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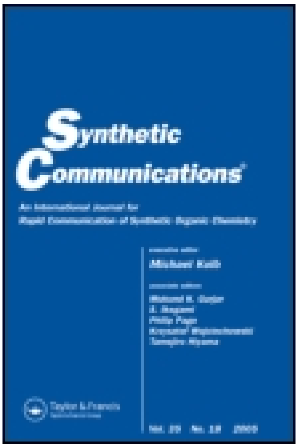

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# $CuFe_2O_4$ Nanoparticles: A Magnetically Recoverable and Reusable Catalyst for the Synthesis of Coumarins via Pechmann Reaction in Water

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# $CuFe_2O_4$ NANOPARTICLES: A MAGNETICALLY RECOVERABLE AND REUSABLE CATALYST FOR THE SYNTHESIS OF COUMARINS VIA PECHMANN REACTION IN WATER

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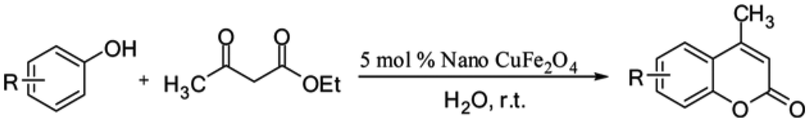
## GRAPHICAL ABSTRACT



**Abstract** *The synthesis of coumarins by hydroxyalkylation of phenols with ethyl acetoacetate (*via *Pechmann reaction) is attempted using magnetically separable and reusable* $CuFe_2O_4$ *nanoparticles in water.*

*[Supplementary materials are available for this article. Go to the publisher's online edition of* Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

**Keywords** Coumarins; $CuFe_2O_4$ nanoparticles; heterogeneous catalyst; Pechmann reaction

## INTRODUCTION

Magnetic nanoparticles are of great interest for researchers from a wide range of disciplines, including magnetic fluids,[1] catalysis,[2] data storage,[3] and environmental remediation.[4] Nanocatalysts have many important benefits in catalyst systems and interesting applications, and they provide a broad range of benefits in catalytic systems. However, in some cases, recovery of the nanocatalysts from the reaction mixtures is so difficult that conventional techniques such as filtration or centrifugation are not enough for an efficient recovery. To overcome this issue, the use of magnetic nanoparticles has emerged as a viable solution; their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the reaction mixture with an external magnet. Magnetic separation is an attractive

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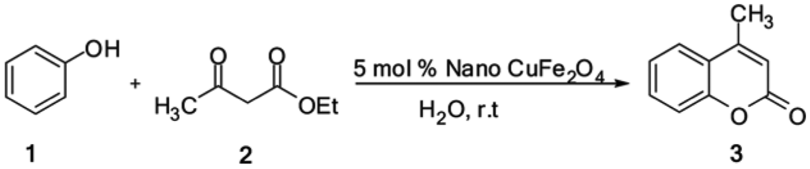


**Scheme 1.** The synthesis of substituted coumarins in the presence of $CuFe_2O_4$ nanoparticles at room temperature.

alternative to filtration or centrifugation as it prevents loss of catalyst and enhances reusability, making the catalyst inexpensive and promising for industrial applications. On the other hand, the use of water as a medium for organic reactions has a number of potential advantages because water is the most abundant, least expensive solvent, nonhazardous and nontoxic, and isolation of the organic products can be performed by simple phase separation.

Coumarin and its derivatives form an important class of benzo-pyrones found in nature and have shown significant biological activities, such as antitumor,[5] anti-HIV,[6] antioxidative,[7] antimicrobial,[8] and anticancer[9] activity. Among the various coumarin derivatives, 7-hydroxy-4-methyl coumarin (β-methylumbelliferone) is used as insecticide, fluorescent brightener, and a standard for fluorometric determination of enzymatic activity and tunable laser dyes.[10] The Pechmann reaction is one of the most widely applied method for synthesizing coumarins using different homogeneous or heterogeneous catalysts such as Amberlyst ion-exchange resins,[11] montmorillonite K-10,[12] nafion resin/silica nanocomposites,[13] nanocrystalline sulfated-zirconia,[14] furic acid,[15] trifluoroacetic acid,[16] phosphorus pentoxide,[17] sulfonic acid functionalized SBA-15 silica,[18] $ZrCl_4$,[19] and $TiCl_4$.[20] However, most of these procedures require a large amount of catalyst long duration, microwave irradiation, and high temperature to complete the reaction. Therefore, the search continues for a better catalyst for the synthesis of coumarins in terms of operational simplicity, reusability, economic viability, and greater selectivity. Herein, we have focused our attention on $CuFe_2O_4$ nanoparticles[21] as heterogeneous catalysts in the synthesis of coumarins in water at room temperature (Scheme 1).

