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Research Article

One-Pot Access to Diverse Functionalized Pyran Annulated Heterocyclic Systems Using SCMNPs@BPy-SO_3H as a Novel Magnetic Nanocatalyst

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Abstract

The SCMNPs@BPy-SO_3H 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(4*H*)-one derivatives. The strategy resulted in the desired products with excellent yields and short reaction times. The SCMNPs@BPy-SO_3H catalyst was readily recovered using a permanent magnetic field and it was reused in six runs with a slight decrease in catalytic activity. Copyright © 2020 BCREC Group. All rights reserved

Keywords: Multicomponent reaction; Solvent-free conditions; Magnetic nanocatalyst; SCMNPs@BPy-SO_3H, pyrano[2,3-*c*]pyrazole; 2-amino-3-cyano-pyrano[3,2-*c*]chromen-5(4*H*)-one

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1. Introduction

In the last decade, considerable attention has been paid to the synthesis of Fe_3O_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_3O_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 acetoacetate, and malononitrile. Some catalysts have been utilized to perform this reaction, such as: DABCO [30], meglumine [31], γ-alumina [32], ionic liquid [33], isonicotinic acid [34], triethylamine [35-36], morpholine triflate (MorT) [37], $Ba(OH)_2$ [38], glycine [39], $Fe_3O_4@SiO_2$-HMTA-SO_3H [40], per-6-amino-β-cyclodextrin (per-6-ABCD) [41], triethylamine [42], cetyltrimethyleammonium chloride (CTACl) [43], urea [44], β-Cyclodextrine-pichlorohydrin [45], molecular sieves [46], and SnO_2 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], ionic liquids [51], MGO [52], Mg/La mixed metal oxides [53], nanosilica [54], and $H_6P_2W_{18}O_{62}.18H_2O$ [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 PXI 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 Fe_3O_4 nanoparticles

In a typical method, a solution of $FeCl_2.4H_2O$ (4.27 g) and $FeCl_3.6H_2O$ (11.65 g) salts was dissolved in 150 mL deionized water and stirred under nitrogen atmosphere at 70 °C. Then, 15 mL NH_4OH (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-$Fe_3O_4@SiO_2$ core shells

The 1 g of Fe_3O_4 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 NH_4OH (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 $Fe_3O_4@SiO_2$-PC magnetic nanoparticles

2 g of $Fe_3O_4@SiO_2$ 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 $Fe_3O_4@SiO_2$-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 rinsed several times to remove the unreacted chemicals; it was then dried in a vacuum.

2.2.6 Preparation of SCMNPs@BPy-SO_3H

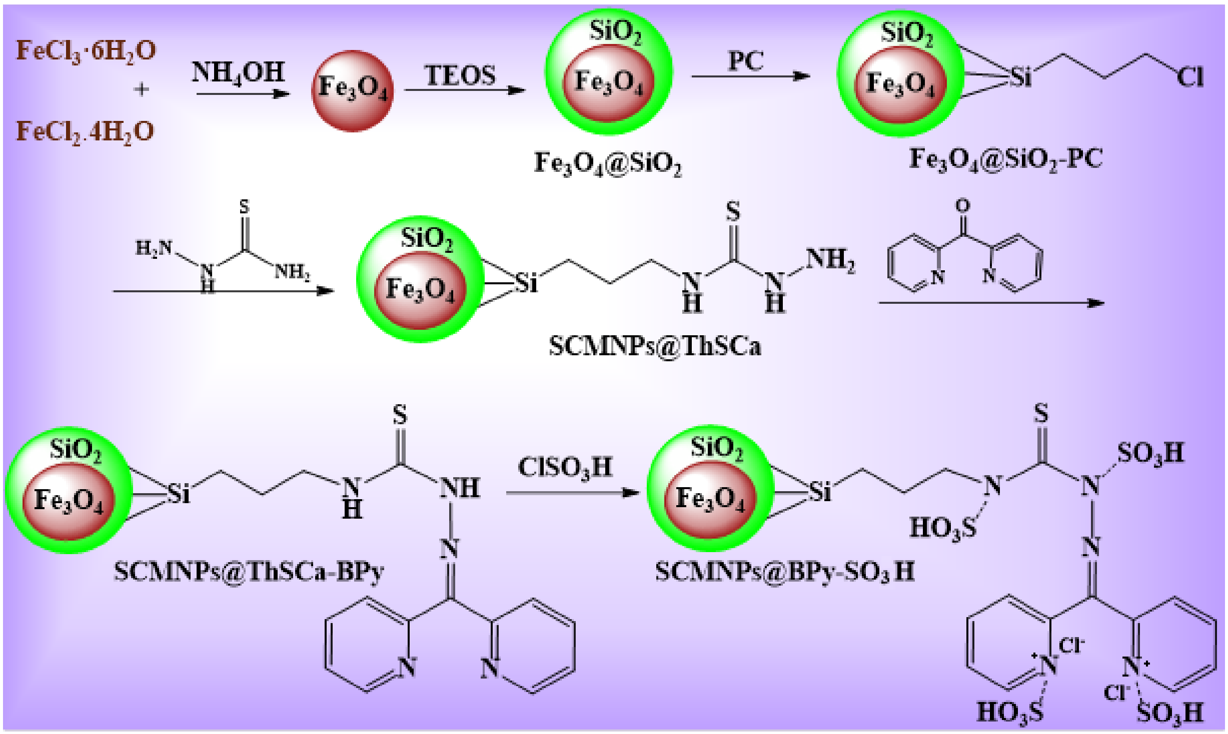
1 g of SCMNPs@ThSCa-BPy was added to 20 mL of dry dichloromethane and ultrasonically dispersed for 30 min. Afterwards, 6 mmol of chlorosulfonic acid was slowly added to the reaction vessel and the achieved mixture was stirred in the ice bath for 6 h. Finally, these precipitates were isolated from the 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-SO_3H synthesis is shown in Scheme 1.

