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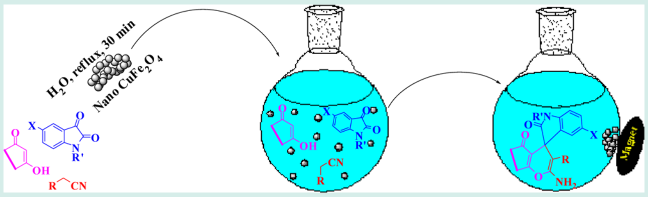
Copper Ferrite Nanoparticles: An Efficient and Reusable Nanocatalyst for a Green One-Pot, Three-component Synthesis of Spirooxindoles in Water

Ayoob Bazgir,[†] Ghaffar Hosseini,[†] and Ramin Ghahremanzadeh*[,‡]

[†]Department of Chemistry, Shahid Beheshti University, G.C., P.O. Box 19396-4716, Tehran 1983963113, Iran

[‡]Nanobiotechnology Research Center, Avicenna Research Institute, ACECR, Tehran 1177-19615, Iran

Supporting Information



ABSTRACT: A green reaction of isatins, active cyanomethanes, and cyclic 1,3-dicarbonyl derivatives for the efficient and simple one-pot three-component synthesis of spirooxindole fused heterocycles in refluxing water by use of magnetically recoverable and reusable catalyst is reported. The features of this procedure are, the use of magnetically recoverable and reusable catalyst, mild reaction conditions, high to excellent product yields, operational simplicity, and easy workup procedures. Most importantly of all, easy magnetic separation of the catalyst eliminates the requirement of catalyst filtration after completion of the reaction. Furthermore, the catalyst remained highly active even after 5 repeated uses.

KEYWORDS: *multicomponent reaction, tandem reaction, spirooxindole, heterocyclic compound, green media, water, magnetic nanoparticles*

Combinatorial chemistry is extensively useful for the discovery of novel biologically active compounds.[1] In this framework, multicomponent reactions (MCRs) are an effective tool in the current drug discovery process in terms of lead finding and lead optimization, but the range of easily accessible and functionalized small heterocycles is rather limited.[2] These strategies have emerged as flexible approaches in organic synthesis due to their advantages over the conventional multistep synthesis. In addition, they are eco-friendly, have superior atom economy, require less time-consuming and costly purification processes and avoid protection−deprotection steps. Because of the range of readily available starting materials, the simplicity of one-pot procedures without the need for isolation of intermediates, and the associated atom economy, MCRs have been broadly employed in the synthesis of heterocyclic compounds.[3−5] Therefore, the design and development of novel, efficient, and green MCRs focused on a target product is one of the most important challenges in organic synthesis. The use of water as a green solvent for organic synthesis has recently attracted considerable attention.[6] Since Breslow demonstrated hydrophobic effects could strongly increase the rate of some organic reactions and fostered the use of water as solvent in organic chemistry in 1980s,[7] there has been a growing recognition that water is an attractive medium for many organic reactions, such as Claisen rearrangement, Diels−Alder, Reformatsky, and pinacol-coupling reactions.[8−10] The use of water can afford the noteworthy benefit of a highly polar environment wherein miscible organic compounds react rapidly and are subsequently easily separated from the solvent. Furthermore, carrying out organic reactions in water, without the use of harmful and flammable organic solvents is appealing to an environmentally conscious society. Numerous studies have focused on finding water-compatible and reusable catalysts.[11−13]

The use of low-cost and readily available species as catalyst plays a significant role for economical feasibility of the chemical processes. Recently, research has been directed toward the synthesis and application of metal oxide nanoparticles in view of their unique properties compared to the bulk metals. Among various metal oxide nanoparticles, magnetic nanoparticles have received considerable attention because of their unusual properties and potential applications in diverse fields. Iron, the most ubiquitous of the transition metals and the fourth most plentiful element in the Earth's crust, is the structural backbone of our modern infrastructure. Magnetic nanoparticles are receiving increasing interest in recent years and are being used widely as a useful group of heterogeneous catalysts for organic synthesis due to their remarkable advantages such as the remarkable catalytic activity, easy synthesis, operational simplicity, eco-friendliness, and recoverability with an external magnetic field. Magnetic separation is an attractive alternative to filtration or centrifugation as it prevents the loss of catalyst and enhances reusability, rendering the catalyst cost-effective and is promising for industrial applications.[14−18] These advantages encouraged us to explore copper ferrite nano-

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particles as a recoverable and reusable catalyst for the synthesis of spirooxindole derivatives.