## RESULTS AND DISCUSSION

To find the optimized condition, the reaction of resorcinol (1 mmol) and ethyl acetoacetate (1.2 mmol) in an aqueous medium at room temperature as a model reaction in the presence of different amounts of $CuFe_2O_4$ nanoparticles (5 mol%) was examined, and variables affecting on the reaction yields were studied.

In the absence of a catalyst, only a trace amount of the desired 7-hydroxy-4-methyl-2*H*-chromen-2-one was obtained under solvent-free conditions even at 70 °C (Table 1, entry 1). In our initial study for the optimization of the reaction conditions, a screening was performed with a variety of different solvents such as ethanol, acetonitrile, dichloromethane, and water at room temperature (Table 1, entries 2–7) as well as under solvent-free conditions with $CuFe_2O_4$ nanoparticles at different temperatures (Table 1, entries 8–10). We noticed that the polar protic solvents

**Table 1.** Effect of temperature, solvent, and amount of catalyst on the synthesis of 7-hydroxy-4-methyl-2*H*-chromen-2-one[a]

| Entry | Amount of catalyst (mol %) | Temperature (°C) | Solvent | Time (min) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | — | 70 | — | 5 h | Trace |
| 2 | 5 | 25 | EtOH | 25 | 70 |
| 3 | 5 | 25 | $CH_3CN$ | 32 | 68 |
| 4 | 5 | 25 | $CH_2Cl_2$ | 30 | 60 |
| 5 | 5 | 25 | $H_2O$ | 15 | 98 |
| 6 | 1 | 25 | $H_2O$ | 20 | 88 |
| 7 | 3 | 25 | $H_2O$ | 20 | 92 |
| 8 | 5 | 25 | — | 25 | 55 |
| 9 | 5 | 45 | — | 25 | 70 |
| 10 | 5 | 70 | — | 25 | 80 |

[a] Reaction conditions: resorcinol (1 mmol) and ethyl acetoacetate (1.2 mmol).

[b] Isolated yield.

afforded better yield than other solvents and the best catalytic activity of $CuFe_2O_4$ nanoparticles (5 mol%) was observed in aqueous medium (Table 1).

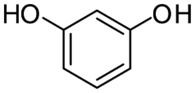
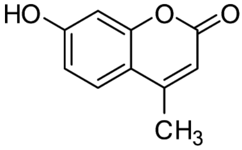
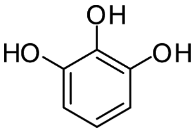
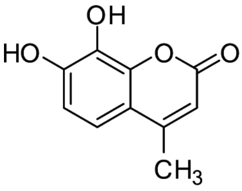
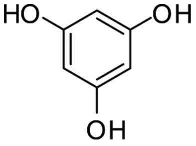
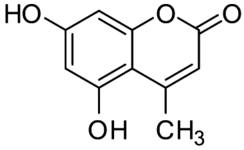
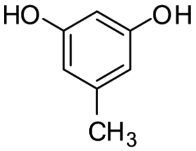
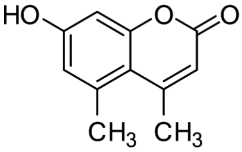
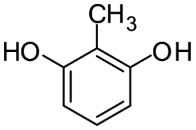
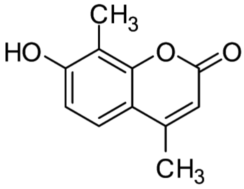
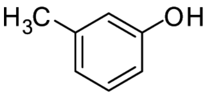
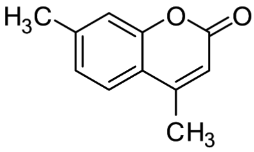
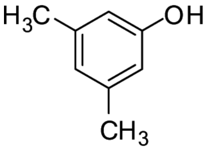
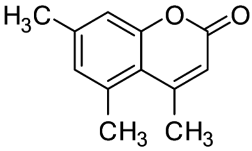
The quantity of the catalyst plays a vital role in the formation of the desired product. To determine the optimum concentration of catalyst, the best yields were found in the presence of just 5 mol% $CuFe_2O_4$ nanoparticles. It was observed that decrease in the amount of catalyst did not improve the results to an appreciable extent.