2.2.7 General process for the synthesis of pyrano[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-SO_3H (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-pyrano[3,2-*c*]chromen-5(4*H*)-ones (7)

A mixture of 4-hydroxycoumarin (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol),



Scheme 1. All stages of the SCMNPs@BPy-SO_3H synthesis.

and SCMNPs@BPy-SO_3H (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-SO_3H

The FT-IR spectrum of the prepared Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-PC, SCMNPs@ThSCa, SCMNPs@ThSCa-BPy, and SCMNPs@BPy-SO_3H is shown in Figure 1. In the spectrum of Fe_3O_4, 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 Fe_3O_4@SiO_2 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 Fe_3O_4@SiO_2-PC exhibits a peak at 2978 cm^{-1} that is indexed 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-SO_3H, the bands at 1033 and 1142 cm^{-1} can be attributed to SO_3H stretching vibration mode.

3.2 Thermal Analysis of SCMNPs@BPy-SO_3H.

Thermogravimetric analysis spectrum of Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-PC, SCMNPs@ThSCa, SCMNPs@ThSCa-BPy and SCMNPs@BPy-SO_3H 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 Fe_3O_4@SiO_2-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-SO_3H show distinct stages of weight loss at temperatures within the range of 330-450 ℃, possibly attributed to the decomposition of attached functional groups to the Fe_3O_4 surface.

3.3 VSM Analysis of SCMNPs@BPy-SO_3H

To study the magnetic properties of the Fe_3O_4, Fe_3O_4@SiO_2, SCMNPs@ThSCa, and SCMNPs@BPy-SO_3H, 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 Fe_3O_4 is 64.79 emu.g^{-1}, which is higher than Fe_3O_4@SiO_2 (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-SO_3H 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 SO_3H groups on the surface of the Fe_3O_4.

3.4 EDX Analysis of SCMNPs@BPy-SO_3H

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

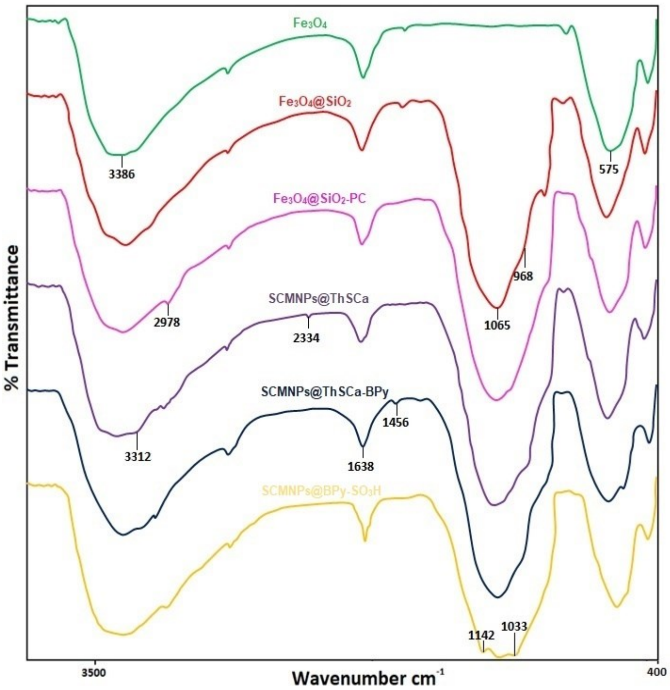


Figure 1. FTIR spectra of Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-PC, SCMNPs@ThSCa, SCMNPs@ThSCa-BPy, and SCMNPs@BPy-SO_3H.

SCMNPs@BPy-SO_3H, as shown in Figure 4.

