

Solvent-free synthesis of 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1*H* benzo[*f*]chromene-2-carbonitrile derivatives by Fe₃O₄@enamine-B(OSO₃H)₂ as an efficient and novel heterogeneous magnetic nanostructure catalyst

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A green procedure for the one-pot three-component synthesis of 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1*H* benzo[*f*]chromene-2-carbonitrile derivatives from the reaction of 2-naphthol, aldehydes, and malononitrile/acetamide in the presence of a catalytic amount of Fe₃O₄@enamine-B(OSO₃H)₂ as an efficient and novel heterogeneous magnetic nanostructure catalyst is described. The catalyst was characterized using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), vibrating sample magnetometry (VSM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). These strategies possess some merits such as simple work-up method, easy preparation of the catalyst, short reaction times, good-to-high yields, and non-use of hazardous solvents during all steps of the reactions. Moreover, due to the magnetic nature of the catalyst, it was readily recovered by magnetic decantation and can be recycled at least six runs with no considerable decrease in catalytic activity.

Keywords: 1-amidoalkyl-2-naphthol, 3-amino-1-phenyl-1*H* benzo[*f*]chromene-2-carbonitrile, solvent-free conditions, magnetic, catalyst.

INTRODUCTION

Energy sources have been used for various processes and systems because this source has played a major role in preventing pollution in our environment¹⁻². Nano small-sized catalysts due to their high surface area can be enhanced the chemical synthesis expediency³⁻⁶. Among the many efforts to find the appropriate support used for the synthesis of heterogeneous catalysis, functionalization of the Fe₃O₄ magnetic nanoparticles (MNPs) due to the ability to adjoin to functional groups with strong connection, high stability and availability have emerged as a thoughtfully route to bridge the gap between homogeneous catalysis and them⁷⁻⁹. Some features of MNPs, such as a tendency to agglomeration due to the strong dipole-dipole attraction and deform during the reaction period will limit their utilization¹⁰⁻¹¹. Thus, in order to increase the efficiency of this kind of nanoparticles in the various special process, functionalization and modification of their surfaces are necessary. Surface modification of the magnetic nanoparticles by silica layers improves their capability to interact with organic compounds through OH groups on the silica surfaces¹²⁻¹⁴. Due to the magnetic nature of the iron oxide nanoparticles, they can provide a variety of potential usages such as drug delivery, MRI contrast agents, hyper thermal agents, and cell sorting¹⁵⁻²⁰. Also, in the catalysts synthesized using these magnetic supports, the final product can be readily isolated from the reaction medium by an external magnet.

The synthesis of 1-amidoalkyl-2-naphthol and its derivatives have attracted much attention of synthetic researchers because of their important biological and pharmacological features such as bradycardia and depressor effects in humans²¹⁻²². Many homogeneous or heterogeneous catalysts have been reported for

the preparation of 1-amidoalkyl-2-naphthol derivatives via three-component condensation of 2-naphthol, acetonitrile, and aldehydes, of which oxalic acid²³, I₂²⁴, Indion-130²⁵, InCl₃²⁶, H₂NSO₃H²⁷, K₅CoW₁₂O₄₀·3H₂O²⁸, TMSCl/NaI²⁹, Fe(HSO₄)₃³⁰, Yb(OTf)₃ in ionic liquid³¹, p-toluenesulfonic acid³², 2,4,6-trichloro-1,3,5-triazine³³, HPMo³⁴, Sr(OTf)₂³⁵, and montmorillonite K₁₀³⁶ are examples. Aminochromene structure moiety has also been successfully employed for the synthesis a variety of derivatives with remarkable biological and pharmacological properties. In addition, Aminochromene derivatives have been introduced to have antimicrobial³⁷⁻³⁸, anticancer³⁹⁻⁴¹, antiviral⁴²⁻⁴³, antibacterial⁴⁴, and central nervous system (CNS)⁴⁵ activities. The synthetic method for the synthesis of substituted 3-amino-1*H*-chromenes is one of the aminochromene derivatives involve: the condensation reaction of 2-naphthol, aldehyde, and malononitrile. There are some methods, such as using CuO-CeO₂⁴⁶, basic ionic liquids⁴⁷⁻⁴⁸, K₂CO₃⁴⁹, Rochelle salt⁵⁰, and DABCO⁵¹ as homogeneous or heterogeneous catalysts which have been presented to the synthesis of 3-amino-1*H*-chromenes derivatives. Some of the above-mentioned catalysts suffer from disadvantages such as Hazardous organic solvents, tedious work-up, long reaction times, low yields of the product, drastic reaction conditions, toxic and corrosive reagent, and use of microwave or ultrasonic irradiation. Therefore, to overcome these drawbacks, there is still much demand to expand an efficient and simple heterogeneous catalytic system for the preparation of amidoalkyl naphthols derivatives.

EXPERIMENTAL

All the pure materials were prepared from Fluka, Merck, and Aldrich chemical companies. The FT-IR

spectra were obtained using a Fourier-transform infrared spectrometer (PerkinElmer PXI spectrometer in KBr wafers). A VSM (VSM; Lake Shore 7200 at 300 K VSM) was used to analyze magnetic susceptibility measurements. The energy dispersive X-ray spectroscopy (EDX) was applied to the chemical composition of synthesized nanoparticles with an (ESEM, Philips, and XL30). The structure of MNPs was examined using a scanning electron microscope (SEM-LEO 1430VP analyzer). Analysis of the crystalline phase was carried out with an X-ray diffraction XRD-6100 Shimadzu, Japan. The thermal stability of the magnetic nanoparticles was accomplished with a TG209 F1; Netzsch, Germany.

CATALYST SYNTHESIS

Synthesis of Magnetic Nanoparticles (Fe_3O_4).

In this way, 2.2 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 5.7 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 60 ml of deionized water in a beaker under vigorous stirring and nitrogen gas protection for 1h. Then 5 ml of ammonium hydroxide solution was added slowly into the reaction mixture until the content of the reaction vessel reached pH 11.0 and the black precipitate was achieved. The reaction was at continued at ambient temperature under agitation for another 1 h. After completion of the reaction, the precipitate was isolated by an appropriate external magnetic field and rinsed three times with deionized water to remove any unreacted chemicals. Finally, the magnetic nanoparticles dried under vacuum oven at 50°C for 18 h and stored in airtight containers.

Synthesis of silica coated magnetic nanoparticles ($\text{Fe}_3\text{O}_4@SiO_2$).

First, 0.1 g of fabricated Fe_3O_4 MNPs was dispersed in a mixture of 50 mL ethanol, 8 mL deionized water and 4 mL of aqueous ammonia (28 wt%) under mechanical stirring for 30 min. The next step was followed by the dropwise addition of 0.5 mL TEOS to the above solution under vigorous sonication for another 30 min. After continuous stirring at 400 rpm for 24 h at room temperatures, the silica coated magnetic nanoparticles were isolated by magnetic decantation and then rinsed several times with the equal values of ethanol and distilled water to remove nonmagnetic byproduct, and finally dried at vacuum conditions at 50°C for 15 h.

Synthesis of Fe_3O_4 bonded aminopropyltriethoxysilane ($\text{Fe}_3\text{O}_4@APTES$).

About 1 g of the $\text{Fe}_3\text{O}_4@SiO_2$ was dispersed in a reaction flask containing 40 mL of dry toluene by ultrasonication vibration for 30 min, followed by the addition of 2 mL of aminopropyltriethoxysilane (APTES). The achieved solution was mechanically stirred at 400 rpm for 24 h under reflux conditions. After reaching the desired product, the precipitates of core-shell $\text{Fe}_3\text{O}_4@APTES$ nanoparticles were isolated by magnetic decantation, rinsed three times with deionized water and anhydrous ethanol, and dried under vacuum oven at 50°C for 15 h.

Synthesis of $\text{Fe}_3\text{O}_4@APTES$ bonded aspartic acid ($\text{Fe}_3\text{O}_4@APTES/ASA$).

1 g of $\text{Fe}_3\text{O}_4@APTES$ nanoparticles was poured in 40 mL ethanol and dispersed by ultrasonic vibration; then, 0.5 g of aspartic acid (ASA) was added, and the achieved solution was mechanically stirred for 24 h under reflux conditions. At the end of the reaction, the $\text{Fe}_3\text{O}_4@APTES/ASA$ nanoparticles were extracted from the reaction vessel using an external magnetic field, washed three times with equal amounts of deionized water and anhydrous ethanol to remove any unreacted organic groups, and dried under vacuum oven at 50°C for 15 h.

