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

Fangping Li¹, Jun Zhang⁴*, Longjiang Wang¹, Weijian Liu¹, Qahtan A. Yousef⁶

¹Guodian Jinshajiang Xulong Hydropower Development Co., Ltd, Chengdu, Sichuan, 610041, China
²University of Science and Technology, School of Civil Engineering, Anshan, Liaoning 114000, China
³Dalian University of Technology, State Key Laboratory of Coastal and Offshore Engineering, Dalian, Liaoning, 116024, China
⁴Zhongyuan University of Technology, Department of Architecture and Engineering, Zhengzhou, Henan, 450007, China
⁵University of Al-Qadisiyah, College of Science, Department of Chemistry, Republic of Iraq
⁶Corresponding author: e-mail: zhangji9888aa@163.com

A green procedure for the one-pot three-component synthesis of 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1H benzo[ʃ]chromene-2-carbonitrile derivatives from the reaction of 2-naphthol, aldehydes, and malononitrile 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-1H benzo[ʃ]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 environment. Nano small-sized catalysts due to their high surface area can be enhanced the chemical synthesis expediency. 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 them. 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 utilization. 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 surfaces. 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 sorting. 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 depessor effects in humans. 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 acid, 1, 2, 3-indion-130, InCl₃, H₂NSO₂H₂P, K₂CoW₁₂O₃₀·3H₂O·2₈, TMSCI/NaP₂, Fe(HSO₄)₃, Yb(OTf)₃ in ionic liquid, p-toluenesulfonic acid, 2,4,6-trichloro-1,3,5-triazine, HPMO₄, Sr(OTf)₂, 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 antimicrobial, antibiotic, antiviral, antioxidant, and central nervous system activities. The synthetic method for the synthesis of substituted 3-amino-1H-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·CeO₂, basic ionic liquids, heterogeneous catalysts which have been presented to the synthesis of 3-amino-1H-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 (Fe₃O₄).**

In this way, 2.2 g of FeCl₂·4H₂O and 5.7 g of FeCl₃·6H₂O were dissolved in 60 ml of deionized water in a beaker under vigorous stirring and nitrogen gas protection for 1 h. 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 (Fe₃O₄@SiO₂).**

First, 0.1 g of fabricated Fe₃O₄ 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 Fe₃O₄ bonded aminopropyltriethoxysilane (Fe₃O₄@APTES).**

About 1 g of the Fe₃O₄@SiO₂ 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 Fe₃O₄@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 Fe₃O₄@APTES bonded aspartic acid (Fe₃O₄@APTES/ASA).**

1 g of Fe₃O₄@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 Fe₃O₄@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 Fe₃O₄@enamine-B(OH)₂.**

About, 1 g of Fe₃O₄@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 Fe₃O₄@enamine-B(OSO₃H)₂.**

To prepare Fe₃O₄@enamine-B(OSO₃H)₂, 2 g of Fe₃O₄@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, the 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 Fe₃O₄@enamine-B(OSO₃H)₂ synthesis are exhibited in Scheme 1.

**FTIR analysis of Fe₃O₄@enamine-B(OSO₃H)₂.**

The FT-IR spectra of the Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@APTES, Fe₃O₄@APTES/ASA, Fe₃O₄@enamine-B(OH)₂, Fe₃O₄@enamine-B(OSO₃H)₂, and recovered Fe₃O₄@enamine-B(OSO₃H)₂ samples in the ranging from 400 to 4000 cm⁻¹ are illustrated in Fig. 1. FT-IR spectra of the Fe₃O₄ exhibited the characteristic Fe-O and the OH groups attached to the iron absorptions at 583 and 3391 cm⁻¹, respectively. In about the Fe₃O₄@SiO₂, 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 Fe₃O₄@APTES, the existence of an anchored alky 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 Fe₃O₄@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 Fe₃O₄@enamine-B(OH)₂ is confirmed by the B-C vibration at 1375 cm⁻¹. Characteristic SO₃H groups are presented at 1098 and 1173 cm⁻¹ in the spectra of Fe₃O₄@enamine-B(OSO₃H)₂. From the spectra of recovered Fe₃O₄@enamine-B(OSO₃H)₂ we
Fe₃O₄@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 Fe₃O₄@APTES/ASA, which can be related to the decomposition of APTES and ASA groups. Fe₃O₄@enamine-B(OH)₂ and Fe₃O₄@enamine-B(OSO₃H)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.