Compounds with an indole moiety exhibit antibacterial and antifungal activities. Furthermore, it has been reported that spiroindoline derivatives have highly enhanced biological activity.[19] The presence of a sterically constrained spiro structure in some natural products also adds to the interest in the investigations of spiro compounds.[20] The development of synthetic methods for these compounds, including the ones with new substitution patterns, is therefore of high importance in organic chemistry. For example, spirotryprostatins **A** and **B** (Figure 1) are cytostatic alkaloids, pteropodine, and isopteropodine have been shown to modulate the function of muscarinic serotonin receptors.[21]

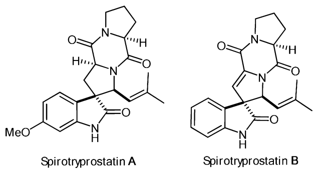
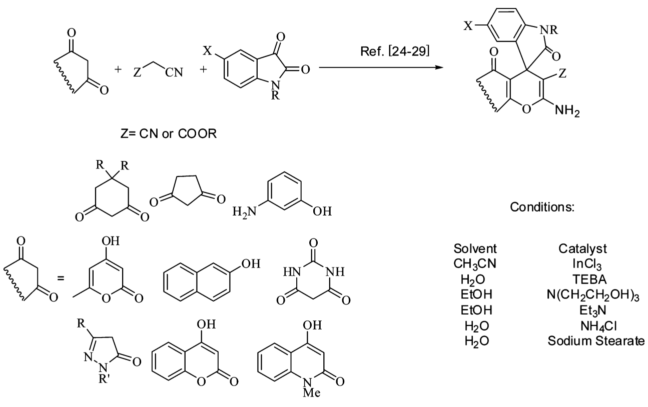


Figure 1. Spirooxindole-containing compounds.

Considering the above reports, the development of simple multicomponent methods for the efficient preparation of spirooxindoles is therefore an interesting challenge. Multicomponent reactions of malononitrile or alkyl cyanoacetate, isatins, and 1,3-dicarbonyl compounds are a powerfull methods for the synthesis of spirooxindoles[22−27] (Scheme 1). In most of these methods expensive catalysts were used, which are incompatible with industrial demands for cost-efficiency. Furthermore, in some cases catalyst recovery is difficult and the prolonged reaction times were needed.

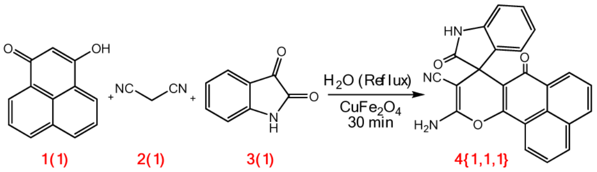
Scheme 1. Previous Synthetic Strategies



In continuation of our investigations on the synthesis of heterocyclic compounds,[28] recently, we have reported efficient methods for spirooxindole synthesis via new multicomponent reactions.[29] Herein, we performed the synthesis of spirooxindole fused heterocycles through tandem three-component reactions of isatins, active cyanomethanes, and cyclic 1,3-dicarbonyl compounds employing water as the reaction medium in the presence of copper ferrite nanoparticles as a powerful catalyst. Compared to alternative reports for preparation of these molecules, the present method not only benfits from magnetically recoverable catalysis but also the products were obtained in higher yields and shorter reaction times. Moreover, as clearly stated by Sheldon, it is generally recognized that "the best solvent is no solvent and if a solvent (diluent) is needed it should preferably be water".[30]