Synthesis of $\text{Fe}_3\text{O}_4@enamine-B(OH)_2$.

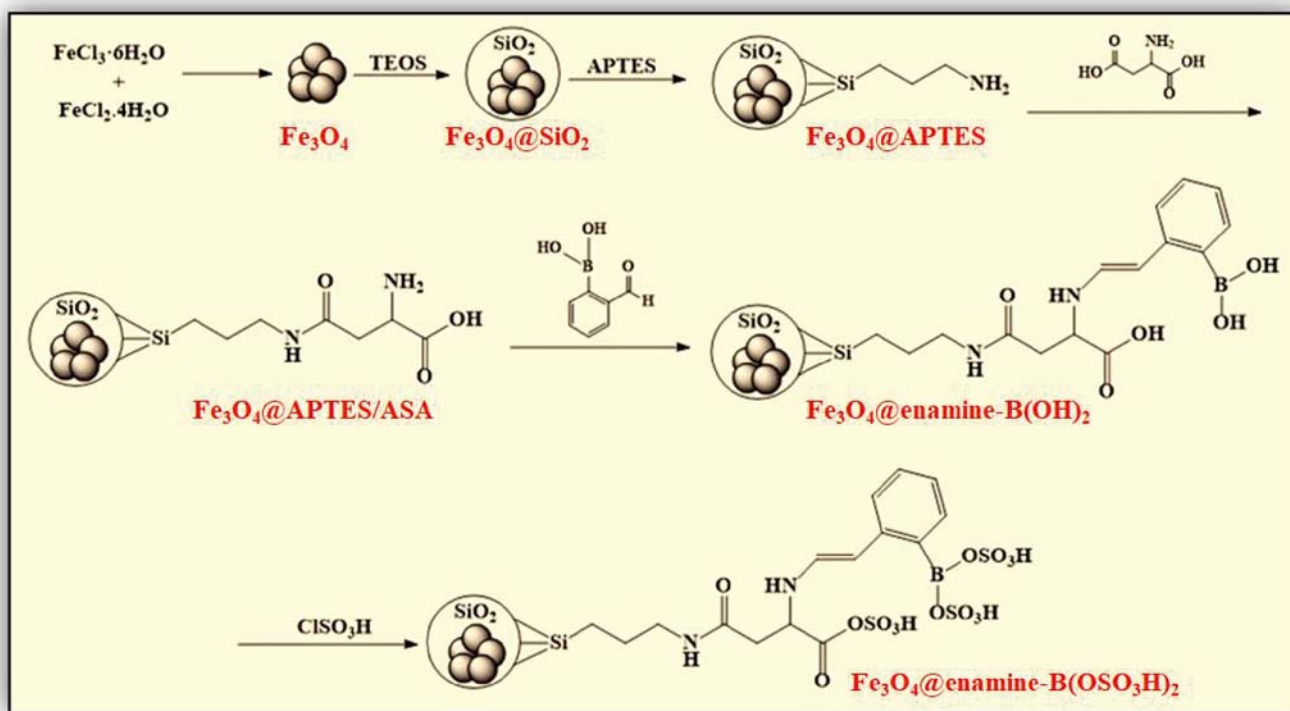
About, 1 g of $\text{Fe}_3\text{O}_4@APTES/ASA$ nanoparticles were dispersed in 50 mL dry ethanol and sonicated for 30 min. Then, 4 mmol of 2-formylbenzeneboronic acid was added into the reaction flask and the solution was refluxed and mechanically stirred for 24 h under a continuous flow of nitrogen gas. Finally, the resultant was collected using an appropriate magnetic field and rinsed three times with equal amounts of distilled water and ethanol to eliminate any unreacted chemicals, and dried under vacuum oven at 50°C for 15 h.

Synthesis of $\text{Fe}_3\text{O}_4@enamine-B(OSO_3H)_2$.

To prepare $\text{Fe}_3\text{O}_4@enamine-B(OSO_3H)_2$, 2 g of $\text{Fe}_3\text{O}_4@enamine-B(OH)_2$ was dispersed in 20 mL of dry dichloromethane for 30 min using ultrasonication. After that, 10 mmol of chlorosulfonic acid was added dropwise to the reaction solution and the obtained mixture was stirred at 0°C for 6 h. Finally, these precipitates were separated with an external magnetic field, rinsed three times with 30 mL of with water and ethanol to eliminate the unreacted residue of the chemicals, and next dried in a vacuum oven at 60°C for 12 h. All stages of the $\text{Fe}_3\text{O}_4@enamine-B(OSO_3H)_2$ synthesis are exhibited in Scheme 1.

FTIR analysis of $\text{Fe}_3\text{O}_4@enamine-B(OSO_3H)_2$.

The FT-IR spectra of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@SiO_2$, $\text{Fe}_3\text{O}_4@APTES$, $\text{Fe}_3\text{O}_4@APTES/ASA$, $\text{Fe}_3\text{O}_4@enamine-B(OH)_2$, $\text{Fe}_3\text{O}_4@enamine-B(OSO_3H)_2$ and recovered $\text{Fe}_3\text{O}_4@enamine-B(OSO_3H)_2$ samples in the ranging from 400 to 4000 cm^{-1} are illustrated in Fig. 1. FT-IR spectra of the Fe_3O_4 exhibited the characteristic Fe-O and the OH groups attached to the iron absorptions at 583 and 3391 cm^{-1} , respectively. In about the $\text{Fe}_3\text{O}_4@SiO_2$, the characteristic absorption band's appeared at 1052 cm^{-1} can be attributed to the stretching vibration of the Si-O-Si group. In the case of $\text{Fe}_3\text{O}_4@APTES$, The existence of an anchored alkyl group is exhibited by the band at about 2984 cm^{-1} , which corresponds to the C-H stretching vibration mode. The achieved FT-IR spectra for $\text{Fe}_3\text{O}_4@APTES/ASA$ contained characteristic stretching and bending vibrations at 1492, and 3307 cm^{-1} related N-H groups, respectively. The presence of the phenylboronic acid in the spectra of $\text{Fe}_3\text{O}_4@enamine-B(OH)_2$ is confirmed by the B-C vibration at 1375 cm^{-1} . Characteristic SO_3H groups are presented at 1098 and 1173 cm^{-1} in the spectra of $\text{Fe}_3\text{O}_4@enamine-B(OSO_3H)_2$. From the spectra of recovered $\text{Fe}_3\text{O}_4@enamine-B(OSO_3H)_2$ we



Scheme 1. Synthetic route of $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$

can see that the catalyst after the third recovery and reuse do not exhibit any difference.

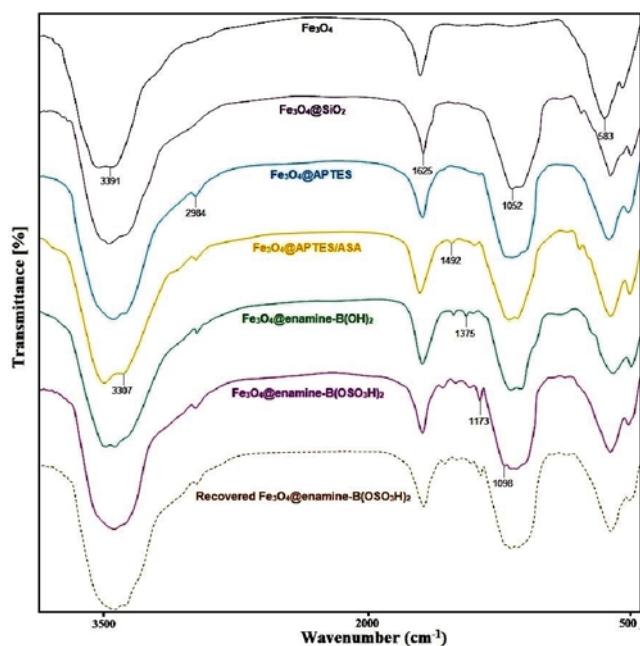


Figure 1. FTIR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{@SiO}_2$, $\text{Fe}_3\text{O}_4\text{@APTES}$, $\text{Fe}_3\text{O}_4\text{@APTES/ASA}$, $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OH})_2$, and $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$

TGA analysis of $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$.