As observed in Fig. 2, thermogravimetric analysis (TGA) was applied for measuring the thermal constancy of the Fe₃O₄, Fe₃O₄@APTES, Fe₃O₄@APTES/ASA, Fe₃O₄@enamine-B(OH)₂ and Fe₃O₄@enamine-B(OSO₃H)₂ at 10°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 H₂O molecules and dehydration of the surface OH groups. In the curve of Fe₃O₄@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 Fe₃O₄@APTES/ASA, which can be related to the decomposition of APTES and ASA groups. Fe₃O₄@enamine-B(OH)₂ and Fe₃O₄@enamine-B(OSO₃H)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.

As can be seen that the catalyst after the third recovery and reuse do not exhibit any difference.

**Scheme 1.** Synthetic route of Fe₃O₄@enamine-B(OSO₃H)₂.

**Figure 1.** FTIR spectra of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@APTES, Fe₃O₄@APTES/ASA, Fe₃O₄@enamine-B(OH)₂, and Fe₃O₄@enamine-B(OSO₃H)₂.

**Figure 2.** TGA curves of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@APTES, Fe₃O₄@APTES/ASA, Fe₃O₄@enamine-B(OH)₂, and Fe₃O₄@enamine-B(OSO₃H)₂.

**EDX analysis of Fe₃O₄@enamine-B(OSO₃H)₂.**

The components of the Fe₃O₄@enamine-B(OSO₃H)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 Fe₃O₄@enamine-B(OSO₃H)₂ illustrates that SO₃H
groups was attached to the functional groups of Fe₃O₄@enamine-B(OH)₂.

VSM analysis of Fe₃O₄@enamine-B(OSO₃H)₂.

The magnetization measurements of the Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@enamine-B(OSO₃H)₂ were surveyed by vibrating sample magnetometer (VSM) at room temperature. As shown on Fig. 4, the saturation magnetization of Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@enamine-B(OSO₃H)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.

RESULTS AND DISCUSSION

In continuation of our investigations and on the basis of the achieved information, Fe₃O₄@enamine-B(OSO₃H)₂ was tested as a separable heterogeneous magnetic nanocatalyst for the synthesis of 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1H-benzo[f]chromene-2-carbonitrile derivatives under solvent-free conditions (Scheme 2).

Firstly, the catalytic efficiency of Fe₃O₄@enamine-B(OSO₃H)₂ was surveyed in a three-component reaction for the preparation of 1-amidoalkyl-2-naphthol and 3-amino-1-phenyl-1H-benzo[f]chromene-2-carbonitrile derivatives. To find the optimal conditions, the reaction between 2-naphtol, 4-chlorobenzaldehyde, and acetamide with 1:1:1 molar ratios and the reaction between 2-naphtol, 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-1H-benzo[f]chromene-2-carbonitrile synthesis reaction (Table 1). As can be seen, in the presence of the catalyst, with different solvents such as H₂O, EtOH, CH₃CN, CHCl₃, 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 Fe₃O₄@enamine-B(OSO₃H)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.
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-naphtol, 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-1H-benzofchromene-2-carbonitrile by the one-pot three-component condensation of 2-naphtol, 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-1H-benzofchromene-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 naphtol 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-naphtol 1 to alkylidemalononitrile 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 (a) and 3-amino-1-phenyl-1H-benzofchromene-2-carbonitrile (b) derivatives. Thus, after completion of the reaction, ethyl acetate as a polar solvent was added to the backer, 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-1H-benzof]chromene-2-carbonitrile (6) derivatives catalyzed by Fe₃O₄@enamine-B(OSO₃H)₂](image-url)
### Table 2. Synthesis of 1-amidoalkyl-2-naphthol (4) derivatives catalyzed by Fe₃O₄@enamine-B(OSO₃H)₂⁺

| Entry | Amide     | Aldehyde (3) | Product | Time [min] | Yield [%] | M.P.(Obas) [°C] | M.P.(Lit) [°C] |
|-------|-----------|--------------|---------|------------|-----------|-----------------|----------------|
| 1     |           |              | ![4a](image) | 12         | 95        | 231-233         | 234-236²⁶      |
| 2     |           | Cl⁻ benzaldehyde | ![4b](image) | 10         | 96        | 262-265         | 265-267²⁶      |
| 3     |           | Cl⁻ benzaldehyde | ![4c](image) | 12         | 96        | 235-237         | 238-239²⁶      |
| 4     | NO₂ benzaldehyde |              | ![4d](image) | 10         | 94        | 233-236         | 237-238²⁶      |
| 5     |           | Br⁻ benzaldehyde | ![4e](image) | 15         | 93        | 187-189         | 182-184²⁶      |
| 6     |           | OMe benzaldehyde | ![4f](image) | 25         | 90        | 211-215         | 214-216²⁸      |
| 7     | MeO benzaldehyde |              | ![4g](image) | 40         | 90        | 238-241         | 238-240²⁵      |
| 8     | Cl⁻ benzaldehyde |              | ![4h](image) | 10         | 94        | 233-235         | 235-236²⁶      |
| 9     | Cl⁻ benzaldehyde |              | ![4i](image) | 25         | 87        | 196-198         | 198-199²⁴      |
| 10    | NO₂ benzaldehyde |              | ![4j](image) | 20         | 90        | 185-189         | 180-182²⁴      |
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-1H-benzof[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-

