Research Article

One-Pot Access to Diverse Functionalized Pyran Annulated Heterocyclic Systems Using SCMNPs@BPy-SO$_3$H as a Novel Magnetic Nanocatalyst

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Abstract

The SCMNPs@BPy-SO$_3$H catalyst was prepared and characterized using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Vibrating Sample Magnetometry (VSM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). Afterwards, its capability was efficiently used to promote the one-pot, three-component synthesis of pyrano[2,3-c]pyrazole and 2-amino-3-cyano-pyrano[3,2-c]chromen-5(4H)-one derivatives. The strategy resulted in the desired products with excellent yields and short reaction times. The SCMNPs@BPy-SO$_3$H catalyst was readily recovered using a permanent magnetic field and it was reused in six runs with a slight decrease in catalytic activity.

Keywords: Multicomponent reaction; Solvent-free conditions; Magnetic nanocatalyst; SCMNPs@BPy-SO$_3$H, pyrano[2,3-c]pyrazole; 2-amino-3-cyano-pyrano[3,2-c]chromen-5(4H)-one

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1. Introduction

In the last decade, considerable attention has been paid to the synthesis of Fe$_3$O$_4$ magnetic nanoparticles (MNPs) in various fields of applications due to their unique features, such as: high surface area, superparamagnetic behavior, low toxicity, biocompatibility, suitability for large-scale generation, simple recovery, and coupling with organic and inorganic molecules [1-9]. Coating an organic (biowastes) or inorganic (bentonite, alumina, silica, zeolite, and metal oxides) support surface on MNPs prevents these nanomaterials from agglomeration due to the strong dipole-dipole attraction; it also improves their efficiency in terms of catalytic activity and simplify separation [10-11]. Surface modifying of Fe$_3$O$_4$ magnetic nanoparticles with silica layer growth the available active sites and ameliorate the chemical stability [12]. Furthermore, because of the presence of active hydroxyl groups on the silica surfaces, a wide range of organic and inorganic linkers can be attached to them and promote their application in many chemical processes.

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Pyran scaffolds have been highlighted as the important heterocyclic molecules because of their widespread presence in natural compounds that made them more important to be used in pharmaceuticals, cosmetics industries, pigments, and biodegradable agrochemicals [13-16]. Pyranopyrazole derivatives, as one of the pyran annulated heterocyclic compounds, have attracted considerable attention in various fields including chemistry, biology, and pharmacology due to their observed features, such as: antimicrobial [17], antiplatelet [18], antiinflammatory [19-21], antitumor [22], anticancer [23], analgesic [24-25], molluscicidal [26], cholinesterases inhibitory activity [27], vasodilator [28], and human Chk1 kinase inhibiting activity [29]. The synthetic strategy to prepare pyranopyrazole derivatives includes utilization of one-pot four-component condensation of hydrazine hydrate, aldehyde, ethyl acetooacetate, and malononitrile. Some catalysts have been utilized to perform this reaction, such as: DABCO [30], meglumine [31], γ-alumina [32], iononic liquid [33], isonicotinic acid [34], triethylamine [35-36], morpholine trflate (MorT) [37], Ba(OH)₂ [38], glycine [39], Fe₃O₄@SiO₂-HMTA-SO₂H [40], per-6-amino-β-cyclodextrin (per-6-ABCD) [41], triethylamine [42], cetyltrimethylammonium chloride (CTACl) [43], urea [44], β-Cyclodextrin-pichlorohydrin [45], molecular sieves [46], and SnO₂ quantum dots [47]. Recently, a one-pot three-component condensation of 4-hydroxycoumarin, malononitrile, and different aryl aldehydes have been reported for the construction of substituted pyrano[3,2-c]coumarins using various catalytic systems, such as: hexadecyltrimethyl ammonium bromide [48], nanoparticles [49], (DAHP) [50], iononic liquids [51], MGO [52], Mg/La mixed metal oxides [53], nanosilica [54], and H₃P₂W₁₈O₆₉.18H₂O [55]. Some of these methods highlight certain merits in reactions, but others also have limitations, such as: long reaction times, the low yield of the products, hard work-up and difficult recoverability.