3.5 XRD Analysis of SCMNPs@BPy-SO_3H

The crystalline nature and surface state of the Fe_3O_4 and SCMNPs@BPy-SO_3H 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 Fe_3O_4, which are revealed to the reflection planes of (220), (311), (400), (422), (511), and (440) with crystalline cubic spinel structure (in a good agreement with the XRD data of Joint Committee on Powder Diffraction Standards No. 19-0629). The XRD-diffraction pattern of the SCMNPs@BPy-SO_3H was similar to the pure Fe_3O_4. Because of this analysis, the SCMNPs@BPy-SO_3H had been prepared successfully without any phase change in Fe_3O_4.

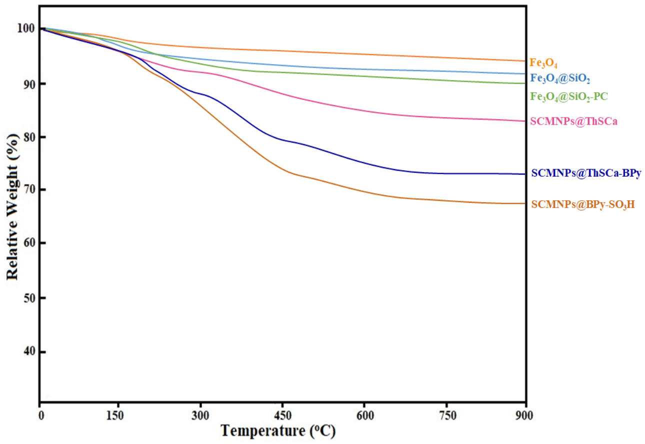


Figure 2. TGA graphs of Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-PC, SCMNPs@ThSCa, SCMNPs@ThSCa-BPy, and SCMNPs@BPy-SO_3H.

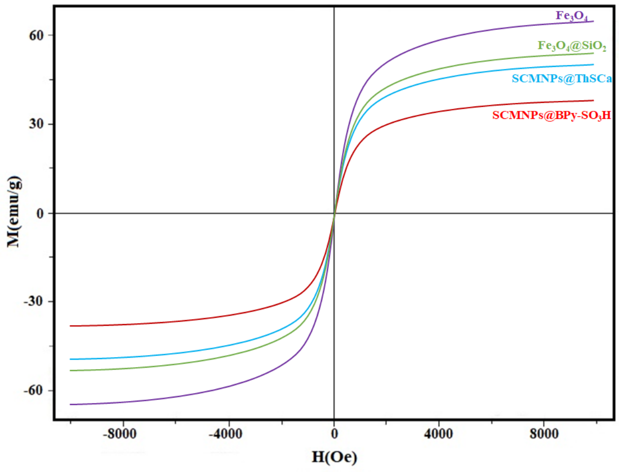


Figure 3. VSM patterns of Fe_3O_4, Fe_3O_4@SiO_2, SCMNPs@ThSCa, and SCMNPs@BPy-SO_3H.

3.6 SEM Analysis of SCMNPs@BPy-SO_3H

The size and morphology of the Fe_3O_4 (A) and SCMNPs@BPy-SO_3H (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(4*H*)-one derivatives using SCMNPs@BPy-SO_3H as an efficient and reusable heterogeneous magnetic nanocatalyst under solvent-free conditions (Scheme 2).

Firstly, the catalytic efficiency of the SCMNPs@BPy-SO_3H 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: H_2O, EtOH, MeOH, $CHCl_3$, CH_3CN, CH_2Cl_2, 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

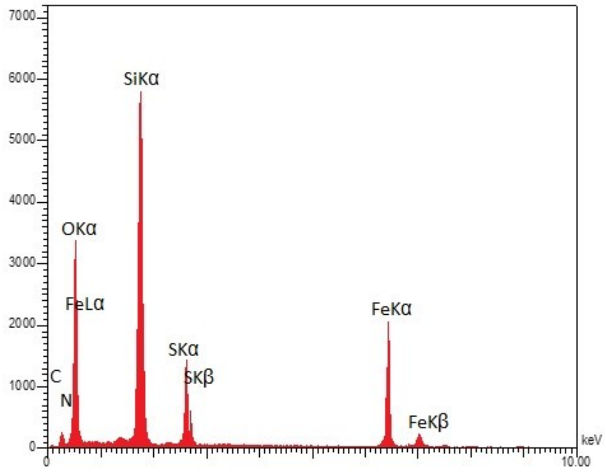


Figure 4. EDX spectra of SCMNPs@BPy-SO_3H.

SCMNPs@BPy-SO_3H (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 Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-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).