As observed in Fig. 2, thermogravimetric analysis (TGA) was applied for measuring the thermal constancy of the Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{@APTES}$, $\text{Fe}_3\text{O}_4\text{@APTES/ASA}$, $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OH})_2$, and $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$ at $10^\circ\text{C min}^{-1}$ of heating rate under a nitrogen atmosphere. As can be seen in all of the samples, the weight loss in the temperature range below 240°C was observed due to evaporation of physically adsorbed H_2O molecules and dehydration of the surface OH groups. In the curve of

$\text{Fe}_3\text{O}_4\text{@APTES}$, a weight loss up to 300°C is also observed, which is associated to the thermal decomposition of APTES group. The weight loss stages up to 350°C were observed in thermogram for $\text{Fe}_3\text{O}_4\text{@APTES/ASA}$, which can be related to the decomposition of APTES and ASA groups. $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OH})_2$ and $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$ have another two weight loss stages up to 450°C , which is associated with the decomposition of functionalized groups on the magnetic nanoparticles surface.

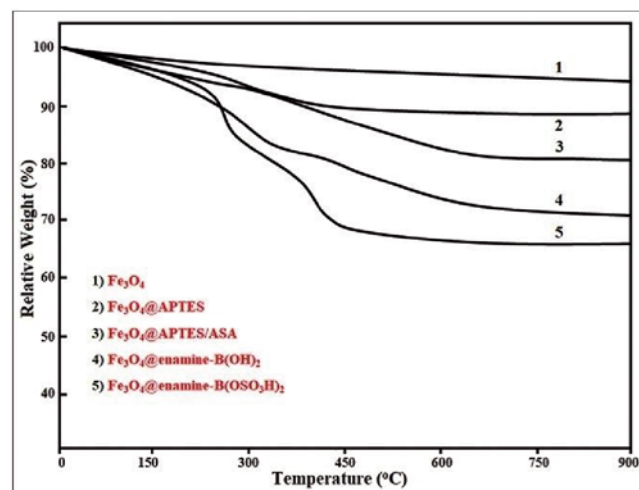


Figure 2. TGA curves of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{@SiO}_2$, $\text{Fe}_3\text{O}_4\text{@APTES}$, $\text{Fe}_3\text{O}_4\text{@APTES/ASA}$, $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OH})_2$, and $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$

EDX analysis of $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$.

The components of the $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$ were characterized by using energy dispersive X-ray spectroscopy (EDX) (Fig. 3). The EDX spectrum exhibits elements, including Fe, Si, C, O, and N, which are present in the catalyst substrate. The existence of sulfur in the $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$ illustrates that SO_3H

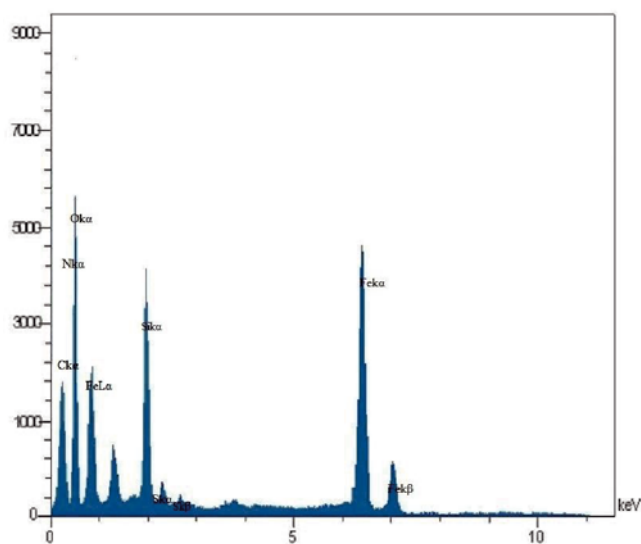


Figure 3. EDX spectra of $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$

groups was attached to the functional groups of $\text{Fe}_3\text{O}_4@enamine-B(\text{OH})_2$.

VSM analysis of $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$.

The magnetization measurements of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@SiO_2$, and $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$ were surveyed by vibrating sample magnetometer (VSM) at room temperature. As shown on Fig. 4, the saturation magnetization of Fe_3O_4 , $\text{Fe}_3\text{O}_4@SiO_2$, and $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$ were found to be at about 61.82, 51.34, and 32.56 emu/g, respectively. The decrease in value of the saturation magnetization can be assigned to the presence of silica-layers, organic groups, and sulfuric acid groups on the surface of the magnetic nanoparticles.

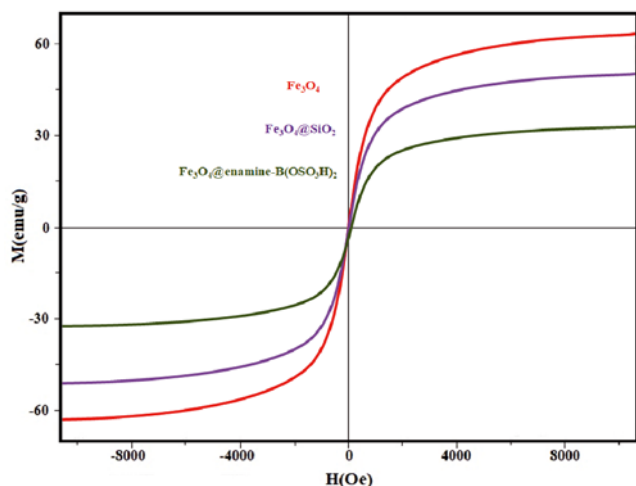


Figure 4. Magnetization curves of Fe_3O_4 , $\text{Fe}_3\text{O}_4@SiO_2$, and $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$

XRD analysis of $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$.

The X-ray diffraction (EDX) patterns of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@enamine-B(\text{OH})_2$, and $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$ indicates the preservation spinel phase of the magnetic nanoparticles during the surface modification (Fig. 5). The reflections of the all samples were found to be 27.65, 33.74, 43.68, 52.87, 58.76 and 64.79 to the (220), (311), (400), (422), (511), and (440) planes, respectively.

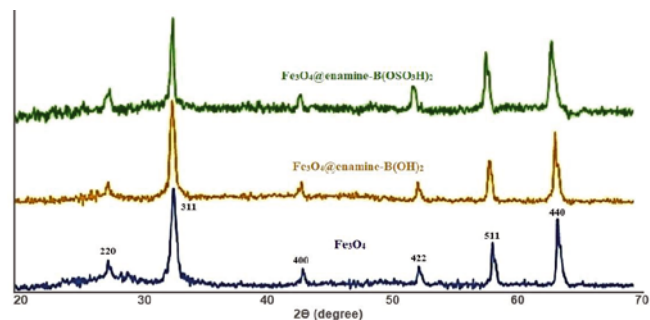
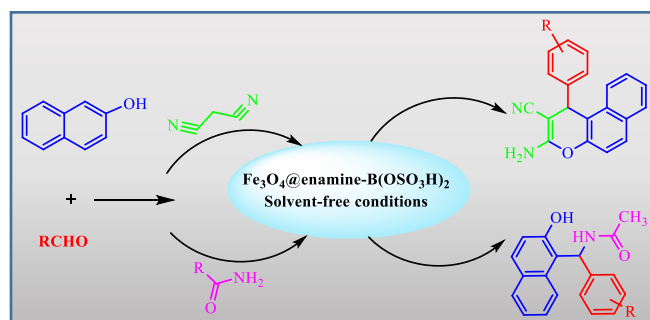


Figure 5. The XRD patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4@enamine-B(\text{OH})_2$, and $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$

RESULTS AND DISCUSSION

In continuation of our investigations and on the basis of the achieved information, $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$ was tested as a separable heterogeneous magnetic nanocatalyst for the synthesis of 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile derivatives under solvent-free conditions (Scheme 2).