2. Materials and Methods

2.1 Experimental

All the pure chemical substances were purchased from Merck and Aldrich Companies and applied without any further purification. Melting points of the substrate were carried out on Electrothermal-9100 apparatus and uncorrected. Fourier transform infrared spectroscopy (FT-IR) was recorded with a PerkinElmer FXI spectrometer using the KBr wafers that was operating in the range of 400-4000 cm⁻¹. X-ray diffraction (XRD) patterns of samples was taken with a Philips instrument with a wavelength of 1.54 Å using Cu-Kα radiation. Thermogravimetric analyses (TGA) were examined by a Du Pont 2000 thermal analysis apparatus under nitrogen atmosphere at a heating rate of 10 °C/min. The magnetic properties were measured by a vibrating sample magnetometry (VSM; Lakeshore 7200 at 300 kVsm) at room temperature. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed for the chemical composition of synthesized nanoparticles (ESEM, Philips, and XL30). Scanning electron microscope (SEM) images were recorded with an SEM-LEO 1430VP instrument about the size, shape and morphology of the nanoparticles.

2.2 Catalyst Synthesis

2.2.1 Preparing Fe₃O₄ nanoparticles

In a typical method, a solution of FeCl₃.4H₂O (4.27 g) and FeCl₂.6H₂O (11.65 g) salts was dissolved in 150 mL deionized water and stirred under nitrogen atmosphere at 70 °C. Then, 15 mL NH₃·H₂O (25%) was slowly dropped into the reaction solution, while being sonicated under nitrogen atmosphere within 30 min. The color of the reaction mixture changed from orange to black. The product of magnetic nanoparticles was isolated magnetically from the reaction solution followed by rinsing several times with deionized water and vacuum-drying.

2.2.2 Preparing nano-Fe₃O₄@SiO₂ core shells

The 1 g of Fe₃O₄ nanoparticles, 65 mL of ethanol and 25 mL of deionized water were added into 250 mL three-neck flask. The reaction solution was sonicated for 20 min. Then, 4 mL of NH₃·H₂O (25%) and 0.5 mL of tetraethylorthosilicate (TEOS) were added dropwise to the flask. The reaction mixture was stirred at ambient temperature for 16 h. Finally, the precipitate was isolated with an external magnetic field, rinsed with distilled water and ethanol, and then dried in a vacuum oven.

2.2.3 Preparation of Fe₃O₄@SiO₂-PC magnetic nanoparticles

2 g of Fe₃O₄@SiO₂ NPs was dispersed in 50 mL of dry toluene in a round-bottom flask using an ultrasonic water for 30 min. Afterwards, 4 mL of 3-chloropropyltriethoxysilane (PC) was
slowly added into the flask and refluxed with mechanical stirring for 24 h under nitrogen gas protection. Afterward, the amino-modified magnetite nanoparticles were gathered using an external magnetic field followed by rinsing several times with ethanol and then being dried under vacuum oven.

2.2.4 Preparation of SCMNPs@ThSCa

1 g of the prepared Fe₃O₄@SiO₂-PC magnetic nanoparticles was dispersed in 75 mL of ethanol using an ultrasonic bath for 30 min and mixed with 5 mL of thiosemicarbazide (ThSCa), and the reaction solution was refluxed for 24 h under a continuous flow of nitrogen gas. The resultant solid precipitates were isolated using a permanent magnetic field that was washed three times with distilled water to eliminate the unreacted chemicals and then dried in a vacuum oven for 17 h.

2.2.5 Preparing SCMNPs@ThSCa-BPy

1 g of the prepared SCMNPs@ThSCa was dispersed in 75 mL of ethanol and mixed with 2.2 mL of 2,2’-bipyridyl ketone (BPy). The reaction solution was stirred under reflux conditions for 12 h and the resultant solid product was separated using an external magnetic field that was washed several times to remove the unreacted chemicals; it was then dried in a vacuum.

2.2.6 Preparation of SCMNPs@BPy-SO₃H

1 g of SCMNPs@ThSCa-BPy was added to 20 mL of dry dichloromethane and ultrasonically dispersed for 30 min. Afterwards, 6 mmol of chlorosulfonic acid was slowly added to the reaction vessel and the achieved mixture was stirred in the ice bath for 6 h. Finally, these precipitates were isolated from the reaction solution with a permanent magnet, washed several times with distilled water, and dried in a vacuum oven at 50 °C for 15 h. All stages of the SCMNPs@BPy-SO₃H synthesis is shown in Scheme 1.