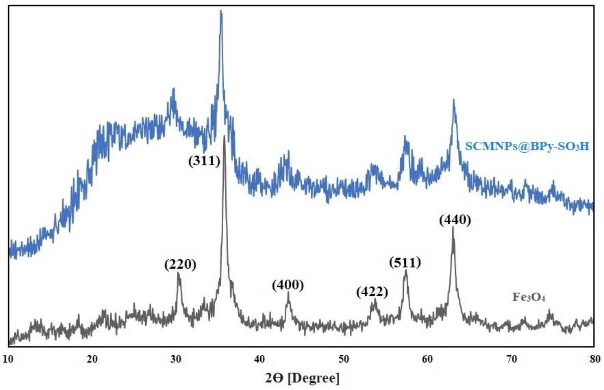


Figure 5. The XRD patterns of Fe_3O_4 and SCMNPs@BPy-SO_3H.

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-SO_3H 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-

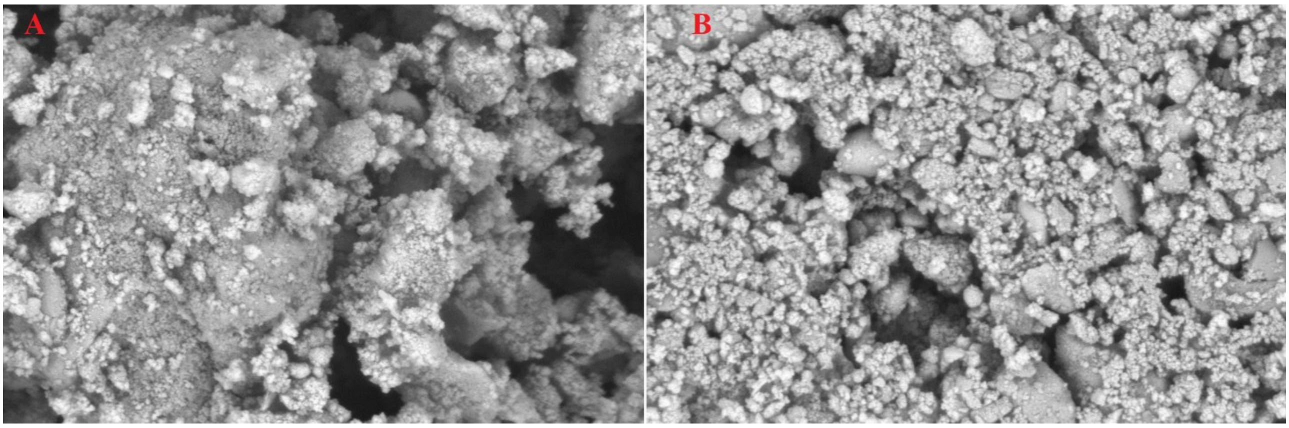
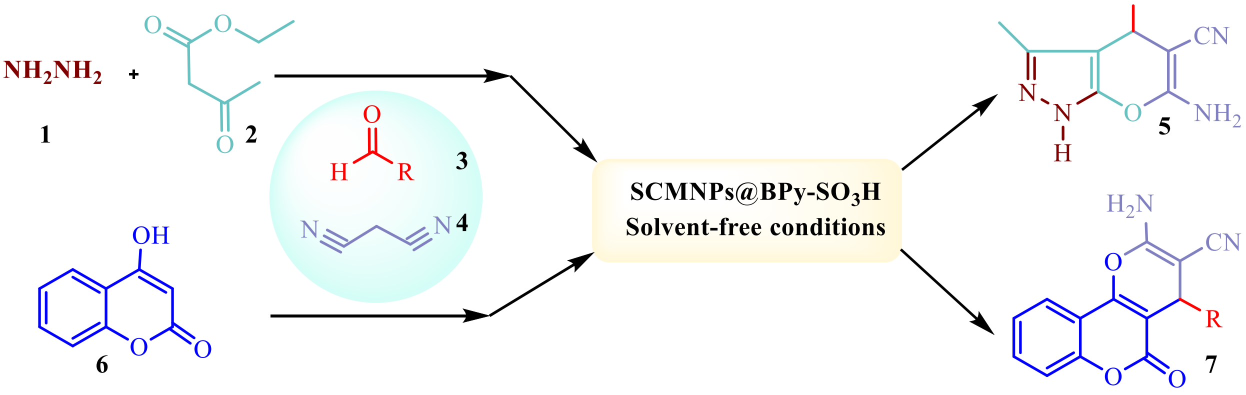


Figure 6. SEM image of Fe_3O_4 (A) and SCMNPs@BPy-SO_3H (B).



Scheme 2. Synthesis of pyrano[2,3-*c*]pyrazole and 2-amino-3-cyano-pyrano[3,2-*c*]chromen-5(4*H*)-one derivatives using SCMNPs@BPy-SO_3H.