Scheme 2. Synthesis of 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile derivatives using $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$

Firstly, the catalytic efficiency of $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$ was surveyed in a three-component reaction for the preparation of 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile derivatives. To find the optimal conditions, the reaction between 2-naphthol, 4-chlorobenzaldehyde, and acetamide with 1:1:1 molar ratios and the reaction between 2-naphthol, 4-chlorobenzaldehyde and malononitrile with 1:1:1.1 molar ratios were selected as the model reactions, respectively. The effects of various factors such as amounts of the catalyst, solvents, and temperatures were studied on the rate and yield of the 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile synthesis reaction (Table 1). As can be seen, in the presence of the catalyst, with different solvents such as H_2O , EtOH, CH_3CN , CHCl_3 , DMF, and toluene, under reflux conditions, the yields of the desired products were low-to-moderate (Table 1, entries 1–6). The outcomes showed that the model reactions using 15 mg of the $\text{Fe}_3\text{O}_4@enamine-B(\text{OSO}_3\text{H})_2$ as the heterogeneous magnetic nanocatalyst at 90°C in the absence of solvent proceeded with the highest yields of the products (Table 1, entry 7). The effect of temperature on the reactions times and products yields are well proved. As can be seen from this table (Table 1, entries 7 and 11–13), the reactions times of the model are significantly reduced and subsequently products yields also increase

Table 1. Optimization one-pot three-component reaction between 2-naphthol, acetamide and 4-chlorobenzaldehyde, and the reaction between 2-naphthol, malononitrile, and 4-chlorobenzaldehyde under different conditions

Entry	Solvent	Catalyst [mg]	Temp.	Time [min]		Yield [%] ^a	
				Method [a]	Method [b]	Method [a]	Method [b]
1	H ₂ O	15	Reflux	70	60	59	65
2	EtOH	15	Reflux	70	60	62	73
3	CH ₃ CN	15	Reflux	95	75	50	56
4	CHCl ₃	15	Reflux	100	90	42	50
5	DMF	15	Reflux	100	90	35	46
6	toluene	15	Reflux	90	80	54	63
7	–	15	90°C	10	12	94	94
8	–	15	25°C	120	75	35	43
9	–	15	50°C	95	60	43	58
10	–	15	60°C	85	45	61	69
11	–	15	70°C	45	30	88	85
12	–	15	80°C	20	20	91	90
13	–	15	100°C	10	10	94	92
14	–	5	90°C	60	55	54	60
15	–	8	90°C	45	30	65	69
16	–	12	90°C	20	15	80	78
17	–	18	90°C	10	12	94	93
18	–	20	90°C	15	20	93	91

^a The yields refer to the isolated product

substantially. Our investigations exhibited that the weaker outcomes can be achieved at temperatures below 70°C, even in the presence of 15 mg of the Fe₃O₄@enamine-B(OSO₃H)₂ (Table 1, entries 8–10). In continue, we investigated the effect of catalyst concentration (such as 5, 8, 12, 15, 18, and 20 mg) on the completion of the reaction (Table 1, entries 7 and 14–18) and as guessed, the yields of the products have decreased remarkably in low concentrations of the catalyst, whereas the reactions times have increased (Table 1, entries 14–16). When the reactions were performed in high concentrations of the catalyst, none of these model reactions were obtained with the highest percentages of the products (Table 1, entries 17–18).

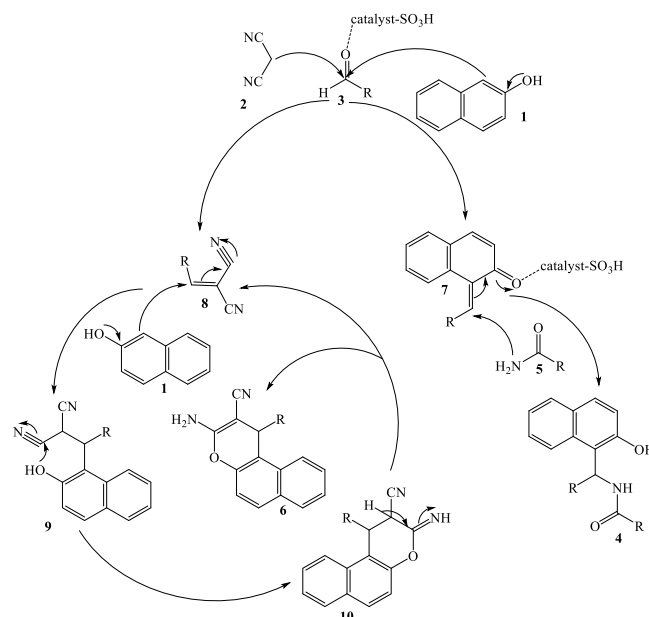
As shown in Table 2, to further explore the efficiency of the heterogeneous magnetic nanocatalyst using these optimized reaction conditions, a range of 1-amidoalkyl-2-naphthols were synthesized by the one-pot three-component condensation of 2-naphthol, acetamide, and aldehydes having electron-donating as well as electron-withdrawing groups, using 15 mg of the Fe₃O₄@enamine-B(OSO₃H)₂ under solvent-free conditions at 90°C in high-to-excellent yields with short reaction times.

After the successful preparation of a series of 1-amidoalkyl-2-naphthols, we decided to explore the effectiveness of the Fe₃O₄@enamine-B(OSO₃H)₂ in the synthesis of 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitriles by the one-pot three-component condensation of 2-naphthol, malononitrile and aldehydes having electron-donating as well as electron-withdrawing groups using 15 mg of the Fe₃O₄@enamine-B(OSO₃H)₂ under solvent-free conditions at 90°C. As shown in Table 3, the final products were achieved in high-to-excellent yields under the above-mentioned conditions.

A suggested mechanism for the preparation of the 1-amidoalkyl-2-naphthol (**4**) and 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile (**6**) derivatives via one-pot three-component condensation is shown in Scheme 3. Initially, Fe₃O₄@enamine-B(OSO₃H)₂, as a heterogeneous magnetic nanocatalyst, activates the carbonyl group of the aldehyde **3** and then naphthol **1** and malononitrile **2** (raw materials that produce **4** and

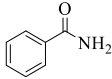

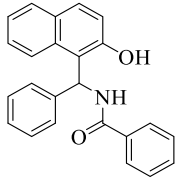
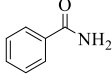
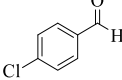
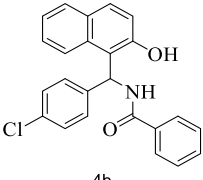
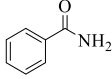
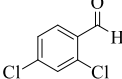
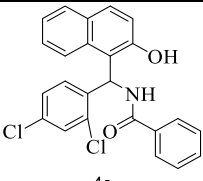
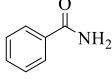
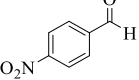
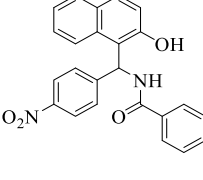
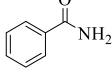
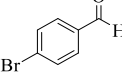
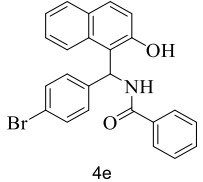
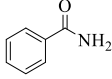

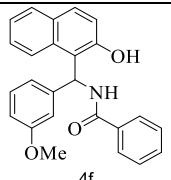
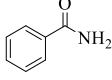
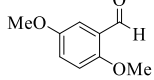
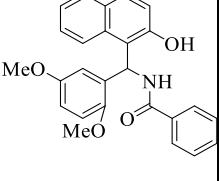

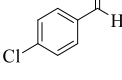
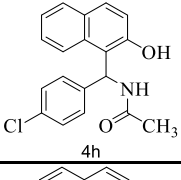

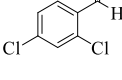
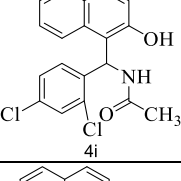


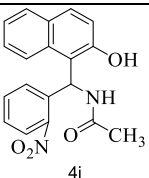
6, respectively) react with the activated aldehyde to give intermediate **7** and **8**. The condensation between intermediate **7** with amide **5** affords product **4**. Also, Intermediate **9** causes by the Michael addition of 2-naphthol **1** to alkylidenemalononitrile **8**, which produces the final product **6** by cyclization and dehydrogenation of intermediate **10**.

Reusability of Fe₃O₄@enamine-B(OSO₃H)₂ as a novel and efficient heterogeneous magnetic nanocatalyst was confirmed in the preparation of 1-amidoalkyl-2-naphthol **4** (a) and 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile **6** (b) derivatives. Thus, after completion of the reaction, ethyl acetate as a polar solvent was added to the beaker, and the reaction mixture was heated for 10 min. Extraction with magnetic decantation was achieved the corresponding product and the catalyst remained in the beaker. The recovered magnetic catalyst was rinsed with distilled water and reused with the negligible decrease in catalytic activity for six runs (Fig. 6).