To assess the generality of this approach for the synthesis of coumarins, various phenols were reacted with ethyl acetoacetate under optimized conditions (Table 2). A series of a variety of functional groups such as ether, hydroxy, nitro, alkyl, and amino groups under the present reaction conditions afforded a wide range of substituted coumarins in good yield. Interestingly, substrates such as phenol, nitro phenols, and cresols showed better reactivity (compared with that previously reported) to afford the respective coumarins with good yields and short reaction times. The reactions of phenols having electron-donating groups furnished greater yields of phenols compared to that without having electron-donating groups or with an electron-withdrawing group. Also, 3-aminophenol reacted to provide 7-amino-4-methyl coumarin in good yield with good chemoselectivity (Table 2, entry 11).

To examine the possible recyclability of the catalyst, the reaction of resorcinol (1 mmol) with ethyl acetoacetate (1.2 mmol) in the presence of 5 mol% $CuFe_2O_4$ nanoparticles in water medium and at room temperature was studied. After 15 min, the reaction was completed and the 7-hydroxy-4-methyl-2*H*-chromen-2-one was obtained in 98% yield. After completion of the reaction (monitored by thin-layer chromatography, TLC), the catalyst was separated from the reaction mixture with an external magnet and water was added to the resulting reaction mixture, followed by extraction with EtOAc. The catalyst could be reused six times for the synthesis of 7-hydroxy-4-methyl-2*H*-chromen-2-one without significant loss of activity (Table 3).

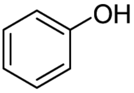
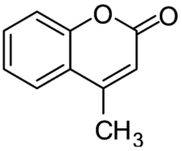
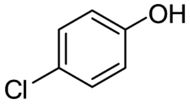
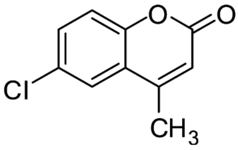
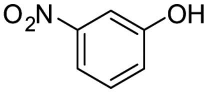
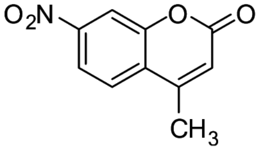
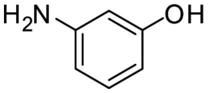
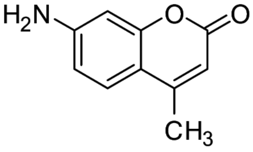
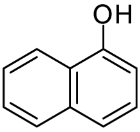
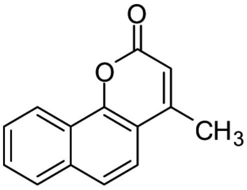
To show the accessibility of the present work we compared this method with other reported catalysts and summarized the results of the preparation of the coumarin derivatives. The results of the synthesis **3a** are collected in Table 4, which shows $CuFe_2O_4$ nanoparticles are more efficient catalysts with respect to the reaction

**Table 2.** Pechmann reactions of various phenols

| Entry | Phenol | Product | Time (min) | Yield (%)[a] | Ref. |
|---|---|---|---|---|---|
| 1 |  |  **3a** | 15 | 98 | [18] |
| 2 |  |  **3b** | 15 | 95 | [22] |
| 3 |  |  **3c** | 18 | 92 | [18] |
| 4 |  |  **3d** | 20 | 92 | [18] |
| 5 |  |  **3e** | 22 | 96 | [22] |
| 6 |  |  **3f** | 18 | 85 | [18] |
| 7 |  |  **3g** | 17 | 82 | [18] |

(*Continued*)

**Table 2.** Continued

| Entry | Phenol | Product | Time (min) | Yield (%)[a] | Ref. |
|---|---|---|---|---|---|
| 8 |  |  **3h** | 20 | 90 | [18] |
| 9 |  |  **3i** | 30 | 85 | [24] |
| 10 |  |  **3j** | 32 | 88 | [24] |
| 11 |  |  **3k** | 30 | 80 | [18] |
| 12 |  |  **3l** | 34 | 85 | [18] |

[a] Isolated yields of pure products.

**Table 3.** Reusability studies of catalysts for the synthesis of compound **3a** (Table 2, entry 1)[a]

| Experiment | Isolated yield (%)[b] |
|---|---|
| 1 | 98 |
| 2 | 96 |
| 3 | 95 |
| 4 | 95 |
| 5 | 92 |
| 6 | 90 |

[a] Reaction condition: resorcinol (1 mmol), ethyl acetoacetate (1.2 mmol), $CuFe_2O_4$ nanoparticles as a catalyst 5 mol% in water.

[b] Isolated yield.

