observations and literature survey [71,74,75], a plausible reaction mechanism for this

Table 4: One-pot reductive acetylation of aromatic nitro compounds promoted by $CuFe_2O_4$ MNPs.



Entry	Substrate	Product	Molar ratio[a]	Time (min)	Yield[b] (%)
1			1:2:1:1	11	97
2			1:2:1:1	14	90
3			1:3:1:2	32	87
4[c]			1:3.5:1.5	22	87
5[c]			1:2:1:2	22	85
6			1:2:1:1.5	32	88
7[c]			1:3:1:1	29	80
8[c]			1:3:1:1	33	88
9[c]			1:3:1:2	33	89
10[c]			1:3:1:1	6	89

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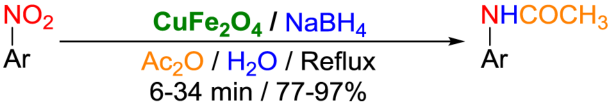
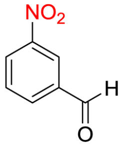
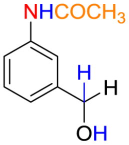
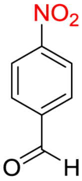
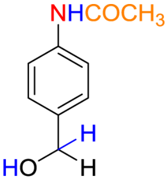
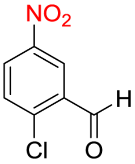
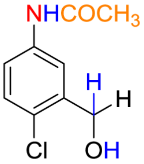
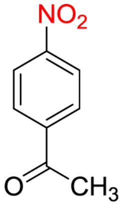
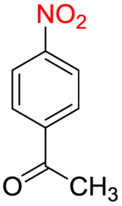
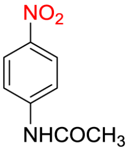
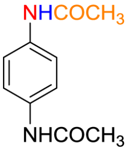
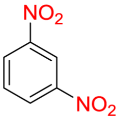
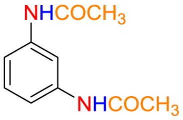
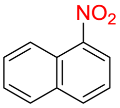
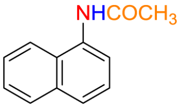