In a pilot experiment, the reaction of 3-hydroxy-1*H*-phenalen-1-one **1**(**1**), malononitrile **2**(**1**), and isatin **3**(**1**) in the presence of $CuFe_2O_4$ (10 mol %) as an inexpensive, magnetically recoverable, and reusable catalyst proceeded rapidly in refluxing water. The progress of the reaction was monitored by TLC. After completion of the reaction (30 min), the product 10′-amino-1,2-dihydro-2,7′-dioxospiro[3*H*-indole-3,8′(7*H*,8*H*)-phenaleno[1,2-*b*]pyran]-9′-carbonitrile **4**{*1,1,1*} was obtained in 90% yield (Scheme 2). ^1H and ^{13}C NMR spectra of the crude product clearly confirmed the formation of spirooxindole **4**{*1,1,1*}.

Scheme 2. Model Reaction



Encouraged by this success and to delineate this approach, particularly in regard to library construction, this methodology was evaluated by using different cyclic 1,3-dicarbonyl compounds, active cyanomethanes and isatins. Four cyclic 1,3-dicarbonyl derivatives **1**(**1**−**4**) four active cyanomethanes **2**(**1**−**4**), and seven substituted isatins **3**(**1**−**7**) were chosen for the library validation (Figure 2). Corresponding 43 spirooxindole fused heterocycles **4** were selectively synthesized by the tandem three-component condensation of cyclic 1,3-dicarbonyls **1**, active cyanomethanes **2** and isatin **3** in good yields in boiling H_2O in the presence of $CuFe_2O_4$ for 30 min. The results can be summarized as shown in Table 1. The yields and

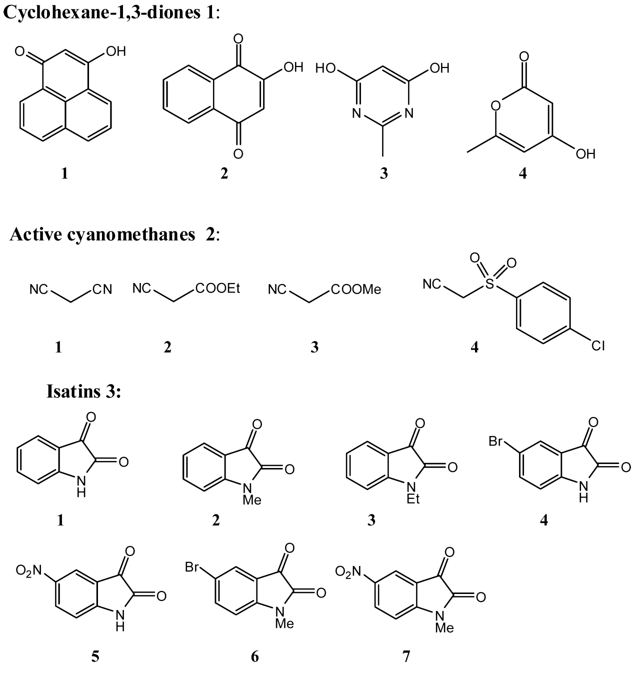
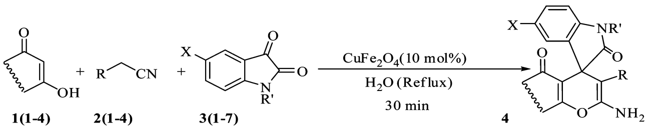


Figure 2. Diversity of reagents.

product purity were remarkable in presence of $CuFe_2O_4$, while without catalyst the yields of products were low (23%).