2.2.7 General process for the synthesis of pyran[2,3-c]pyrazoles (5)

A mixture of hydrazine hydrate (1 mmol), acetoacetic ester (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol) and SCMNPs@BPy-SO₃H (20 mg) was stirred at 80 °C under solvent-free conditions for the appropriate time. After completion of the reaction, the catalyst was removed using an external magnetic field and the achieved product was purified by recrystallization in aqueous ethanol.

2.2.8 General process for the synthesis of 2-amino-3-cyano-pyran[3,2-c]chromen-5(4H)-ones (7)

A mixture of 4-hydroxycoumarin (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol),
and SCMNPs@BPY-SO₃H (15 mg) was stirred at 80 °C under solvent-free conditions for the appropriate time. After completion of the reaction, the catalyst was removed using an external magnetic field and the achieved product was purified by re-crystallization in aqueous ethanol.

3. Results and Discussion

3.1 FTIR Analysis of SCMNPs@BPY-SO₃H

The FT-IR spectrum of the prepared Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂·PC, SCMNPs@ThSCa, SCMNPs@ThSCa-BPY, and SCMNPs@BPY-SO₃H is shown in Figure 1. In the spectrum of Fe₃O₄, the characteristic bands of the stretching vibration of the Fe-O-Fe and O-H were found at 575 cm⁻¹ and 3386 cm⁻¹, respectively. The FT-IR spectrum of the Fe₃O₄@SiO₂ showed associated absorption bands at 968 and 1065 cm⁻¹ due to Si-O-Si and Si-OH stretching vibrations, respectively. The FT-IR spectrum of the Fe₃O₄@SiO₂·PC exhibits a peak at 2978 cm⁻¹, which is attributed to the C-H stretching vibration mode. The C=S and N-H stretching vibrations of the SCMNPs@ThSCa could be observed at around 2334 cm⁻¹ and 3312 cm⁻¹, respectively. Additionally, the FT-IR spectrum shows a strong band at 1456 and 1638 cm⁻¹ due to the C=C and C=N stretching vibrations, respectively, revealing the functionalization of the magnetic cores with organic groups. In the case of SCMNPs@BPY-SO₃H, the bands at 1033 and 1142 cm⁻¹ can be attributed to SO₃H stretching vibration mode.

3.2 Thermal Analysis of SCMNPs@BPY-SO₃H

Thermogravimetric analysis spectrum of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂·PC, SCMNPs@ThSCa, SCMNPs@ThSCa-BPY and SCMNPs@BPY-SO₃H was surveyed using TGA under nitrogen atmosphere at 10 °C/min of heating rate. The results are shown in Figure 2. In the TGA graph of all of the samples, a weight loss of about 3% observed that is related to desorption of physically adsorbed water and dehydration of the surface hydroxyl groups. The TGA of Fe₃O₄@SiO₂·PC and SCMNPs@ThSCa undergoes other weight loss stages, which can be seen in the range between 330-460 °C, probably related to the elimination of attached 3-chloropropyltriethoxysilane (PC) and thiosemicarbazide (ThSCa) molecules. The TGA curves of SCMNPs@ThSCa-BPY and SCMNPs@BPY-SO₃H show distinct stages of weight loss at temperatures within the range of 330-450 °C, possibly attributed to the decomposition of attached functional groups to the Fe₃O₄ surface.

3.3 VSM Analysis of SCMNPs@BPY-SO₃H

To study the magnetic properties of the Fe₃O₄, Fe₃O₄@SiO₂, SCMNPs@ThSCa, and SCMNPs@BPY-SO₃H, magnetic measurements were done at room temperature by a vibrating sample magnetometer (VSM). As shown in VSM patterns (Figure 3), the saturation magnetization (Ms) of the Fe₃O₄ is 64.79 emu.g⁻¹, which is higher than Fe₃O₄@SiO₂ (52.34 emu.g⁻¹) and SCMNPs@ThSCa (48.65 emu.g⁻¹). This significant decrease in the Ms confirms the formation of the silica shell around the MNPs and organic groups on the surface of the SCMNPs. However, the saturation magnetization of SCMNPs@BPY-SO₃H was 37.68 emu.g⁻¹, which is lower than that of SCMNPs. This additional decrease in the value of Ms is due to the formation of organic and SO₃H groups on the surface of the Fe₃O₄.