Scheme 3. A suggested mechanism for the synthesis of 1-amidoalkyl-2-naphthol (**4**) and 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile (**6**) derivatives catalyzed by Fe₃O₄@enamine-B(OSO₃H)₂

Table 2. Synthesis of 1-amidoalkyl-2-naphthol (**4**) derivatives catalyzed by $\text{Fe}_3\text{O}_4@\text{enamine-B}(\text{OSO}_3\text{H})_2^{\text{a}}$

Entry	Amide	Aldehyde (3)	Product	Time [min]	Yield [%] ^b	M.P.(Obsd) [°C]	M.P. (Lit) [°C]
1			 4a	12	95	231-233	234-236 ³²
2			 4b	10	96	262-265	265-267 ⁵²
3			 4c	12	96	235-237	238-239 ⁵²
4			 4d	10	94	233-236	237-239 ⁵²
5			 4e	15	93	187-189	182-184 ⁵³
6			 4f	25	90	211-215	214-216 ²⁸
7			 4g	40	90	239-241	238-240 ⁵³
8			 4h	10	94	233-235	235-236 ⁵⁵
9			 4i	25	87	196-198	198-199 ⁵⁴
10			 4j	20	90	185-189	180-182 ⁵⁴

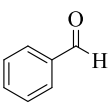
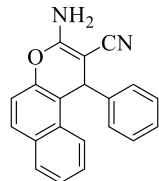
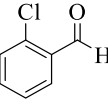
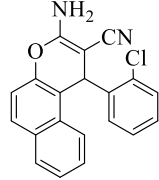
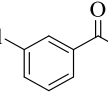
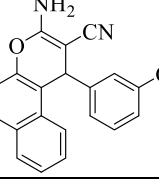
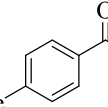
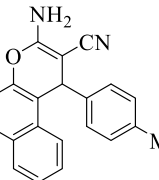
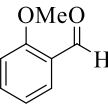
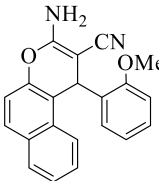
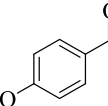
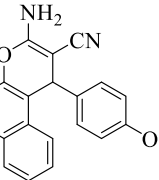
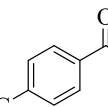
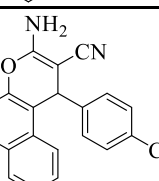
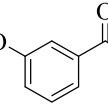
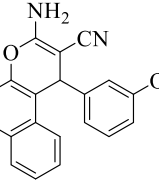
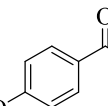
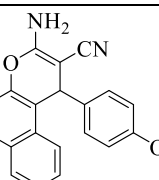
11				15	93	246-249	248-250 ³⁰
12				20	95	228-230	229-231 ⁵³
13				20	91	247-249	251-253 ³⁶
14				30	95	215-218	220-221 ³⁶
15				25	92	227-229	235-236 ⁵⁵
16				15	93	200-202	203-205 ⁵⁷
17				15	93	238-240	241-243 ⁵⁴
18				35	89	172-174	176-175 ⁵⁶
18				35	88	170-172	168-169 ²⁷
18				35	84	165-168	163-165 ⁵⁸

^a Reaction conditions: 2-naphthol (1 mmol), aldehyde (1 mmol), amide (1 mmol), Fe₃O₄@enamine-B(OSO₃H)₂ (15 mg).

A comparison between the previously reported methods and our procedure could highlight the efficiency of the synthesized catalyst Fe₃O₄@enamine-B(OSO₃H)₂ for the preparation of 1-amidoalkyl-2-naphthol (**4**) and 3-amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile

(**6**) derivatives. To ensure the safety, cleanliness and simplicity of classical strategies, solvent-free procedures from the perspective of green chemistry are important. The outcomes tabulated in Table 4 show that our pro-

Table 3. Preparation of 3-amino-1-phenyl-1*H*-benzo[*h*]chromene-2-carbonitrile (**6**) derivatives using Fe₃O₄@enamine-B(OSO₃H)₂ as a catalysta

Entry	Product	Aldehyde (3)	Product	Time [min]	Yield[%] ^b	M.P.(Obtd) [°C]	M.P. (Ref) [°C]
1	6a			18	92	277-279	279-280 ⁵⁹
2	6b			12	92	273-275	271-272 ⁵⁹
3	6c			15	92	210-212	202-204 ⁶⁴
12	6l			25	92	272-274	273-274 ⁵⁹
13	6m			25	93	220-222	219-222 ⁶²
14	6n			20	92	195-197	185-187 ⁶⁰
15	6o			20	94	210-212	215-217 ⁶⁴
16	6p			15	91	281-283	280-282 ⁶⁴
17	6q			20	96	285-287	288-290 ⁶³

^a Reaction conditions: 2-naphthol (1 mmol), aldehyde (1 mmol), malononitrile (1.1 mmol), Fe₃O₄@enamine-B(OSO₃H)₂ (15 mg).

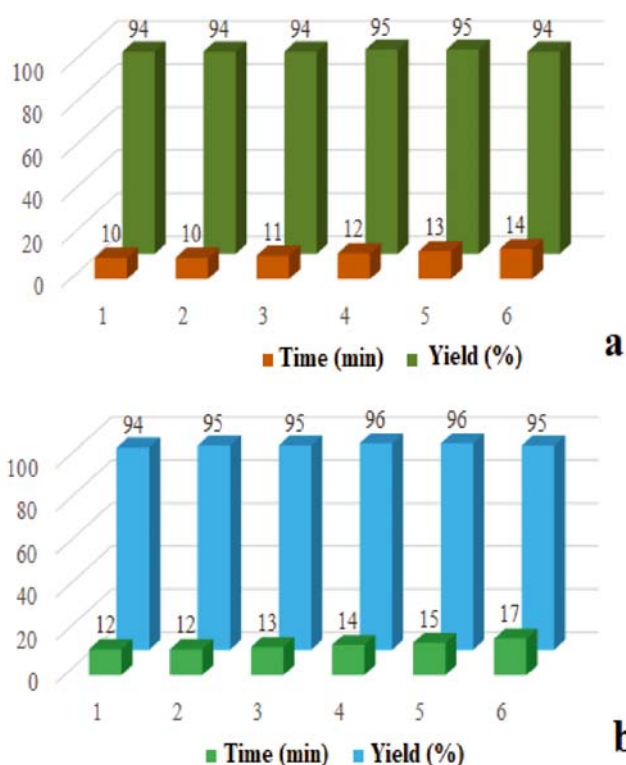


Figure 6. The recycling of $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$ in the synthesis of 1-amidoalkyl-2-naphthol **4** (a) and 3-amino-1-phenyl-1H-benzof[chromene-2-carbonitrile **6** (b) derivatives

Table 4. Different catalysts for the preparation of 1-amidoalkyl-2-naphthol (**4**) and 3-amino-1-phenyl-1H-benzof[chromene-2-carbonitrile (**6**) derivatives

1-amidoalkyl-2-naphthol (entries 1-9)	
1) KH_2SO_4 /Solvent-free/ 100°C 1h, 90%, Ref:65	2) $\text{Fe}(\text{HSO}_4)_3$ /Solvent-free/ 85°C 25h, 56%, Ref:30
3) I_2 /Solvent-free/ 125°C 5.5h, 85%, Ref:24	4) Succinic acid /Solvent-free/ 120°C 25 min, 93%, Ref:66
5) $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$ /Solvent-free/ 125°C 2h, 86%, Ref:28	6) $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ /Solvent-free/ 100°C 1h, 91%, Ref:67
7) $\text{Ba}_3(\text{PO}_4)_2$ /Solvent-free/ 100°C 45 min, 87%, Ref:68	8) Nano SnO_2 /Solvent-free/ 25°C 35 min, 81%, Ref:69
9) $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$ /Solvent-free/ 90°C , 15 min, 93%, Ref: This work	
3-amino-1-phenyl-1H-benzof[chromene-2-carbonitrile (entries 10-16)	
10) Morpholine/ H_2O /r.t. 3h, 87%, Ref:70	11) DABCO/ EtOH /r.t. 7h, 72%, Ref:51
12) $\text{Fe}(\text{HSO}_4)_3$ / CH_3CN /Reflux 4h, 85%, Ref:71	13) $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ / H_2O /Reflux 80 min, 85%, Ref:62
14) Nanozeolite CP/ H_2O /Reflux 20 min, 92%, Ref:72	15) Methanesulfonic acid/ CH_3CN /Reflux 4h, 91%, Ref:73
16) $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$ /Solvent-free/ 90°C , 12 min, 94%, Ref: This work	

cedure, utilizing $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$, provided the highest yields of the products in low reaction times.