Table 1. Synthesis of Spiro[indoline-pyrazolopyridopyrimidine] Derivatives



product **4**	yield (%)	product **4**	yield (%)
4{*1,1,1*}	90	**4**{*2,2,1*}	89
4{*1,1,2*}	83	**4**{*2,2,2*}	92
4{*1,1,3*}	85	**4**{*2,2,5*}	94
4{*1,1,4*}	94	**4**{*2,3,4*}	92
4{*1,1,5*}	90	**4**{*2,4,1*}	85
4{*1,1,6*}	92	**4**{*2,4,4*}	87
4{*1,1,7*}	96	**4**{*2,4,5*}	89
4{*1,2,1*}	90	**4**{*3,1,1*}	87
4{*1,2,4*}	91	**4**{*3,1,5*}	82
4{*1,3,5*}	95	**4**{*3,1,7*}	81
4{*1,4,1*}	88	**4**{*3,3,1*}	94
4{*1,4,4*}	85	**4**{*3,3,5*}	92
4{*2,1,1*}	90	**4**{*4,1,1*}	84
4{*2,1,2*}	97	**4**{*4,1,5*}	82
4{*2,1,3*}	88	**4**{*4,1,7*}	81
4{*2,1,4*}	86	**4**{*4,2,1*}	91
4{*2,1,5*}	85	**4**{*4,3,1*}	93
4{*2,1,6*}	93	**4**{*4,3,4*}	96
4{*2,1,7*}	94	**4**{*4,3,5*}	93

As shown in Table 1, it was found that the method works with a wide variety of substrates, and this made it possible to synthesize a series of spirooxindole fused heterocycles.

We expect this method to find extensive application in the field of combinatorial chemistry, diversity-oriented synthesis, and drug discovery. This method, based on green tandem three-component $CuFe_2O_4$-catalyzed reaction in water, is the most simple, convenient and would be applicable for the synthesis of different types of spirooxindole fused heterocycles.

The yields and product purity were remarkable in presence of $CuFe_2O_4$, while without catalyst the yields of products were low. We reconsider the model reaction in absence of any catalyst and the yield of product was determined 23% after purification by a column chromatography. We also evaluated the amount of catalyst required for this transformation. The model reaction was performed in the presence of 2, 5, 10, 15, and 20 mol % of catalyst. It was found that using 10 mol % copper ferrite nanoparticles as a catalyst in water is sufficient to push the reaction forward. Increasing the amount of nano $CuFe_2O_4$ particles to more than 10 mol % showed no substantial improvement in the yield. Thus, 10 mol % of catalyst was chosen as suitable quantity of the catalyst for the reaction (Table 2).

Table 2. Different Amount of the $CuFe_2O_4$ Nanoparticles As Catalyst in Model Reaction[a]

entry	$CuFe_2O_4$ nanoparticles (mol %)	time (min)	yield (%)[b]
1	2	60	78
2	5	60	86
3	10	30	90
4	15	30	90
5	20	45	89

[a]The reaction was carried out using isatin (1 mmol), malononitrile (1 mmol), and 2-hydroxynaphthalene-1,4-dione (1 mmol) in the presence of catalyst and H_2O (5 mL). [b]Isolated yield of the pure compound.

Finally, The possibility of recycling the magnetic catalyst was examined by using the reaction of isatin **3**(**1**), malononitrile **2**(**1**), and 2-hydroxynaphthalene-1,4-dione **1**(**2**) as model substrates under optimized conditions. After completion of the reaction, while the reaction mixture is still hot enough to keep the product in solution, the catalyst was removed from the hot reaction solution immediately with an external magnet, washed with acetone, and the recycled catalyst was saved for the next reaction runs. The procedure was repeated and the results indicated the recycled catalyst could be used five times. The isolated yields were similar and remained with no detectable loss, until the fifth recycling, 90%, 90%, 89%, 88%, and 80% (Figure 3).

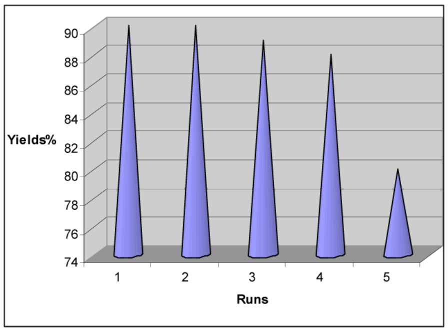


Figure 3. Recyclability of $CuFe_2O_4$ on the synthesis of product **4**{*2,1,1*}.

The workup of these very clean reactions involves only a filtration and simple washing step with EtOH. After completion of the reaction, the mixture was magnetically concentrated with the aid of a magnet to separate the catalyst. Using this simple purification protocol the desired products are obtained in high purity. Compounds **4** are stable solids whose structures were established by IR, ^1H, ^{13}C NMR spectroscopy, and elemental analysis.