3.4 EDX Analysis of SCMNPs@BPY-SO₃H

The presence of functionalized groups on the surface of magnetic nanoparticles was also confirmed by the energy-dispersive X-ray spectroscopy (EDX) spectra showing the presence of Fe, C, N, S, Si, and O elements in the
SCMNPs@BPy-SO₃H, as shown in Figure 4.

3.5 XRD Analysis of SCMNPs@BPy-SO₃H

The crystalline nature and surface state of the Fe₃O₄ and SCMNPs@BPy-SO₃H were confirmed by powder X-ray diffraction (XRD) (Figure 5). As shown, six characteristic peaks at 2θ = 31.56°, 36.26°, 42.75°, 53.25°, 56.87°, and 63.25° were observed in the XRD pattern of the Fe₃O₄, which are revealed to the reflection planes of (220), (311), (400), (422), (511), and (440) with crystalline cubic spinel structure (in good agreement with the XRD data of Joint Committee on Powder Diffraction Standards No. 19-0629). The XRD diffraction pattern of the SCMNPs@BPy-SO₃H was similar to the pure Fe₃O₄. Because of this analysis, the SCMNPs@BPy-SO₃H had been prepared successfully without any phase change in Fe₃O₄.

3.6 SEM Analysis of SCMNPs@BPy-SO₃H

The size and morphology of the Fe₃O₄ (A) and SCMNPs@BPy-SO₃H (B) were investigated to determine the variations in the surface of the magnetic nanoparticles by the scanning electron microscopy (SEM) analysis. As shown in Figure 6, prepared magnetic nanoparticles in all the samples have nearly a spherical structure indicating the nanoparticles with a large surface area. In this research, we reported our outcomes for the efficient and rapid preparation of pyrano[2,3-c]pyrazole and 2-amino-3-cyano-pyrano[3,2-c]chromen-5(4H)-one derivatives using SCMNPs@BPy-SO₃H as an efficient and reusable heterogeneous magnetic nanocatalyst under solvent-free conditions (Scheme 2).

Firstly, the catalytic efficiency of the SCMNPs@BPy-SO₃H was studied in the synthesis of pyrano[2,3-c]pyrazole derivatives. To discover the appropriate reaction conditions, a one-pot four-component condensation of hydrazine hydrate (1 mmol), acetoacetic ester (1 mmol), 4-chlorobenzaldehyde (1 mmol), and malononitrile (1 mmol) was selected and tested as a model reaction under different conditions. We used various solvents, such as: H₂O, EtOH, MeOH, CHCl₃, CH₂CN, CH₂Cl₂, and acetone under reflux conditions (Table 1, entries 1-7). These observations illustrated that the reaction performed in the absence of solvent serves as the best result according to the principles of green chemistry for this synthesis (Table 1, entry 12). Although, EtOH with respect to having a polarity compared to other nonpolar solvents used in this reaction gave a moderate yield of the product (Table 1, entry 2). For the synthesis completion, different amounts of the
SCMNPs@BPy-SO₃H (5, 8, 12, 16, 20, and 25 mg) examined that 20 mg of the nanocatalyst is sufficient (Table 1, entries 8-13). By increasing and decreasing the catalyst concentration, the final yields of the product were decreased to 92, 86, 75, 64, and 59%, respectively (Table 1, entries 8-11 and 13). To define the role of temperature as a factor accelerating the reaction, the model reaction was done using temperatures ranging from 25 to 100 °C (Table 1, entries 12 and 14-19). It was found that reaction in 80 °C led to a better yield of the desired product than others (Table 1, entry 12). Finally, when the model reaction was done in the presence of 20 mg of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-PC, SCMNPs@ThSCa, and SCMNPs@ThSCa-BPy under the optimized conditions, the final yields of the products were 78, 73, 68, 81, and 85, respectively (Table 1, entries 20-24).

In order to establish the efficiency of the optimum conditions (Table 1, Entry 12) in previously reported reactions, we surveyed the generality of this procedure with both electron-withdrawing and electron-donating aldehydes and the results are depicted in Table 2. All the investigated aldehydes afforded corresponding products in excellent yields and short reaction times.