|   |     |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|-----|
| 11 | C₂H₅NH₂ | O₂N | C₂H₅NH₂ | O₂N | 15 | 93 | 248-249 | 248-250°c |
| 12 | C₂H₅NH₂ | Br | C₂H₅NH₂ | O₂N | 20 | 95 | 228-230 | 229-231°c |
| 13 | C₂H₅NH₂ | (Me₂N)₂ | C₂H₅NH₂ | O₂N | 20 | 91 | 247-249 | 251-253°c |
| 14 | C₂H₅NH₂ | MeO | C₂H₅NH₂ | O₂N | 30 | 95 | 215-218 | 220-221°c |
| 15 | C₂H₅NH₂ | MeO | C₂H₅NH₂ | O₂N | 25 | 92 | 227-229 | 235-236°c |
| 16 | C₂H₅NH₂ | OMe | C₂H₅NH₂ | O₂N | 15 | 93 | 200-202 | 203-205°c |
| 17 | C₂H₅NH₂ | OMe | C₂H₅NH₂ | O₂N | 15 | 93 | 238-240 | 241-243°c |
| 18 | H₃N | O | C₂H₅NH₂ | O₂N | 35 | 89 | 172-174 | 176-175°c |
| 19 | H₃N | Cl | C₂H₅NH₂ | O₂N | 35 | 88 | 170-172 | 168-169°c |

*Reaction conditions: 2-naphthol (1 mmol), aldehyde (1 mmol), amide (1 mmol), Fe₃O₄@enamine-B(OSO₃H)₂ (15 mg).*
Table 3. Preparation of 3-amino-1-phenyl-1H-benzo[ ]chromene-2-carbonitrile (6) derivatives using Fe₃O₄@enamine-B(OSO₃H)₂ as a catalyst

| Entry | Product | Aldehyde (3) | Product | Time [min] | Yield[%] | M.P.(Obtd) [°C] | M.P. (Ref) [°C] |
|-------|---------|--------------|---------|------------|----------|----------------|----------------|
| 1     | 6a      |              |         | 18         | 92       | 277-279        | 279-280\(^{39}\) |
| 2     | 6b      | Cl-O        |         | 12         | 92       | 273-275        | 271-272\(^{39}\) |
| 3     | 6c      | Cl-Cl       |         | 15         | 92       | 210-212        | 202-204\(^{44}\) |
| 12    | 6l      | Me-O        |         | 25         | 92       | 272-274        | 273-274\(^{39}\) |
| 13    | 6m      | OMe-O       |         | 25         | 93       | 220-222        | 219-222\(^{52}\) |
| 14    | 6n      | Me-OMe      |         | 20         | 92       | 195-197        | 185-187\(^{50}\) |
| 15    | 6o      | F₃C-        |         | 20         | 94       | 210-212        | 215-217\(^{44}\) |
| 16    | 6p      | HO-          |         | 15         | 91       | 281-283        | 280-282\(^{24}\) |
| 17    | 6q      | HO-          |         | 20         | 96       | 285-287        | 288-290\(^{50}\) |

*Reaction conditions: 2-naphtol (1 mmol), aldehyde (1 mmol), malononitrile (1.1 mmol), Fe₃O₄@enamine-B(OSO₃H)₂ (15 mg).
procedure, utilizing Fe3O4@enamine-B(OSO3H)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 Fe3O4@enamine-B(OSO3H)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**

This research was funded by the National Key Research and Development Plan of China (2017YFC1503103) and the State Key Laboratory of Water Resource Protection and Utilization in Coal Mining (SHJT-17-42.15).

**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., Dadjou, 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 Fe3O4@ SiO2@ 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. Mobarakia, A., Movassaghi, 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 Comb. 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. Skylesh, S., Schönemann, 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. & Nasseri, M.A. (2013). Methylene dipyridine nanoparticles stabilized on Fe3O4 as catalysts for efficient, green, and one-pot synthesis of pyrazolophthalazinyl spirooxindoles. *Cataylsis Today* 217, 80–85. DOI: 10.1016/j.cattod.2013.07.018.