CONCLUSIONS

The prepared magnetic nanocatalyst was characterized by several techniques such as FTIR, TGA, VSM, EDX and XRD analysis. Magnetic recovery of the catalyst $\text{Fe}_3\text{O}_4\text{@enamine-B}(\text{OSO}_3\text{H})_2$ was discovered to be

a highly effective and economically sustainable catalyst for the synthesis of a wide range of substituted 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1H benzo[f]chromene-2-carbonitrile derivatives through a one-pot three component condensation reaction. The main properties of these procedures are a simple work-up method, easy preparation of the catalyst, short reaction times, good-to-high yields, and non-use of hazardous solvents during all steps of the reactions.

ACKNOWLEDGEMENTS

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LITERATURE CITED

1. Abedinia, O., Zareinejad, M., Doranehgard, M.H., Fathi, G. & Ghadimi, N. (2019). Optimal offering and bidding strategies of renewable energy based large consumer using a novel hybrid robust-stochastic approach. *J. Cleaner Prod.* 215, 878–889. DOI: 10.1016/j.jclepro.2019.01.085.
2. Bagal, H.A., Soltanabad, Y.N., Dadjuo, M., Wakil, K. & Ghadimi, N. (2018). Risk-assessment of photovoltaic-wind-battery-grid based large industrial consumer using information gap decision theory. *Solar Energy* 169, 343–352. DOI: 10.1016/j.solener.2018.05.003.
3. Shao, M., Ning, F., Zhao, J., Wei, M., Evans, D.G. & Duan, X. (2012). Preparation of $\text{Fe}_3\text{O}_4\text{@SiO}_2$ layered double hydroxide core-shell microspheres for magnetic separation of proteins. *J. Amer. Chem. Soc.* 134(2), 1071–1077. DOI: 10.1021/ja2086323.
4. Deng, Y., Deng, C., Qi, D., Liu, C., Liu, J., Zhang, X. & Zhao, D. (2009). Synthesis of core/shell colloidal magnetic zeolite microspheres for the immobilization of trypsin. *Adv. Mater.* 21(13), 1377–1382. DOI: 10.1002/adma.200801766.
5. Mobaraki, A., Movassagh, B. & Karimi, B. (2014). Magnetic solid sulfonic acid decorated with hydrophobic regulators: A combinatorial and magnetically separable catalyst for the synthesis of α -aminonitriles. *ACS Combin. Sci.* 16(7), 352–358. DOI: 10.1021/co500022g.
6. Safaei-Ghomi, J., Javidan, A., Ziarati, A. & Shahbazi-Alavi, H. (2015). Synthesis of new 2-amino-4H-pyran-3, 5-dicarboxylate derivatives using nanocrystalline M II Zr 4 (PO 4) 6 ceramics as reusable and robust catalysts under microwave irradiation. *J. Nanopartic. Res.* 17(8), 338. DOI: 10.1007/s11051-015-3142-y.
7. Shylesh, S., Schünemann, V. & Thiel, W.R. (2010). Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis. *Angew. Chemie Internat. Edit.* 49(20), 3428–3459. DOI: 10.1002/anie.200905684.
8. Tucker-Schwartz, A.K., Farrell, R.A. & Garrell, R.L. (2011). Thiol-ene click reaction as a general route to functional trialkoxysilanes for surface coating applications. *J. Amer. Chem. Soc.* 133(29), 11026–11029. DOI: 10.1021/ja202292q.
9. Sadeghzadeh, S.M. & Nasserri, M.A. (2013). Methylene dipyridine nanoparticles stabilized on Fe_3O_4 as catalysts for efficient, green, and one-pot synthesis of pyrazolophthalaziny spirooxindoles. *Catalysis Today* 217, 80–85. DOI: 10.1016/j.cattod.2013.07.018.
10. Vayssieres, L., Chanéac, C., Tronc, E. & Jolivet, J.P. (1998). Size tailoring of magnetite particles formed by aqueous precipitation: an example of thermodynamic stability of nanometric oxide particles. *J. Colloid Inter. Sci.* 205(2), 205–212. DOI: 10.1006/jcis.1998.5614.
11. Hong, R.Y., Feng, B., Liu, G., Wang, S., Li, H.Z., Ding, J.M., ... & Wei, D.G. (2009). Preparation and characterization of Fe_3O_4 /polystyrene composite particles via inverse emulsion