Next, the catalyst efficiency of SCMNPs@BPy-SO₃H was surveyed in the one-pot three-component condensation of 4-hydroxycoumarin (1 mmol), 4-chlorobenzaldehyde (1 mmol), and malononitrile (1 mmol) for the preparation of 2-amino-

![Figure 5. The XRD patterns of Fe₃O₄ and SCMNPs@BPy-SO₃H.](image)

![Figure 6. SEM image of Fe₃O₄ (A) and SCMNPs@BPy-SO₃H (B).](image)

![Scheme 2. Synthesis of pyrano[2,3-c]pyrazole and 2-amino-3-cyano-pyrano[3,2-c]chromen-5(4H)-one derivatives using SCMNPs@BPy-SO₃H.](image)
4-(4-chlorophenyl)-5-oxo-4H,5H-pyran[3,2-c]chromene-3-carbonitrile. Optimization of the above-mentioned model reaction was performed under different conditions and the outcomes are presented in Table 3. To investigate the effect of various solvents, such as: H₂O, EtOH, MeOH, CHCl₃, CH₃CN, CH₂Cl₂, acetone, and solvent-free conditions (Table 3, entries 1-8), the model reaction was done in the presence of these solvents and the best outcome was achieved in the absence of solvent (Table 3, entry 8). To illustrate the importance of temperature in the model reaction, the reaction was performed under different temperatures ranging from 25 to 100 °C (Table 3, entries 8 and 12-14). The yields of the desired product were increased and the reaction times were decreased with increased temperature up to 80 °C (Table 3, entries 8 and 9-12). In addition, the results show that the use of 90 and 100 °C led to slight decreases compared to 80 °C in terms of the product yields (Table 3, entries 13-14). To discover the best amounts of catalyst on the model reaction, organic transformation was done in the presence of 5, 8, 12, 15, 20, and 25 mg of SCMNPs@BPy-SO₃H (Table 3, entries 8 and 15-20) and the highest yield of the product was achieved in the presence of 15 mg of catalyst (Table 3, entry 8). Also, when the model reaction was done in the presence of 15 mg of.

**Table 1. Optimization of one-pot four-component condensation of hydrazine hydrate, acetoacetic ester, 4-chlorobenzaldehyde, and malononitrile under different conditions.**

| Entry | Solvent | Catalyst (mg) | Temperature (°C) | Time (min) | Yield (%) |
|-------|---------|---------------|------------------|------------|-----------|
| 1     | H₂O     | 20            | reflux           | 50         | 64        |
| 2     | EtOH    | 20            | reflux           | 35         | 75        |
| 3     | MeOH    | 20            | reflux           | 60         | 56        |
| 4     | CHCl₃   | 20            | reflux           | 80         | 49        |
| 5     | CH₃CN   | 20            | reflux           | 75         | 51        |
| 6     | CH₂Cl₂  | 20            | reflux           | 80         | 45        |
| 7     | acetone | 20            | reflux           | 75         | 54        |
| 8     | ...     | 5             | 80               | 10         | 59        |
| 9     | ...     | 8             | 80               | 10         | 64        |
| 10    | ...     | 12            | 80               | 10         | 75        |
| 11    | ...     | 16            | 80               | 10         | 86        |
| 12    | ...     | 20            | 80               | 10         | 94        |
| 13    | ...     | 25            | 80               | 10         | 92        |
| 14    | ...     | 20            | 25               | 75         | 42        |
| 15    | ...     | 20            | 50               | 45         | 56        |
| 16    | ...     | 20            | 60               | 25         | 69        |
| 17    | ...     | 20            | 70               | 15         | 87        |
| 18    | ...     | 20            | 90               | 10         | 94        |
| 19    | ...     | 20            | 100              | 10         | 93        |
| 20    | ...     | Fe₃O₄ (20)    | 80               | 10         | 78        |
| 21    | ...     | Fe₃O₄@SiO₂ (20)| 80              | 10         | 73        |
| 22    | ...     | Fe₃O₄@SiO₂-PC (20)| 80      | 10         | 68        |
| 23    | ...     | SCMNPs@ThSCa (20)| 80          | 10         | 81        |
| 24    | ...     | SCMNPs@ThSCa-BPy (20)| 80      | 10         | 85        |