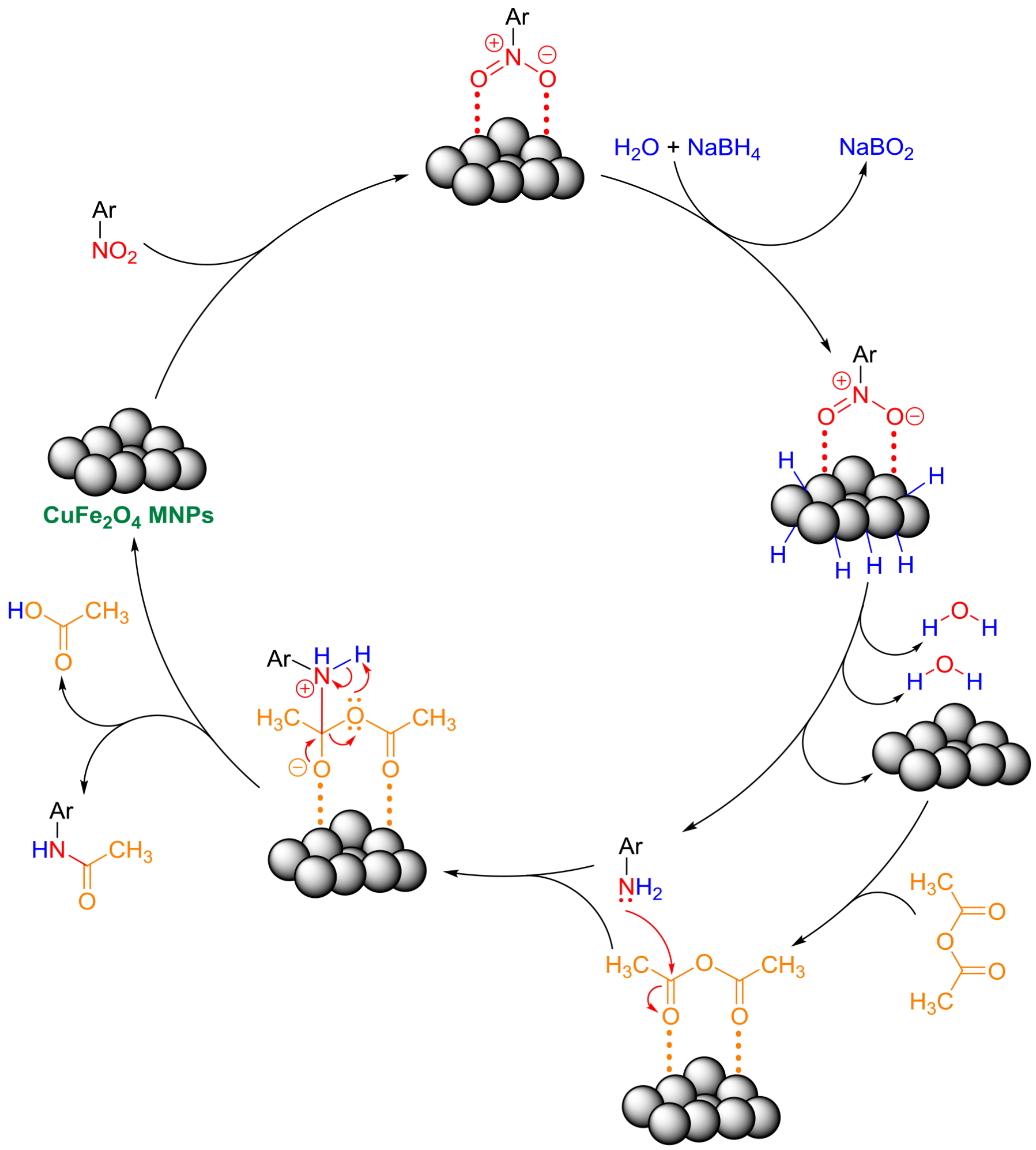
Entry	Substrate	Product	Molar ratio[a]	Time (min)	Yield[b] (%)
11			1:3:1:2	11	87
12[c]			1:3:1:1	17	89
13[c]			1:2:1:1.5	12	84
14[c]			1:4:1:2	24	80
15[c]			1:2.5:1:1	27	80
16[c]			1:3:1:2	34	77
17			1:2:1:1	27	78

[a] Substrate:$NaBH_4$:$CuFe_2O_4$:Ac_2O.

[b] Yields refer to isolated pure products.

[c] In these reactions, $NaBH_4$ was added portion-wisely.

reaction is presented in Scheme 2. Firstly, nitroarene and hydrogen which is obtained from the reaction of $NaBH_4$ and water absorbed on the surface of $CuFe_2O_4$ NPs. After completion of the reduction process which was accompanied by the elimination of two molecules of water, gene-



Scheme 2: Plausible mechanism for the one-pot reductive acetylation of nitroarenes promoted by $CuFe_2O_4$ MNPs.

rated arylamine intermediate attacked to Ac_2O (which was activated by $CuFe_2O_4$) caused the formation of desired amide compound along with carboxylic acid as an only side product.

2.4 Reusability

The recoverability and reusability of the $CuFe_2O_4$ NPs were studied using the *N*-acetylation of aniline and also one-pot reductive acetylation of nitrobenzene reactions. After completion of the reaction, the catalyst separated by an external magnet and reused for the subsequent runs without significant loss of its catalytic activity (Figures 10 and 11).

3 Experimental

3.1 Preparation of the $CuFe_2O_4$ MNPs

$CuFe_2O_4$ MNPs were synthesized based on a previously reported method by Jia and co-workers [76]. First of all, copper(II) acetate, iron(III) nitrate, sodium hydroxide, and sodium chloride were mixed in a molar ratio 1:2:8:2 and grounded in a simple agate mortar and pestle. After about 50 min, the resultant mixture was washed with deionized water several times. After removal of sodium chloride by washing, the wet nanocomposite was dried for 2 h at 80°C. Finally, the powders were calcinated