- polymerization. *J. Alloys Comp.* 476(1–2), 612–618. DOI: 10.1016/j.jallcom.2008.09.060.
12. Rostamnia, S. & Doustkhah, E. (2015). Synthesis of water-dispersed magnetic nanoparticles (H₂O-DMNPs) of β -cyclodextrin modified Fe₃O₄ and its catalytic application in Kabachnik–Fields multicomponent reaction. *J. Magnet. Magnet. Mater.* 386, 111–116. DOI: 10.1016/j.jmmm.2015.03.064.
13. Rostamzadeh, S., Shadjou, N., Azad, M. & Jalali, N. (2012). (α -Fe₂O₃)-MCM-41 as a magnetically recoverable nanocatalyst for the synthesis of pyrazolo [4, 3-c] pyridines at room temperature. *Catal. Commun.* 26, 218–224. DOI: 10.1016/j.catcom.2012.05.022.
14. Zhang, F., Jin, J., Zhong, X., Li, S., Niu, J., Li, R. & Ma, J. (2011). Pd immobilized on amine-functionalized magnetite nanoparticles: a novel and highly active catalyst for hydrogenation and Heck reactions. *Green Chem.* 13(5), 1238–1243. DOI: 10.1039/C0GC00854K.
15. Berry, C.C., & Curtis, A.S. (2003). Functionalisation of magnetic nanoparticles for applications in biomedicine. *J. Phys. D: Appl. Phys.* 36(13), R198. DOI: 10.1088/0022-3727/36/13/203.
16. Nasongkla, N., Bey, E., Ren, J., Ai, H., Khemtong, C., Guthi, J.S. & Gao, J. (2006). Multifunctional polymeric micelles as cancer-targeted, MRI-ultrasensitive drug delivery systems. *Nano Letters* 6(11), 2427–2430. DOI: 10.1021/nl061412u.
17. Arruebo, M., Fernández-Pacheco, R., Ibarra, M.R. & Santamaría, J. (2007). Magnetic nanoparticles for drug delivery. *Nano Today* 2(3), 22–32. DOI: 10.1016/S1748-0132(07)70084-1.
18. Dobson, J. (2006). Magnetic nanoparticles for drug delivery. *Drug Development Res.* 67(1), 55–60. DOI: 10.1002/ddr.20067.
19. Lewin, M., Carlesso, N., Tung, C.H., Tang, X.W., Cory, D., Scadden, D.T. & Weissleder, R. (2000). Tat peptide-derivatized magnetic nanoparticles allow in vivo tracking and recovery of progenitor cells. *Nature Biotechnol.* 18(4), 410. DOI: 10.1038/74464.
20. Govan, J. & Gun'ko, Y.K. (2014). Recent advances in the application of magnetic nanoparticles as a support for homogeneous catalysts. *Nanomaterials*, 4(2), 222–241. DOI: 10.3390/nano4020222.
21. Shen, A.Y., Tsai, C.T. & Chen, C.L. (1999). Synthesis and cardiovascular evaluation of N-substituted 1-aminomethyl-2-naphthols. *Europ. J. Med. Chem.* 34(10), 877–882. DOI: 10.1016/S0223-5234(99)00204-4.
22. Sztatmari, I. & Fulop, F. (2004). Syntheses and transformations of 1-(α -aminobenzyl)-2-naphthol derivatives. *Current Org. Synthesis* 1(2), 155–165. DOI: 10.2174/1570179043485402.
23. Ansari, S.A.M.K., Sangshetti, J.N., Kokare, N.D., Wakte, P.S. & Shinde, D.B. (2010). Oxalic acid catalyzed solvent-free synthesis of α -amidoalkyl- β -naphthols. *Ind. J. Chem. Technol.* 17(1), 71–73.
24. Das, B., Laxminarayana, K., Ravikanth, B. & Rao, B.R. (2007). Iodine catalyzed preparation of amidoalkyl naphthols in solution and under solvent-free conditions. *J. Molec. Catal. A: Chem.* 261(2), 180–183. DOI: 10.1016/j.molcata.2006.07.077.
25. Patil, S.B., Singh, P.R., Surpur, M.P., & Samant, S.D. (2007). Cation-Exchanged Resins: Efficient Heterogeneous Catalysts for Facile Synthesis of 1-Amidoalkyl-2-naphthols from One-Pot, Three-Component Condensations of Amides/Ureas, Aldehydes, and 2-Naphthol. *Synt. Commun.* 37(10), 1659–1664.
26. Chavan, N.L., Naik, P.N., Nayak, S.K. & Kusrurkar, R.S. (2010). Indium (III) chloride: an efficient catalyst for the synthesis of amidoalkyl naphthols. *Synt. Commun.* 40(19), 2941–2947. DOI: 10.1080/00397910903340702.
27. Patil, S.B., Singh, P.R., Surpur, M.P. & Samant, S.D. (2007). Ultrasound-promoted synthesis of 1-amidoalkyl-2-naphthols via a three-component condensation of 2-naphthol, ureas/amides, and aldehydes, catalyzed by sulfamic acid under ambient conditions. *Ultrasonics Sonochem.* 14(5), 515–518. DOI: 10.1016/j.ulsonch.2006.09.006.
28. Nagarapu, L., Baseeruddin, M., Apuri, S. & Kantavari, S. (2007). Potassium dodecatungstocobaltate trihydrate (K₅CoW₁₂O₄₀·3H₂O): A mild and efficient reusable catalyst for the synthesis of amidoalkyl naphthols in solution and under solvent-free conditions. *Catal. Commun.* 8(11), 1729–1734. DOI: 10.1016/j.catcom.2007.02.008.
29. Arundhathi, K., Sudhakar, K., Sastry, B.S. & Yadav, J.S. (2010). A novel three-component one-pot reaction involving β -naphthol, aldehydes, and urea promoted by TMSCl/NaI. DOI: 10.1002/jhet.328.
30. Shaterian, H.R., Yarahmadi, H. & Ghashang, M. (2008). An efficient, simple and expedition synthesis of 1-amidoalkyl-2-naphthols as 'drug like' molecules for biological screening. *Bioorg. & Med. Chem. Letters* 18(2), 788–792. DOI: 10.1016/j.bmcl.2007.11.035.
31. Kumar, A., Rao, M.S., Ahmad, I. & Khungar, B. (2009). A simple and facile synthesis of amidoalkyl naphthols catalyzed by Yb (OTf) 3 in ionic liquids. *Canad. J. Chem.* 87(6), 714–719. DOI: 10.1139/V09-049.
32. Khodaei, M.M., Khosropour, A.R. & Moghanian, H. *Synlett.*, 2006, 132, 916.
33. Zhang, P. & Zhang, Z.H. (2009). Preparation of amidoalkyl naphthols by a three-component reaction catalyzed by 2, 4, 6-trichloro-1, 3, 5-triazine under solvent-free conditions. *Monatshfte für Chem.- Chem. Monthly* 140(2), 199. DOI: 10.1007/s00706-008-0059-5.
34. Jiang, W.Q., An, L.T., & Zou, J.P. (2008). Molybdophosphoric Acid: An Efficient Keggin-type Heteropolyacid Catalyst for the One-pot Three-Component Synthesis of 1-Amidoalkyl-2-naphthols. *Chin. J. Chem.* 26(9), 1697–1701. DOI: 10.1002/cjoc.200890307.
35. Su, W.K., Tang, W.Y. & Li, J.J. (2008). Strontium(II) triflate catalyzed condensation of β -naphthol, aldehyde and urea or amides: a facile synthesis of amidoalkyl naphthols. *Chem. Res.* 123–128. DOI: 10.3184/030823408X298508.
36. Kantavari, S., Vuppalapati, S.V. & Nagarapu, L. (2007). Montmorillonite K10 catalyzed efficient synthesis of amidoalkyl naphthols under solvent free conditions. *Catalysis Communications* 8(11), 1857–1862. DOI: 10.1016/j.catcom.2007.02.022.
37. Khafagy, M.M., El-Wahab, A.H.A., Eid, F.A. & El-Agrody, A.M. (2002). Synthesis of halogen derivatives of benzo [h] chromene and benzo [a] anthracene with promising antimicrobial activities. *Il Farmaco* 57(9), 715–722. DOI: 10.1016/S0014-827X(02)01263-6.
38. Jeso, V. & Nicolaou, K.C. (2009). Total synthesis of tovophyllin B. *Tetrahedron letters* 50(11), 1161–1163. DOI: 10.1016/j.tetlet.2008.12.096.
39. Skommer, J., Wlodkowic, D., Mättö, M., Eray, M. & Pelkonen, J. (2006). HA14-1, a small molecule Bcl-2 antagonist, induces apoptosis and modulates action of selected anticancer drugs in follicular lymphoma B cells. *Leukemia Res.* 30(3), 322–331. DOI: 10.1016/j.leukres.2005.08.022.
40. Mohr, S.J. (1975). Chirigos, MA, Fuhrman, FS, and Pryor, JW Pyran Copolymer as an Effective Adjuvant to Chemotherapy against a Murine Leukemia and Solid Tumor. *Cancer Res.* 35, 3750–3754.
41. Wang, J.L., Liu, D., Zhang, Z.J., Shan, S., Han, X., Srinivasula, S.M., ... & Huang, Z. (2000). Structure-based discovery of an organic compound that binds Bcl-2 protein and induces apoptosis of tumor cells. *Proceed. Nat. Acad. Sci.* 97(13), 7124–7129. DOI: 10.1073/pnas.97.13.7124.
42. Martínez-Grau, A., & Marco, J. (1997). Friedländer reaction on 2-amino-3-cyano-4H-pyrans: Synthesis of derivatives of 4H-pyran [2, 3-b] quinoline, new tacrine analogues. *Bioorg. & Medic. Chem. Letters* 7(24), 3165–3170. DOI: 10.1016/S0960-894X(97)10165-2.
43. Smith, P.W., Sollis, S.L., Howes, P.D., Cherry, P.C., Starkey, I.D., Cobley, K.N., ... & Wyatt, P. (1998). Dihydropyran-carboxamides related to zanamivir: A new series of inhibitors of influenza virus sialidases. 1. Discovery, synthesis, biological

activity, and structure– activity relationships of 4-guanidino- and 4-amino-4 H-pyran-6-carboxamides. *J. Med. Chem.* 41(6), 787–797. DOI: 10.1021/jm970374b.

44. Kidwai, M., Saxena, S., Khan, M.K.R. & Thukral, S.S. (2005). Aqua mediated synthesis of substituted 2-amino-4H-chromenes and in vitro study as antibacterial agents. *Bioorg. & Med. Chem. Letters* 15(19), 4295–4298. DOI:10.1016/j.bmcl.2005.06.041.

45. Eiden, F. & Denk, F. (1991). Synthesis of CNS-activity of pyran derivatives: 6, 8-dioxabicyclo (3, 2, 1) octane. *Arch. Pharm.* 324(6), 353–354. DOI: 10.1002/ardp.19913240606.

46. Albadi, J., Razeghi, A., Mansournezhad, A. & Azarian, Z. (2013). CuO-CeO 2 nanocomposite catalyzed efficient synthesis of aminochromenes. *J. Nanostr. Chem.* 3(1), 85.

47. Rao, M.S., Chhikara, B.S., Tiwari, R., Shirazi, A.N., Parang, K. & Kumar, A. (2012). A greener synthesis of 2-aminochromenes in ionic liquid and evaluation of their antiproliferative activities.

48. Gong, K., Wang, H.L., Fang, D. & Liu, Z.L. (2008). Basic ionic liquid as catalyst for the rapid and green synthesis of substituted 2-amino-2-chromenes in aqueous media. *Catal. Commun.* 9(5), 650–653. DOI: 10.1016/j.catcom.2007.07.010.

49. Abdolmohammadi, S., Afsharpour, M. & Keshavarz-Fatideh, S. (2014). An Efficient Green Synthesis of 3-Amino-1 H-chromenes Catalyzed by ZnO Nanoparticles Thin-film. *South Afric. J. Chem.* 67(1), 203–210.