4-(4-chlorophenyl)-5-oxo-4*H*,5*H*-pyrano[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: H_2O, EtOH, MeOH, $CHCl_3$, CH_3CN, CH_2Cl_2, 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 9-14). 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-SO_3H (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.[a]

Entry	Solvent	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)[b]
1	H_2O	20	Reflux	50	64
2	EtOH	20	Reflux	35	75
3	MeOH	20	Reflux	60	56
4	$CHCl_3$	20	Reflux	80	49
5	CH_3CN	20	Reflux	75	51
6	CH_2Cl_2	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	---	Fe_3O_4 (20)	80	10	78
21	---	Fe_3O_4@SiO_2 (20)	80	10	73
22	---	Fe_3O_4@SiO_2-PC (20)	80	10	68
23	---	SCMNPs@ThSCa (20)	80	10	81
24	---	SCMNPs@ThSCa-BPy (20)	80	10	85

[a]Reaction conditions: hydrazine hydrate (1 mmol), acetoacetic ester (1 mmol), 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), and required amount of the catalysts. [b]The yields refer to the isolated product.

Table 2. Synthesis of pyrano[2,3-*c*] pyrazoles catalyzed by SCMNPs@BPy-SO$_3$H.[a]

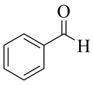
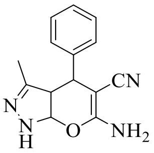
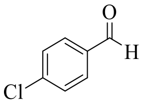
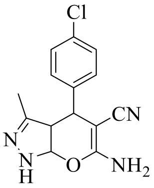
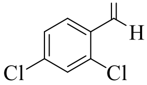
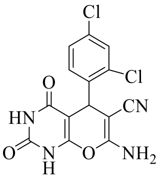
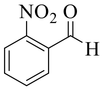
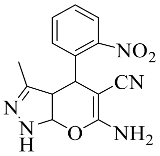
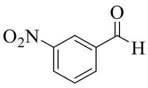
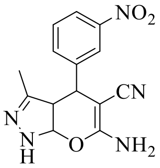
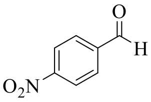
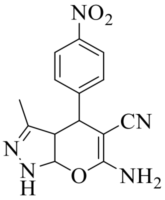
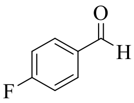
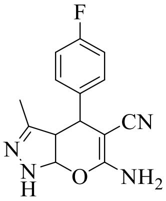
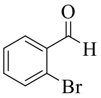
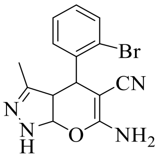
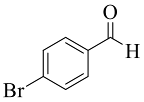
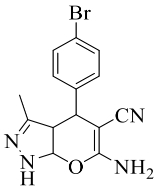
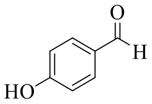
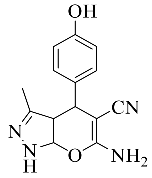
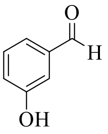
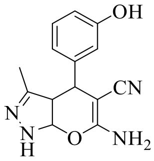
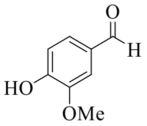
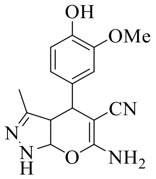
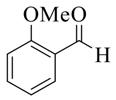
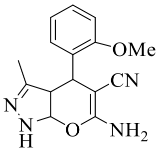
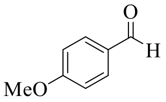
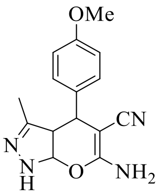
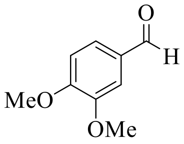
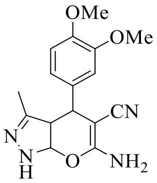
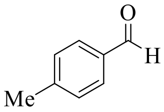
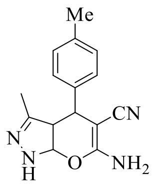
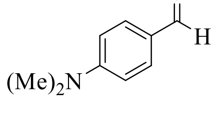
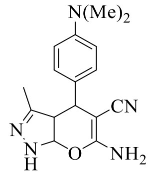
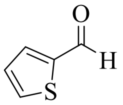
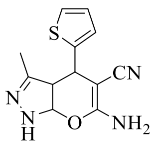
Entry	Product	Aldehyde (3)	Product	Time (min)	Yield (%)[b]	M.P(Obsd) (°C)	M.P (Lit) (°C)
1	**5a**			12	91	239-242	244-245[56]
2	**5b**			10	94	230-232	233-234[56]
3	**5c**			15	90	229-231	230-232[56]
4	**5d**			12	93	221-223	222-224[57]
5	**5e**			15	92	197-199	191[58]
6	**5f**			12	95	201-203	195[58]
7	**5g**			15	94	209-211	240-242[59]
8	**5h**			20	90	253-255	259-261[34]
9	**5i**			15	93	192-194	179-180[59]

Table 2. … (continued)

Entry	Product	Aldehyde (3)	Product	Time (min)	Yield (%)[b]	M.P(Obsd) (°C)	M.P (Lit) (°C)
10	**5j**			20	91	221-224	223-226[61]
11	**5k**			25	87	245-247	248-249[20]
12	**5l**			25	89	239-241	234-236[60]
13	**5m**			15	92	257-259	260-263[34]
14	**5n**			15	94	179-181	174[58]
15	**5o**			15	91	199-201	195[58]
16	**5p**			15	92	182-185	170-172[56]
17	**5q**			20	90	217-219	191[62]
18	**5r**			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.

Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-PC, SCMNPs@ThSCa, SCMNPs@ThSCa-BPy, and SCMNPs@BPy-SO_3H under the optimized conditions, the final yields of the product were 81, 75, 73, 84, and 87, respectively (Table 1, entries 21-25). After optimization of the reaction conditions for the model reaction, various 2-amino-3-cyano-pyrano[3,2-*c*]chromen-5(4*H*)-ones were prepared with an array of aromatic aldehydes bearing either electron-withdrawing or electron-donating substituents by this procedure (Table 4).

The plausible mechanism for the synthesis of pyrano[2,3-*c*]pyrazole and pyrano[3,2-*c*]chromen derivatives is shown in Scheme 3. In both cases, benzylidenemalononitrile **8** was achieved because of a Knoevenagel condensation between activated carbonyl group of aldehyde **3** by the SCMNPs@BPy-SO_3H nanocatalyst and malononitrile **4**. In the case of pyrano[2,3-*c*]pyrazole derivatives, hydrazine hydrate **1** reacted with activated carbonyl group of acetoacetic ester **2** by the catalyst to form pyrazolone **9** via condensation reaction. After that, activated benzylidenemalononitrile **8** by the catalyst condense with 4-hydroxycoumarin **6** and pyrazolone **9** through Michael addition. The obtained **10** and **11** intermediates from these additions undergo cyclization and tautomerization (**12** and **13**) to develop the desired products **5** and **7**.

The recyclability potential of SCMNPs@BPy-SO_3H was tested for the synthesis of 6-amino-4-(4-chlorophenyl)-3-methyl-1,3a,4,7a-tetrahydropyrano[2,3-*c*]pyrazole-5-carbonitrile (a) and 2-amino-4-(4-chlorophenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile (b) under the optimized conditions. Upon detection of reaction completion of the appeared product stain on the TLC, the catalyst was filtered out from the reaction solution using an appropriate magnet-

Table 3. Optimization of one-pot three-component condensation of 4-hydroxycoumarin, 4-chlorobenzaldehyde, and malononitrile, under different conditions.[a]

Entry	Solvent	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)[b]
1	H_2O	15	Reflux	40	73
2	EtOH	15	Reflux	35	81
3	MeOH	15	Reflux	45	70
4	$CHCl_3$	15	Reflux	60	59
5	CH_3CN	15	Reflux	60	54
6	CH_2Cl_2	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	---	Fe_3O_4 (15)	80	15	81
22	---	Fe_3O_4@SiO_2 (15)	80	15	75
23	---	Fe_3O_4@SiO_2-PC (15)	80	15	73
24	---	SCMNPs@ThSCa (15)	80	15	84
25	---	SCMNPs@ThSCa-BPy (15)	80	15	87

[a] Reaction conditions: 4-hydroxycoumarin (1 mmol), 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), and required amount of the catalysts. [b] The yields refer to the isolated product.

Table 4. Synthesis of 2-amino-3-cyano-pyrano[3,2-*c*]chromen-5(4*H*)-ones using SCMNPs@BPy-SO_3H as a catalyst.[a]