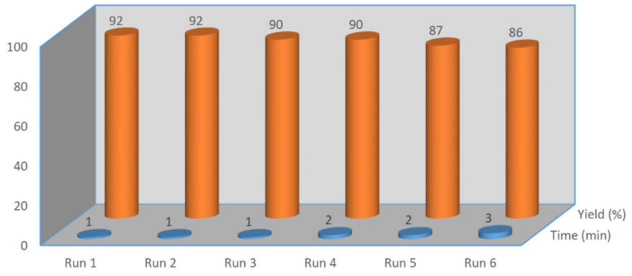


Figure 10: Reusability of the $CuFe_2O_4$ MNPs in the *N*-acetylation of aniline.

for 2 h at 300, 500, 600, 700, 800, and 900°C to obtain $CuFe_2O_4$ MNPs.

3.2 General experimental procedure for the synthesis of *N*-arylacetamides via *N*-acetylation of arylamines

To the synthesis of *N*-phenylacetamide as a representative example, a mixture of aniline (1 mmol, 0.093 g) and H_2O (3 mL) was prepared in a round-bottom flask (15 mL) which equipped with a magnetic stirrer. Then, ferromagnetic $CuFe_2O_4$ (0.3 mmol, 0.072 g) was added into the reaction flask, and the resulting mixture was stirred at reflux. Subsequently, Ac_2O (1 mmol, 0.102 g) was added to the prepared mixture followed by stirring for 1 min at the same temperature conditions. Then, the mixture was cooled to room temperature, and the $CuFe_2O_4$ was separated by a magnet from the reaction environment. Then, the reaction mixture was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. Finally, evaporation of the solvent under reduced pressure afforded the pure *N*-phenylacetamide which was characterized by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy techniques.

3.3 General procedure for the synthesis of *N*-arylacetamides via one-pot reductive acetylation of aromatic nitro compounds

As an example, nitrobenzene (1 mmol, 0.123 g) was dissolved in 2 mL of H_2O in a 15 mL round-bottom flask which equipped with a magnetic stirrer. Then, $CuFe_2O_4$ (1 mmol, 0.237 g) was added, and the mixture was stirred. Then, $NaBH_4$ (2 mmol, 0.075 g) was added, and the resulting mixture was stirred under reflux conditions for 10 min. Completion of the reduction reaction was monitored by TLC using *n*-CCl_4:Et_2O (5:2) as an eluent. Afterward, acetic anhydride (1 mmol, 0.102 g) was added to the reaction mixture followed by stirring for an additional 1 min at the same temperature conditions. Afterward, the mixture was cooled to room temperature, and the mentioned nanocomposite was separated by a magnet from the reaction environment. The reaction mixture was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. Finally, evaporation of the solvent under reduced pressure afforded the pure *N*-phenylacetamide which was characterized by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy techniques.

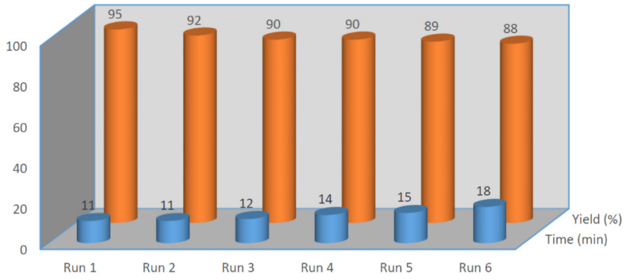


Figure 11: Reusability of the $CuFe_2O_4$ MNPs in the one-pot reductive acetylation of nitrobenzene.

4 Conclusions

In this research, we have developed simple, efficient, cost-effective and environmentally benign protocols for the synthesis of various *N*-arylacetamides via *N*-acetylation of arylamines and straightforward one-pot reductive acetylation of aromatic nitro compounds promoted by $CuFe_2O_4$ MNPs in water at reflux. Use of water as a green solvent, good to excellent yield of desired products, implementation of the cost-effective promoter which can reusable for several runs are advantages of the current protocols for the synthesis of *N*-arylacetamide derivatives. It is worthy to note that the catalytic applications of the modified and non-modified $CuFe_2O_4$ MNPs in various organic transformations under investigations in our lab, and will be reported in due course of the time.

Conflict of interest: The authors declare no conflict of interest.

Acknowledgement: Authors gratefully acknowledge the financial support from Urmia University.

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