*Reaction conditions: hydrazine hydrate (1 mmol), acetoacetic ester (1 mmol), 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), and required amount of the catalysts. The yields refer to the isolated product. Copyright © 2020, BCREC, ISSN 1978-2993*
Table 2. Synthesis of pyrano[2,3-c] pyrazoles catalyzed by SCMNPs@BPy-\(\text{SO}_3\)H.\(^a\)

| Entry | Product | Aldehyde (3) | Product | Time (min) | Yield (%)\(^b\) | M.P (Obsd) (°C) | M.P (Lit) (°C) |
|-------|---------|-------------|---------|------------|----------------|----------------|----------------|
| 1     | 5a      | ![Image of Aldehyde (3)] | ![Image of Product] | 12         | 91             | 239-242        | 244-245\(^{56}\) |
| 2     | 5b      | ![Image of Aldehyde (3)] | ![Image of Product] | 10         | 94             | 230-232        | 233-234\(^{56}\) |
| 3     | 5c      | ![Image of Aldehyde (3)] | ![Image of Product] | 15         | 90             | 229-231        | 230-232\(^{56}\) |
| 4     | 5d      | ![Image of Aldehyde (3)] | ![Image of Product] | 12         | 93             | 221-223        | 222-224\(^{57}\) |
| 5     | 5e      | ![Image of Aldehyde (3)] | ![Image of Product] | 15         | 92             | 197-199        | 191\(^{58}\) |
| 6     | 5f      | ![Image of Aldehyde (3)] | ![Image of Product] | 12         | 95             | 201-203        | 195\(^{58}\) |
| 7     | 5g      | ![Image of Aldehyde (3)] | ![Image of Product] | 15         | 94             | 209-211        | 240-242\(^{59}\) |
| 8     | 5h      | ![Image of Aldehyde (3)] | ![Image of Product] | 20         | 90             | 253-255        | 259-261\(^{54}\) |
| 9     | 5i      | ![Image of Aldehyde (3)] | ![Image of Product] | 15         | 93             | 192-194        | 179-180\(^{59}\) |
Table 2. ... (continued)

| Entry | Product | Aldehyde (3) | Product | Time (min) | Yield (%) | M.P.(Obsd) (°C) | M.P.(Lit) (°C) |
|-------|---------|--------------|---------|------------|------------|-----------------|----------------|
| 10    | 5j      | ![Product](image1) | ![Product](image2) | 20         | 91         | 221-224         | 223-226\(^{61}\) |
| 11    | 5k      | ![Product](image3) | ![Product](image4) | 25         | 87         | 245-247         | 248-249\(^{20}\) |
| 12    | 5l      | ![Product](image5) | ![Product](image6) | 25         | 89         | 239-241         | 234-236\(^{60}\) |
| 13    | 5m      | ![Product](image7) | ![Product](image8) | 15         | 92         | 257-259         | 260-263\(^{34}\) |
| 14    | 5n      | ![Product](image9) | ![Product](image10) | 15         | 94         | 179-181         | 174\(^{58}\) |
| 15    | 5o      | ![Product](image11) | ![Product](image12) | 15         | 91         | 199-201         | 195\(^{58}\) |
| 16    | 5p      | ![Product](image13) | ![Product](image14) | 15         | 92         | 182-185         | 170-172\(^{56}\) |
| 17    | 5q      | ![Product](image15) | ![Product](image16) | 20         | 90         | 217-219         | 191\(^{62}\) |
| 18    | 5r      | ![Product](image17) | ![Product](image18) | 20         | 91         | 221-224         | 223-225\(^{20}\) |

\(^{a}\)Reaction conditions: hydrazine hydrate (1 mmol), acetoacetic ester (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol), and required amount of the catalysts. \(^{b}\)The yields refer to the isolated product.
**Table 3.** Optimization of one-pot three-component condensation of 4-hydroxycoumarin, 4-chlorobenzaldehyde, and malononitrile, under different conditions.