**Table 4.** Comparison of the catalytic efficiency of $CuFe_2O_4$ nanoparticles with some reported catalysts in the synthesis of compound **3a**

| Entry | Catalyst | Time (min) | Yield (%) | Ref. |
|---|---|---|---|---|
| 1 | PMSCl, 7 mol%, 130 °C | 60 | 94 | [25] |
| 2 | Zr(IV)-HMNQ@ASMPs, solvent-free, 110 °C | 10 | 96 | [26] |
| 3 | $ZrOCl_2 \cdot 8H_2O/SiO_2$, 10 mol%, 90 °C | 40 | 94 | [27] |
| 4 | Zirconium(IV)-modified silica gel, 10 mol%, 130 °C | 30 | 94 | [28] |
| 5 | $GaI_3$, 10 mol%, reflux, $CH_2Cl_2$ | 42 | 96 | [29] |
| 6 | $InCl_3$, 10 mol%, 65 °C | 30 | 98 | [23] |
| 7 | $Sm(NO_3)_3 \cdot 6H_2O$, 10 mol%, 80 °C | 20 | 98 | [30] |
| 8 | $Bi(NO_3)_3 \cdot 5H_2O$, 5 mol%, 80 °C | 15 | 94 | [31] |
| 9 | Ionic liquid anhydrous $FeCl_3$, 20 mol%, 70 °C | 12 | 80 | [32] |
| 10 | $CuFe_2O_4$ nanoparticles, rt, water, 5 mol% | 15 | 98 | — |

time and require lower catalyst content under very mild conditions at room temperature in aqueous media. They exhibited broad applicability in terms of yields.

## CONCLUSION

In summary, we have described here the synthesis of coumarin derivatives using $CuFe_2O_4$ nanoparticles as catalysts in water at room temperature. The methodology has several advantages such as using water as solvent, high reaction rates, excellent yields, simplicity in the extraction of the product, magnetically separable catalysts, and elimination of catalyst filtration after completion of the reaction.

## EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and used without further purification. The $CuFe_2O_4$ nanoparticles were prepared according to the procedure described in the literature.[21] Melting points were measured with an Electrothermal 9100 apparatus. $^1H$ and $^{13}C$ spectra were measured with Bruker DRX-400 Avance spectrometers, and infrared (IR) spectra were recorded on a FT-IR Bruker Vector 22 spectrometer.

### General Procedure for the Preparation of Coumarins

Resorcinol (1 mmol) and ethyl acetoacetate (1.2 mmol) were placed in a 10 ml, round-bottomed flask in $H_2O$ (3 mL). Sequentially $CuFe_2O_4$ (5 mol%, 12 mg) was added. After completion of the reaction, the catalyst was separated from the reaction mixture with an external magnet, and the catalyst was washed several times with $H_2O$ and dried under vacuum. Water (10 mL) was added to the resulting reaction mixture, followed by extraction with EtOAc (3 × 5 mL). The collected organic phases were dried with $Na_2SO_4$, and the solvent was removed under vacuum to give the corresponding coumarin, which did not require any further purification. The physical data (mp, NMR) of these known compounds were found to be identical with those reported in the literature. Spectroscopic data for selected examples are shown.

**7-Hydroxy-4-methyl-2*H*-chromen-2-one (3a).** Colorless solid, mp 185–186 °C; IR (KBr): $\nu$ 3165, 1675, 1383, 1237, 1067, 985, 856, 758, 572, 525, 426 cm$^{-1}$; $^1$H NMR (400 MHz; DMSO-$d_6$; TMS): $\delta_H = 10.52$ (brs, 1H), 7.35 (d, $J = 8.4$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.65 (s, 1H), 6.10 (brs, 1H), 2.29 (brs, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$; TMS): $\delta_C = 161.6$, 160.7, 155.2, 153.8, 126.9, 113.6, 112.8, 110.4, 102.2, 18.8.

**7-Amino-4-methyl-2*H*-chromen-2-one (3k).** Light yellow solid, mp 224–225 °C; IR (KBr): $\nu$ 3436, 3353, 3250, 1617, 1543, 1448, 1389, 1263, 1213, 1155, 1056, 835, 710, 649, 539, 452 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$; TMS): $\delta_H = 7.42$ (d, $J = 8.0$ Hz, 1H), 6.43 (dd, $J = 7.2$ Hz, $J = 2.5$ Hz, 1H), 6.42 (d, $J = 2.5$ Hz, Hz, 1H), 6.12 (brs, 2H), 5.92 (s, 1H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$; TMS): $\delta_C = 163.2$, 154.9, 154.1, 153.5, 125.7, 111.6, 109.5, 107.6, 97.9, 18.2.

