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ARTICLE



Fe₃O₄@SiO₂@sulfated boric acid as superparamagnetic and recyclable nanocatalyst-assisted, one-pot, *pseudo* four-component synthesis of 5-amino-2-aryl-3*H*-chromeno[4,3,2-*de*][1,6] naphthyridine-4-carbonitrile derivatives

Zeynab Khosravi | Hadi Mohammadi | Hamid Reza Shaterian

Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan, Iran

Correspondence

Hamid Reza Shaterian, Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran. Email: hrshaterian@chem.usb.ac.ir

Abstract

The catalytic performance of the superparamagnetic nanocatalyst $Fe_3O_4@SiO_2@$ Sulfated boric acid as a green, recyclable, and acidic solid catalyst in the synthesis of chromeno[4,3,2-*de*][1,6]naphthyridine derivatives has been studied. Chromeno [4,3,2-*de*][1,6]naphthyridine derivatives via a *pseudo* four-component reaction from aromatic aldehydes (1 mmol), malononitrile (2 mmol), and 2'-hydroxyacetophenone in the presence of $Fe_3O_4@SiO_2@Sulfated$ boric acid (0.004 g) as a nanocatalyst in 3 mL of water as a green solvent at 80°C has been synthesized. The advantages of this method are higher product yields in shorter reaction times, easy recyclability and reusability of the catalyst, and easy work-up procedures. The nanocatalyst was reused at least six times. The nanocatalyst retained its stability in the reaction, and after reusability, it was separated easily from the reaction by an external magnet.

KEYWORDS

2'-hydroxyacetophenone, chromeno[4,3,2-*de*][1,6]naphthyridine, Fe₃O₄@SiO₂@Sulfated boric acid, nanocatalyst, *Pseudo* four-component reaction, water

1 | **INTRODUCTION**

Nanomaterials have been widely utilized as solid support materials for the design of environmentally benign heterogeneous catalysts for various economic and environmental reactions.^[1] Magnetic core interest to researce including catalysi resonance imagin remediation.^[7–10] been extensively i panoparticles as catalyst interact easily with reactants and intermediates which cause to increase the reaction rate, and conversion of reactants to the desired product(s).^[3] One of the important and significant groups of nanoparticles is magnetic

nanoparticles (MNPs), which show very particular properties such as high surface areas and ease separation of the catalyst by external magnet in work-up stage.^[4–6]

Magnetic core-shell structures of silica are of great interest to researchers from a wide range of disciplines, including catalysis, biotechnology/biomedicine, magnetic resonance imaging, data storage, and environmental remediation.^[7-10] In recent years, MNPs (e.g., Fe₃O₄) have been extensively investigated as an inorganic catalyst support in the synthesis of organic-inorganic hybrid catalysts^[11-13] because of their good stability, easy synthesis and functionalization, and high surface area, as well as low toxicity and price.^[13-16]

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Silica-coated nanoparticles such as $Fe_3O_4@SiO_2$ can be easily connected to linker groups, which can functionalized by a range of different organocatalysts.^[17] Function-based sulfonic acid is a significant branch of MNPs.^[18] Various solid acid catalysts with a variety of acid sites were considered in many different processes.^[19,20]

Multicomponent reactions are a promising design in the novel combinatorial chemistry due to some advantages such as their ability to synthesize the desired products with high atom economy through the reaction of three or more starting materials in a one-pot procedure. In addition, this technical skill improves the synthetic efficiency and simplicity of the formation of complex molecules with respect to the conventional organic reactions.^[21–23]

Chromenes and their fused heterocyclic derivatives have attracted a great deal of interest due to their wide applications in the field of pharmaceuticals. A literature survey demonstrated that several catalysts were reported for the preparation of chromeno[4,3,2-*de*][1,6]naphthyridine derivatives.^[24–27]

In continuation of our research on organocatalysts immobilized on nonmagnetic materials and their applications in organic reactions, especially the synthesis of chromeno [4,3,2-de][1,6]naphthyridine derivatives,^[24,27] here, we report the preparation of 5-amino-2-aryl-3*H*-chromeno [4,3,2-de][1,6]naphthyridine-4-carbonitrile derivatives via cascade *pseudo* four-component condensation reaction of malononitrile (2 mmol) and 2'-hydroxyacetophenone (1 mmol) with various aromatic aldehydes (1 mmol) in the presence of the catalytic amount of superparamagnetic $Fe_3O_4@SiO_2@Sulfated boric acid as a nanocatalyst under$ green conditions in aqueous media (Scheme 1).