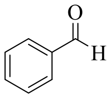
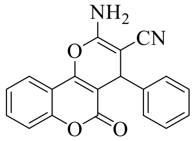
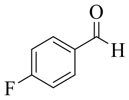
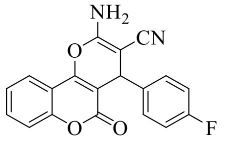
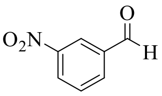
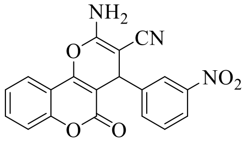
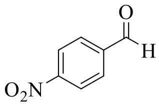
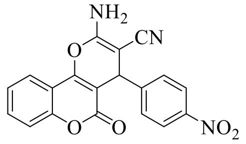
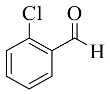
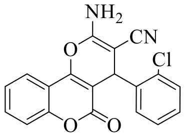
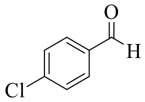
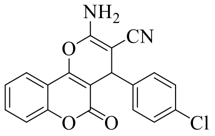
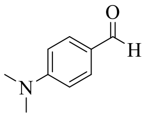
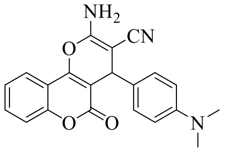
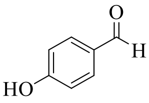
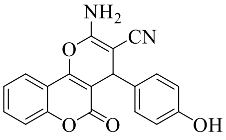
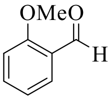
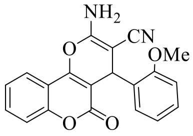
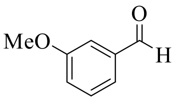
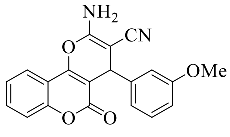
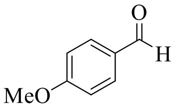
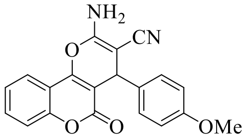
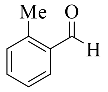
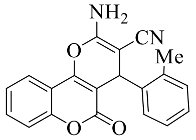
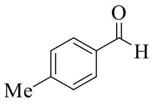
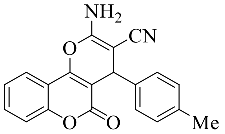
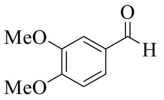
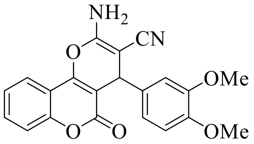
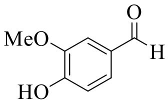
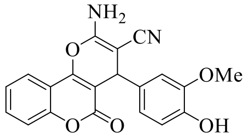
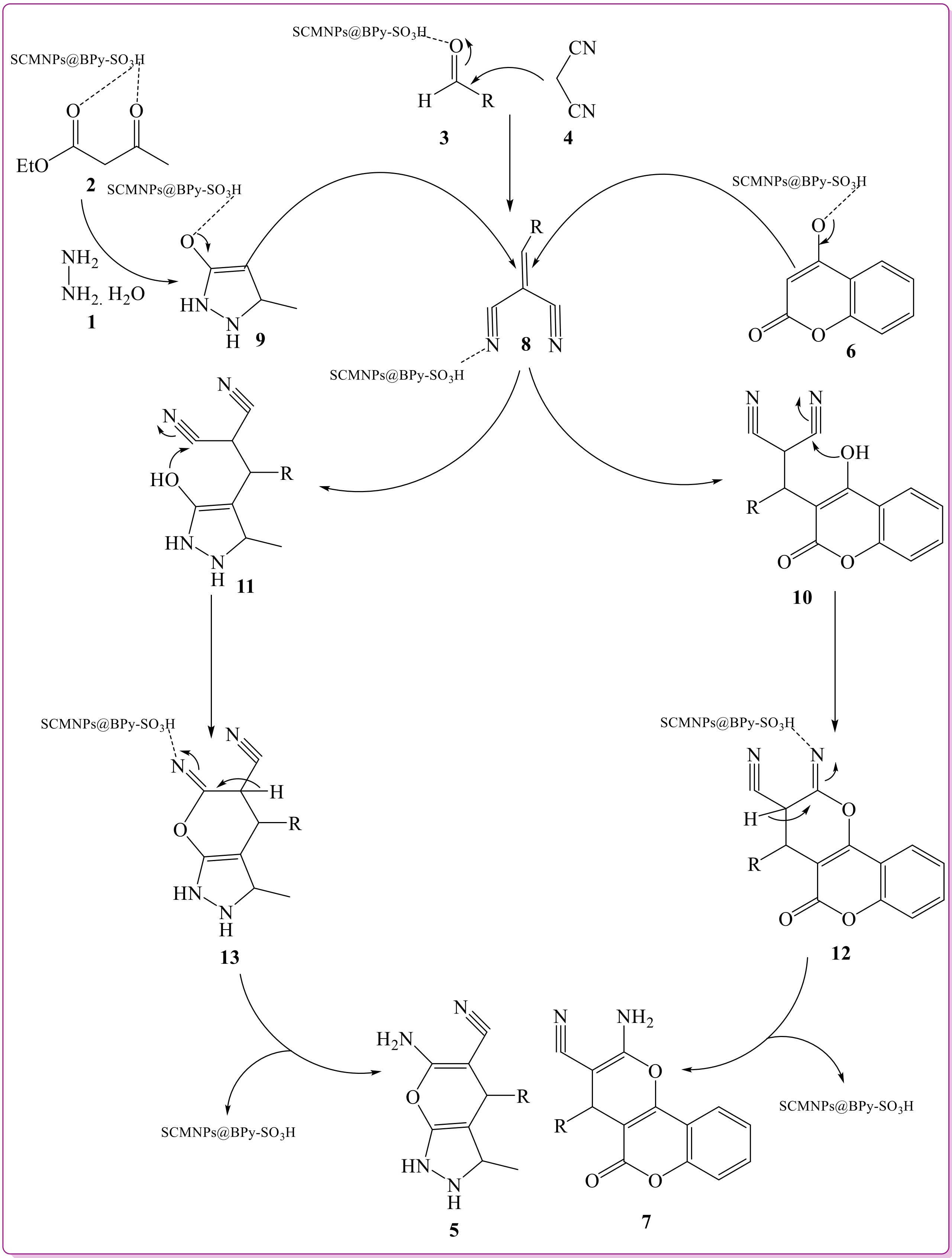
Entry	Product	Aldehyde (3)	Product	Time (min)	Yield (%)[b]	M.P(Obtd) (°C)	M.P (Ref) (°C)
1	**7a**			25	95	251-253	256-258[63]
2	**7b**			18	97	254-256	260-262[63]
3	**7c**			25	95	269-271	260-262[64]
4	**7d**			15	94	242-244	250-252[64]
5	**7e**			15	95	238-240	244-246[65]
6	**7f**			15	97	259-261	263-265[66]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