In conclusion, an efficient, clean, atom-economical and simple method for the preparation of spirooxindoles using readily available starting materials by tandem one-pot three-component reaction is reported. Prominent among the advantages of this new method are operational simplicity, high to excellent product yields and easy workup procedures employed. Most important of all, easy magnetic separation of the catalyst eliminates the requirement of catalyst filtration after completion of the reaction, which is an additional green attribute of this reaction.

■ EXPERIMENTAL PROCEDURES

General. Melting points were measuring on an Electrothermal 9100 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a *BRUKER DRX-300 AVANCE* spectrometer at 300.13 and 75.47 MHz, respectively. ^1H and ^{13}C NMR spectra were obtained on solutions in DMSO-d_6 using TMS as internal standard. IR spectra were recorded using an FTIR apparatus. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer.

The chemicals used in this study were obtained from Fluka and Merck and were used without purification.

Typical Experimental Procedure for the Preparation of Catalyst. $CuFe_2O_4$ nanoparticles were prepared by coprecipitation of $Cu(NO_3)_2$ and $Fe(NO_3)_3$ in water in the presence of sodium hydroxide. Briefly, a solution of $Fe(NO_3)_3\cdot 9H_2O$ (2.02 g, 5 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.604 g, 2.5 mmol) in distiller water (10 mL) was treated with aqueous NaOH (4M, 7.5 mL, 30 mmol) at room temperature over a period of 10 min to form a reddish-black precipitate. The reaction mixture was warmed to 90 °C and stirred. After 2 h, it was cooled to room temperature and the formed magnetic particles were separated by a magnetic separator. Then, the catalyst was washed with water and kept in air oven overnight at 80 °C. Then the catalyst was ground in a mortar-pestle and kept in a furnace at 800 °C at a heating rate of (2 °C/min) and cooled to 100 °C at (5 °C/min) in air. The XRD patterns of calcinated precipitate indicate that the powder is mainly composed of $CuFe_2O_4$ (Figure 4).[31] The position and relative intensities of all peaks confirm well with standard XRD pattern of $CuFe_2O_4$ (JCPDS card No. 34-0425) indicating characteristic of the tetragonall structure, the copper ferrite nanoparticles calcinated at 800 °C present a particle size of 35 nm, calculated from the broadening of the peak at 2θ = 35.31 using the Scherrer equation.

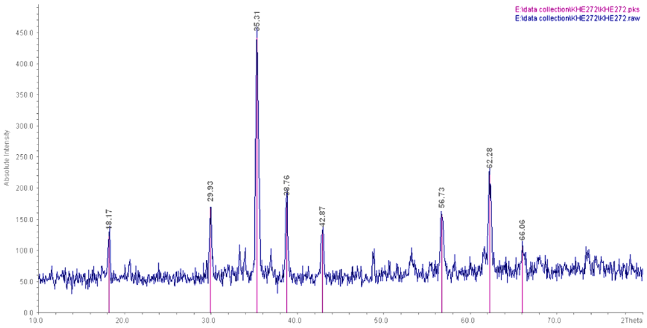


Figure 4. XRD patterns of calcinated $CuFe_2O_4$.

Typical Procedure for the Preparation of Spirooxindoles (4). A mixture of malononitrile (1 mmol), isatins (1 mmol), cyclic 1,3-dicarbonyl compounds (1 mmol), and $CuFe_2O_4$ (0.1 mmol) was heated to reflux in water (5 mL) for 30 min. Upon reaction completion (TLC, silica, EtOAc/hexane, 1:3), the catalyst was separated from the hot reaction mixture with the aid of an external magnet. The solution was decanted into the beaker, before the desired product precipitated. The recovered catalyst was washed several times with chloroform followed by water, then dried under vacuum and reutilized four times for the same reaction. The solution was cooled to room temperature. Then, the precipitated product was filtered and washed with water (10 mL) and ethanol (5 mL) to afford the pure product **4**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional materials including NMR data and additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +98-21-22432020; Fax; +98-21-22432021. E-mail: r.ghahremanzadeh@avicenna.ac.ir,.

Notes

The authors declare no competing financial interest.

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