### Preparation of Nano $CuFe_2O_4$

$CuFe_2O_4$ nanoparticles were prepared by thermal decomposition of $Cu(NO_3)_2$ and $Fe(NO_3)_3$ in water in the presence of sodium hydroxide. Briefly, to a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (3.34 g, 8.2 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (1 g, 4.1 mmol) in 75 ml of distilled water, 3 g (75 mmol) of NaOH dissolved in 15 ml of water was added at room temperature over a period of 10 min, during which a reddish-black precipitate was formed. Then the reaction mixture was warmed to 90 °C and stirred. After 2 h, it was cooled to room temperature, and the magnetic particles so formed were separated by a magnetic separator. It was then washed with water (3 × 30 ml), and the catalyst was kept in an air oven overnight at 80 °C. Then the catalyst was ground in a mortar and pestle, kept in a furnace at 700 °C for 5 h (step up temperature 20 °C/min), and then cooled to room temperature slowly; 820 mg of magnetic $CuFe_2O_4$ nanoparticles were obtained.

### Catalyst Characterizations

The systematic characterization of $CuFe_2O_4$ catalyst was carried out by x-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscopy (TEM). The XRD analysis was done in a Philips PW 1830 x-ray diffractometer with CuK$\alpha$ source ($\lambda = 1.5418$ Å) in a range of Bragg's angle (5–60°) at room temperature. The XRD pattern of the calcined sample (Fig. 1) perfectly matches with the expected cubic spinel structure of $CuFe_2O_4$. The average crystallite size (L) was calculated from X-ray line broadening using (3 1 1) peak and Debye-Sherrer's equation; $L = 0.89\lambda/\beta\cos\theta$, where $\beta$ is the FWHF and $\lambda$ is the wavelength of the radiation, found to be $L = 10.3$ nm. SEM picture was taken using a Jeol JSM-5300 microscope (acceleration voltage 10 kV). The sample powder was deposited on a carbon tape before mounting on a sample holder. To reduce the charge developed on the sample, gold sputtering was done for 3 min. The SEM of the $CuFe_2O_4$ sample is shown in Fig. 2a. As indicated in this figure, small agglomerated nanoparticles of disordered surface morphology are observed. The TEM were obtained with a Philips CM-10 microscope. The $CuFe_2O_4$ sample for TEM was prepared by dispersing the powdered sample in ethanol by sonication and then drop drying on a copper grid

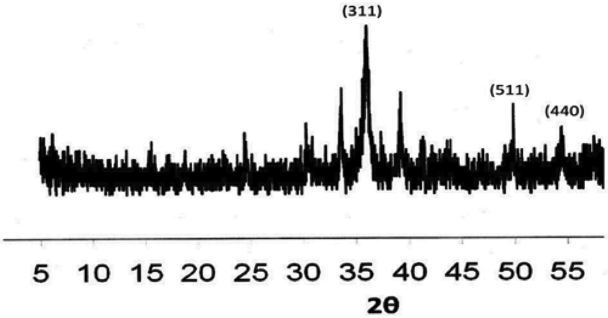
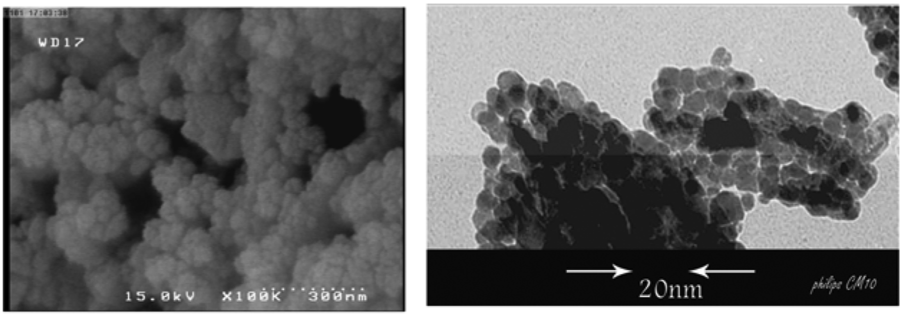


**Figure 1.** X-ray diffraction pattern of $CuFe_2O_4$ nanoparticles.



(a) (b)

**Figure 2.** (a) SEM image of $CuFe_2O_4$ nanoparticles. (b) TEM image of $CuFe_2O_4$ nanoparticles.

(400 mesh) coated with carbon film. As the TEM figure shows, the average size of particles resulted from this method is approximately 5–15 nm. The particle sizes obtained from TEM are in good agreement with XRD measurement (Fig. 2b).

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