50. El-Maghraby, A.M. (2014). Green chemistry: new synthesis of substituted chromenes and benzochromenes via three-component reaction utilizing Rochelle salt as novel green catalyst. *Org. Chem. Internat.* DOI: 10.1155/2014/715091.

51. Balalaie, S., Ramezanzpour, S., Bararjanian, M. & Gross, J.H. (2008). DABCO-catalyzed efficient synthesis of naphthopyran derivatives via One-Pot three-component condensation reaction at room temperature. *Synt. Commun.* 38(7), 1078–1089. DOI: 10.1080/00397910701862865.

52. Wang, M., Zhang, T.T., Liang, Y. & Gao, J.J. (2012). Efficient synthesis of mono-and disubstituted 2, 3-dihydroquinazolin-4 (1H)-ones using copper benzenesulfonate as a reusable catalyst in aqueous solution. *Monatshefte für Chem.-Chem. Monthly* 143(5), 835–839. DOI: 10.1007/s00706-011-0648-6.

53. Hajipour, A.R., Ghayeb, Y., Sheikhan, N. & Ruoho, A.E. (2009). Brønsted acidic ionic liquid as an efficient and reusable catalyst for one-pot synthesis of 1-amidoalkyl 2-naphthols under solvent-free conditions. *Tetrahedron Letters* 50(40), 5649–5651. DOI: 10.1016/j.tetlet.2009.07.116.

54. Selvam, N.P. & Perumal, P.T. (2006). A new synthesis of acetamido phenols promoted by Ce (SO₄)₂. *Tetrahedron Letters* 47(42), 7481–7483. DOI: 10.1016/j.tetlet.2006.08.038.

55. Nandi, G.C., Samai, S., Kumar, R. & Singh, M.S. (2009). Atom-efficient and environment-friendly multicomponent synthesis of amidoalkyl naphthols catalyzed by P2O₅. *Tetrahedron Letters* 50(51), 7220–7222. DOI: 10.1016/j.tetlet.2009.10.055.

56. Shaterian, H.R., Yarahmadi, H. & Ghashang, M. (2008). Silica supported perchloric acid (HClO₄-SiO₂): an efficient and recyclable heterogeneous catalyst for the one-pot synthesis of amidoalkyl naphthols. *Tetrahedron* 64(7), 1263–1269. DOI: 10.1016/j.tet.2007.11.070.

57. Luo, J. & Zhang, Q. (2011). A one-pot multicomponent reaction for synthesis of 1-amidoalkyl-2-naphthols catalyzed by PEG-based dicationic acidic ionic liquids under solvent-free conditions. *Monatshefte für Chem.-Chem. Monthly* 142(9), 923. DOI: 10.1007/s00706-011-0522-6.

58. Ghorbani-Vaghei, R. & Malaekhepour, S.M. (2010). Efficient and solvent-free synthesis of 1-amidoalkyl-2-naphthols using N, N, N', N'-tetrabromobenzene-1, 3-disulfonamide. *Central Europ. J. Chem.* 8(5), 1086–1089. DOI: 10.2478/s11532-010-0077-0.

59. Moosavi-Zare, A.R., Zolfigol, M.A., Khaledian, O., Khakyzadeh, V., Beyzavi, M.H. & Kruger, H.G. (2014). Tandem Knoevenagel–Michael–cyclocondensation reaction of

malononitrile, various aldehydes and 2-naphthol over acetic acid functionalized ionic liquid. *Chem. Engin. J.* 248, 122–127. DOI: 10.1016/j.cej.2014.03.035.

60. Dekamin, M.G., Eslami, M. & Maleki, A. (2013). Potassium phthalimide-N-oxyl: a novel, efficient, and simple organocatalyst for the one-pot three-component synthesis of various 2-amino-4H-chromene derivatives in water. *Tetrahedron* 69(3), 1074–1085. DOI: 10.1016/j.tet.2012.11.068.

61. Nabinia, N., Shirini, F., Tajik, H., Mashhadinezhad, M. & Langarudi, M.S.N. (2018). An affordable DABCO-based ionic liquid efficiency in the synthesis of 3-amino-1-aryl-1H-benzo [f] chromene-2-carbonitrile, 1-(benzothiazolylamino) phenylmethyl-2-naphthol, and 1-(benzoimidazolylamino) phenylmethyl-2-naphthol derivatives. *J. Iranian Chem. Soc.* 15(9), 2147–2157. DOI: 10.1007/s13738-018-1408-x.

62. Behbahani, F.K. & Maryam, S. (2013). On Water CuSO₄ 4. 5H₂O-catalyzed Synthesis of 2-amino-4H-chromenes. *J. Korean Chem. Soc.* 57(3), 357–360.

63. Sadeghi, B. & Zarepour, I. (2015). Nano-sawdust–BF₃ as a new, cheap, and effective nano catalyst for one-pot synthesis of 2-amino benzo [h] chromene derivatives. *J. Nanostruc. Chem.* 5(3), 305–311. DOI: 10.1007/s40097-015-0162-1.

64. Akandi, A.S., Balali, E., Mosavat, T., Ghanbari, M.M. & Eazabadi, A. (2014). The One-Step Synthesis of 3, 4-Dihydroprano [F] Chromene Derivatives in Under Grinding as an Environmentally Friendly Alternative. *Oriental J. Chem.* 30(2). DOI: 10.13005/ojc/300225.

65. Cai, X.H., Guo, H. & Xie, B. (2011). One-pot multi-component synthesis of amidoalkyl naphthols with potassium hydrogen sulfate as catalyst under solvent-free condition. *Jordan J. Chem.* 146(602), 1–4.

66. Hazeri, N., Maghsoudlou, M.T., Habii-Khorassani, S.M., Aboonajmi, J. & Safarzi, M. (2013). A green protocol for one-pot three-component synthesis of amidoalkyl naphthols catalyzed by succinic acid. *Chem. Sci. Transac.* 2(S1), S330–S336. DOI: 10.7598/cst2013.426.

67. Chinna Ashalua, K. & Nageshwar Rao, J. (2013). MgSO₄ catalyzed one-pot multi-component reaction: Synthesis of amidoalkyl naphthols. *J. Chem. Pharm. Res.* 5, 44.

68. Taghrir, H., Ghashang, M. & Biregan, M.N. (2016). Preparation of 1-amidoalkyl-2-naphthol derivatives using barium phosphate nano-powders. *Chin. Chem. Letters* 27(1), 119–126. DOI: 10.1016/j.ccl.2015.08.011.

69. Zolfigol, M.A., Baghery, S., Moosavi-Zare, A.R., Vahdat, S.M., Alinezhad, H. & Norouzi, M. (2015). Design of 1-methylimidazolium tricyanomethanide as the first nanostructured molten salt and its catalytic application in the condensation reaction of various aromatic aldehydes, amides and β-naphthol compared with tin dioxide nanoparticles. *RSC Adv.* 5(56), 45027–45037. DOI: 10.1039/C5RA02718G.

70. Heravi, M.M., Hosseinnejad, T., Faghihi, Z., Shiri, M., & Vazinfard, M. (2017). Synthesis of 2-amino-3-cyano 4-H-chromenes containing quinoline in water: computational study on substituent effects. *J. Iranian Chem. Soc.* 14(4), 823–832. DOI: 10.1007/s13738-016-1032-6.

71. Eshghi, H., Damavandi, S. & Zohuri, G.H. (2011). One pot synthesis of pyran-based heterocycles from benzyl halides as key reagents. *Inorg. Met. Org. NanoMet. Chem.* 41, 1067.

72. Baghbanian, S.M., Rezaei, N., & Tashakkorian, H. (2013). Nanozeolite clinoptilolite as a highly efficient heterogeneous catalyst for the synthesis of various 2-amino-4 H-chromene derivatives in aqueous media. *Green Chem.* 15(12), 3446–3458. DOI: 10.1039/C3GC41302K.

73. Heravi, M.M., Baghernejad, B. & Oskooie, H.A. (2008). A Novel and Efficient Catalyst to One-Pot Synthesis of 2-Amino-4H-Chromenes by Methanesulfonic. *Acid. J. Chin. Chem. Soc.* 55(3), 659–662. DOI: 10.1002/jccs.200800098.