10. Vaysseires, L., Chanéac, C., Trone, 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 Fe3O4/polystyrene composite particles via inverse emulsion
activity, and structure—activity relationships of 4-guanidino-4-amino-4-H-pyran-6-carboxamides. J. Med. Chem. 41(6), 787–797. DOI: 10.1021/jm900374b.

44. Kidwai, M., Saxena, S., Khan, M.K.R. & Thukral, S.S. (2005). Aqua mediated synthesis of substituted 2-amino-4-H-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/arpd.199913240606.

46. Albadi, J., Raseghi, A., Mansournizad, A. & Azarian, Z. (2013). CuO-CeO2 nanocomposite catalyzed efficient synthesis of aminochrome. J. Nanostr. Chem. 3(1), 85.

47. Rao, M.S., Chikara, B.S., Tiwari, R., Shirini, A.N., Parang, K. & Kumar, A. (2012). A greener synthesis of 2-aminochromenes in ionic liquid and evaluation of their anti proliferative 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-4H-chromenes in aqueous media. Catal. Commun. 9(5), 650–653. DOI: 10.1016/j.catcom.2007.07.010.

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

50. El-Maghraby, A.M. (2014). Green chemistry: new synthesis of substituted 2-amino and 2-benzylchromenes and benzochromens via three-component reaction utilizing Rochelle salt as novel green catalyst. Org. Chem. Int. 10.1155/2014/715091.

51. Balalaei, S., Ramezanpoor, S., Baranjari, M. & Gross, J.H. (2008). DABCO-catalyzed efficient synthesis of naphthypan derivatives via One-Pot three-component condensation reaction at room temperature. Synt. Commun. 38(7), 1078–1089. DOI: 10.1080/03997910701862865.

52. Wang, M., Zing, T.T., Liang, Y. & Gao, J.J. (2012). Efficient synthesis of mono-and substituted 2, 3-dihydroquinazolin-4(1H)-ones using copper benzenesulfonate as a reusable catalyst in aqueous solution. Monatshfte 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. (2015). Design of 1-methyl-1H-chromenes as key reagents. Tetrahedron Letters 57(3), 357–360. DOI:10.1016/j.tetlet.2015.07.010.

54. Selvam, N.P. & Perumal, P.T. (2006). A new synthesis of acetamido phenols promoted by Ce (SO4)2. Monatshefte für Chem. 137(5), 659–662. DOI: 10.1007/s00706-008-0077-0.

55. Ghorbani-Vaghei, R. & Malekehpour, S.M. (2010). Efficient and solvent-free synthesis of 1-amidoalkyl-2-naphthols catalyzed by PEG-based dicationic acidic ionic liquids under solvent-free conditions. Monatshfte für Chem.-Chem. Monthly 142(9), 923. DOI: 10.1007/s00706-011-0522-6.

56. Moosavi-Zare, A.R., Zolfogli, M.A., Khaleld, O., Khayyazadeh, 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.

57. 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-4-H-chromene derivatives in water. Tetrahedron 69(3), 1074–1085. DOI: 10.1016/j.tet.2012.11.068.

58. 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-(benzoazolylamino) phenethyl-2-naphthol, and 1-((benzoimidazolylamino) phenethyl-2-naphthol derivatives. J. Iranian Chem. Soc. 15(9), 2147–2157. DOI:10.1007/s13738-018-1408-x.

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

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

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

62. Grass, C.H., Gross, H. & Xie, B. (2011). One-pot multicomponent synthesis of amidicyanlated naphthols with potassium hydroxide as a catalyst under solvent-free condition. Jordan J. Chem. 146(602), 1–4.

63. Hazeri, N., Maghsoudlou, M.T., Habib-Khorassani, S.M., Aboonajimi, J. & Safarzef, M. (2013). A green protocol for one-pot three-component synthesis of amidicyanlated naphthols catalyzed by succinic acid. Chem. Sci. Transac. 2(S1), S330–S336. DOI:10.7598/cst2013.1426.

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

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

66. Zolfogli, 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.

67. Heravi, M.M., Hosseinnejad, T., Faghihi, Z., Shirini, M. & Vazinward, 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.

68. 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.

69. Baghbanian, S.M., Rezaei, N. & Tashkhoranian, H. (2013). Nanozolite clonitopilite 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.

70. Heravi, M.M., Hosseinnejad, T., Faghihi, Z., Shirini, M. & Vazinward, M. (2017). A Novel and Efficient Catalyst to One-Pot Synthesis of 2-Amiino-4H-Chromenes by Methanesulfonic Acid. J. Chin. Chem. Soc. 55(3), 659–662. DOI: 10.1002/jccs.20080099.