Table 4. … (continued)

Entry	Product	Aldehyde (3)	Product	Time (min)	Yield (%)^b	M.P(Obtd) (°C)	M.P (Ref) (°C)
11	**7k**			35	95	225-227	221-223[65]
12	**7l**			25	93	262-264	260-262[63]
13	**7m**			25	92	250-252	252-254[63]
14	**7n**			30	92	229-232	228-230[63]
15	**7o**			25	96	257-259	253-254[70]

[a]Reaction conditions: 4-hydroxycoumarin (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol), and required amount of the catalysts. [b]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-tetrahydropyrano[2,3-*c*]pyrazole-5-carbonitrile and 2-amino-4-(4-chlorophenyl)-5-oxo-4*H*,5*H*-pyrano[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.

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-pyrano[3,2-*c*]chromen-5(4*H*)-one derivatives in the presence of an environmental 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.

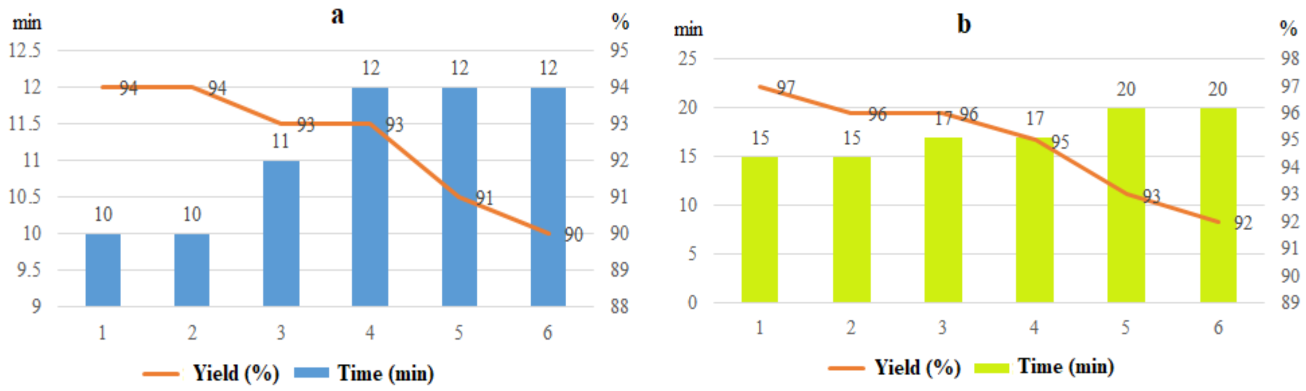
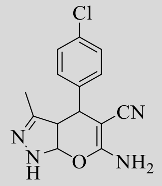
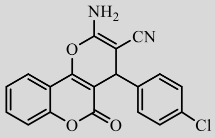


Figure 7. Recycling of SCMNPs@BPy-SO$_3$H in the synthesis of 6-amino-4-(4-chlorophenyl)-3-methyl-1,3a,4,7a-tetrahydropyrano[2,3-*c*]pyrazole-5-carbonitrile (a) and 2-amino-4-(4-chlorophenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile (b) derivatives.

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

	Entry	Catalyst and Conditions	Reaction time (min)	Yield (%)^b	Ref.
 (entries 1-6)	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
 (entries 7-12)	7	CuO nanoparticles/H$_2$O/100 °C	6	93	[71]
	8	[Sipim]HSO$_4$/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 Al$_2$O$_3$/EtOH	300	89	[74]
	12	SCMNPs@BPy-SO$_3$H/---/80 °C	15	97	This work

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