| Entry | Solvent | Catalyst (mg) | Temperature (°C) | Time (min) | Yield (%) |
|-------|---------|---------------|-----------------|------------|-----------|
| 1     | H₂O     | 15            | Reflux          | 40         | 73        |
| 2     | EtOH    | 15            | Reflux          | 35         | 81        |
| 3     | MeOH    | 15            | Reflux          | 45         | 70        |
| 4     | CHCl₃   | 15            | Reflux          | 60         | 59        |
| 5     | CH₂CN   | 15            | Reflux          | 60         | 54        |
| 6     | CH₂Cl₂  | 15            | Reflux          | 60         | 48        |
| 7     | acetone | 15            | Reflux          | 60         | 52        |
| 8     |         | 15            | 80              | 15         | 97        |
| 9     |         | 15            | 25              | 70         | 42        |
| 10    |         | 15            | 50              | 55         | 76        |
| 11    |         | 15            | 60              | 45         | 84        |
| 12    |         | 15            | 70              | 20         | 91        |
| 13    |         | 15            | 90              | 15         | 96        |
| 14    |         | 15            | 100             | 15         | 93        |
| 15    |         | 5             | 80              | 15         | 62        |
| 16    |         | 8             | 80              | 15         | 71        |
| 17    |         | 12            | 80              | 15         | 89        |
| 19    |         | 20            | 80              | 15         | 95        |
| 20    |         | 25            | 80              | 15         | 91        |
| 21    |         | Fe₃O₄(15)     | 80              | 15         | 81        |
| 22    |         | Fe₃O₄@SiO₂(15)| 80              | 15         | 75        |
| 23    |         | Fe₃O₄@SiO₂-PC (15) | 80 | 15 | 73 |
| 24    |         | SCMNPs@ThSCa (15) | 80 | 15 | 84 |
| 25    |         | SCMNPs@ThSCa-BPy (15) | 80 | 15 | 87 |

*Reaction conditions: 4-hydroxycoumarin (1 mmol), 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), and required amount of the catalysts. The yields refer to the isolated product.*
### Table 4. Synthesis of 2-amino-3-cyano-pyran[3,2-c]chromen-5(4H)-ones using SCMNPs@BPy-\(\text{SO}_3\text{H}\) as a catalyst.\(^a\)

| Entry | Product | Aldehyde (3) | Product | Time (min) | Yield (%)\(^b\) | M.P(Obtd) (°C) | M.P (Ref) (°C) |
|-------|---------|--------------|---------|------------|----------------|----------------|----------------|
| 1     | 7a      |             | 7a      | 25         | 95             | 251-253        | 256-258\(^{63}\) |
| 2     | 7b      | F            | 7b      | 18         | 97             | 254-256        | 260-262\(^{63}\) |
| 3     | 7c      | O\(_2\)N     | 7c      | 25         | 95             | 269-271        | 260-262\(^{64}\) |
| 4     | 7d      | O\(_2\)N     | 7d      | 15         | 94             | 242-244        | 250-252\(^{64}\) |
| 5     | 7e      | Cl           | 7e      | 15         | 95             | 238-240        | 244-246\(^{65}\) |
| 6     | 7f      | Cl           | 7f      | 15         | 97             | 259-261        | 263-265\(^{66}\) |
| 7     | 7g      | N            | 7g      | 25         | 92             | 260-262        | 265-267\(^{63}\) |
| 8     | 7h      | OH           | 7h      | 20         | 96             | 249-252        | 259-261\(^{67}\) |
| 9     | 7i      | OMe          | 7i      | 25         | 95             | 235-237        | 236-238\(^{68}\) |
| 10    | 7j      | MeO          | 7j      | 30         | 95             | 232-235        | 242-244\(^{69}\) |

\(^a\) Synthesis of 2-amino-3-cyano-pyran[3,2-c]chromen-5(4H)-ones using SCMNPs@BPy-\(\text{SO}_3\text{H}\) as a catalyst.

\(^b\) Yield is reported as the percentage of the product obtained relative to the starting material.
| Entry | Product | Aldehyde (3) | Product | Time (min) | Yield (%)<sup>b</sup> | M.P (Obtd) (°C) | M.P (Ref) (°C) |
|-------|---------|--------------|---------|------------|----------------|----------------|----------------|
| 11    | 7k      | ![Aldehyde](image) | ![Product](image) | 35         | 95             | 225-227        | 221-223<sup>65</sup> |
| 12    | 7l      | ![Aldehyde](image) | ![Product](image) | 25         | 93             | 262-264        | 260-262<sup>63</sup> |
| 13    | 7m      | ![Aldehyde](image) | ![Product](image) | 25         | 92             | 250-252        | 252-254<sup>63</sup> |
| 14    | 7n      | ![Aldehyde](image) | ![Product](image) | 30         | 92             | 229-232        | 228-230<sup>63</sup> |
| 15    | 7o      | ![Aldehyde](image) | ![Product](image) | 25         | 96             | 257-259        | 253-254<sup>70</sup> |

<sup>a</sup>Reaction conditions: 4-hydroxycoumarin (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol), and required amount of the catalysts.

<sup>b</sup>The yields refer to the isolated product.
Scheme 3. A plausible mechanism for the preparation of pyrano[2,3-c]pyrazole 5 and pyrano[3,2-c]chromen 7 derivatives catalyzed by SCMNPs@BPy-SO$_3$H.
ic field. The recovered SCMNPs@BPy-SO$_3$H nanoparticles were rinsed several times with water/ethanol (1:1), oven-dried at 50 °C for 24 h, and reused for six runs with a slight decrease in catalytic activity (Figure 7).

To assess the efficiency of this catalytic system, the achieved outcome for the synthesis of 6-amino-4-(4-chlorophenyl)-3-methyl-1,3a,4,7a-tetrahydropyran0[2,3-c]pyrazole-5-carbonitrile and 2-amino-4-(4-chlorophenyl)-5-oxo-4H,5H-pyran0[3,2-c]chromene-3-carbonitrile derivatives by this strategy was compared with those of the previously reported homogeneous and heterogeneous catalysts in the literature. As shown in Table 5, the use of SCMNPs@BPy-SO$_3$H leads to an improved procedure in terms of reaction time, catalyst amount, product yield, and compatibility with the environment.

![Figure 7](image.png)

**Figure 7.** Recycling of SCMNPs@BPy-SO$_3$H in the synthesis of 6-amino-4-(4-chlorophenyl)-3-methyl-1,3a,4,7a-tetrahydropyran0[2,3-c]pyrazole-5-carbonitrile (a) and 2-amino-4-(4-chlorophenyl)-5-oxo-4H,5H-pyran0[3,2-c]chromene-3-carbonitrile (b) derivatives.

### 4. Conclusion

We described an effective, easy, and eco-friendly strategy for a wide range of biologically and pharmacologically interesting diverse functionalized pyrano[2,3-c]pyrazole and 2-amino-3-cyano-pyran0[3,2-c]chromen-5(4H)-one derivatives in the presence of an environmentally friendly and reusable heterogeneous magnetic nanocatalyst (SCMNPs@BPy-SO$_3$H) via an eco-friendly multicomponent reaction under solvent-free conditions. This strategy has various merits, including lower loading of the catalyst, the usage of a green catalyst, easy work-up, no organic solvent, and excellent yields.

### Table 5. Comparison of the current strategy with other reported procedures for synthesizing 6-amino-4-(4-chlorophenyl)-3-methyl-1,3a,4,7a-tetrahydropyran0[2,3-c]pyrazole-5-carbonitrile and 2-amino-4-(4-chlorophenyl)-5-oxo-4H,5H-pyran0[3,2-c]chromene-3-carbonitrile derivatives.

| Entry | Catalyst and Conditions | Reaction time (min) | Yield (%) | Ref. |
|-------|-------------------------|---------------------|-----------|------|
| 1     | Ba(OH)$_2$/H$_2$O/Reflux | 90                  | 93        | [38] |
| 2     | CTACl/H$_2$O/90 °C      | 240                 | 88        | [43] |
| 3     | MorT/EtOH:H$_2$O/Reflux | 540                 | 92        | [37] |
| 4     | γ-Alumina/H$_2$O/Reflux | 35                  | 90        | [32] |
| 5     | Isonicotinic acid/---/85 °C | 10                 | 90        | [34] |
| 6     | SCMNPs@BPy-SO$_3$H/---/80 °C | 20                 | 94        | This work |
| 7     | CuO nanoparticles/H$_2$O/100 °C | 6               | 93        | [71] |
| 8     | [Sipim]HSO$_3$/100 °C  | 30                  | 90        | [72] |
| 9     | ZnO NPs/EtOH/Reflux    | 10                  | 80        | [73] |
| 10    | SDS/H$_2$O/60 °C       | 150                 | 88        | [63] |
| 11    | Nano AlO$_2$/EtOH      | 300                 | 89        | [74] |
| 12    | SCMNPs@BPy-SO$_3$H/---/80 °C | 15               | 97        | This work |

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