2 | RESULTS AND DISCUSSION

2.1 | Catalyst

The FT-IR spectrum of $Fe_3O_4@SiO_2-O-B(OSO_3H)_2$ is presented in Figure 1. The Fe–O stretching vibration was observed at 550–650 cm⁻¹, and the stretching mode of Si– O-Si showed a strong broad peak at about 1,099–1,220 cm⁻¹. The functionalization of SO₃H groups



SCHEME 1 Synthesis of 5-amino-2-aryl-3*H*-chromeno[4,3,2-*de*] [1,6]naphthyridine-4-carbonitrile derivatives in the presence of Fe₃O₄@SiO₂@sulfated boric acid as a nanocatalyst



FIGURE 1 FT-IR spectra: (a) $Fe_3O_4@SiO_2$; (b) $Fe_3O_4@SiO_2$ -Cl; (c) $Fe_3O_4@SiO_2$ -O-B(OH)₂; (d) $Fe_3O_4@SiO_2$ -O-B(OSO₃H)₂

on the boric acid surface was approved by the absorption band S–O, and the S=O stretching bands of $-SO_3H$ moiety are asserted with 998–1,220 cm⁻¹ bands in the FT-IR spectrum. In addition, in the spectrum of Fe₃O₄@SiO₂-O-B (OSO₃H)₂, the peak at 3,405 cm⁻¹ was attributed to the SO₃–H groups.

2.2 | Optimization of the reaction conditions

To evaluate the activity of the nanocatalyst $Fe_3O_4@SiO_2-O-B(OSO_3H)_2$, the one-pot, *pseudo* four-component reaction of benzaldehyde (1 mmol), malononitrile (2 mmol), and 2'-hydroxyacetophenone (1 mmol) in water in the presence of $Fe_3O_4@SiO_2-O-B(OSO_3H)_2$ as a nanocatalyst was selected as a model (Scheme 2).

First, the reaction was carried out in presence of $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2@Boric$ acid, $Fe_3O_4@SiO_2@$ Sulfated boric acid, and without a catalyst at 80°C in aqueous media. The results are summarized in Table 1. It was found that the sequence of activity of the catalysts is: $Fe_3O_4@SiO_2 < Fe_3O_4@SiO_2@Boric$ acid $< Fe_3O_4@SiO_2@$ Sulfated boric acid. Comparing the catalyst activity of $Fe_3O_4@SiO_2@Sulfated$ boric acid as a nanocatalyst with other catalysts in Table 1, the reaction was completed in 60 min and with 90% yield (Table 1, Entry 4).

To select the appropriate solvent, the activity of $Fe_3O_4@SiO_2@Sulfated$ boric acid as a nanocatalyst was investigated in water, water: ethanol mixture, and under solvent-free conditions. According to the results, the highest yield of the desired product and maximum performance of the catalyst was obtained once the reaction was carried out



SCHEME 2 Synthesis of 5-amino-2-phenyl-3*H*-chromeno [4,3,2-*de*][1,6]naphthyridine-4-carbonitrile

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TABLE 1 Preparation of 5-amino-2-phenyl-3*H*-chromeno [4,3,2-de][1,6]naphthyridine-4-carbonitrile in the presence of Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@boric acid, Fe₃O₄@SiO₂@sulfated boric acid, and without a catalyst at 80°C in aqueous media

Entry	Catalyst	Amount catalyst (g)	Time (min)	Yield (%) ^{a,b}
1	Catalyst-free	_	360	13
2	Fe ₃ O ₄ @SiO ₂	0.004	110	80
3	Fe ₃ O ₄ @SiO ₂ @boric acid	0.004	80	85
4	Fe ₃ O ₄ @SiO ₂ @sulfated boric acid	0.004	60	90

^a*Reaction conditions*: benzaldehyde (1 mmol), malononitrile (2 mmol), and 2'-hydroxyacetophenone (1 mmol) with different catalysts in water (3 mL). ^bYield refers to isolated pure products.

TABLE 2 Preparation of 5-amino-2-phenyl-3*H*-chromeno [4,3,2-de][1,6]naphthyridine-4-carbonitrile in the presence of Fe₃O₄@SiO₂@sulfated boric acid in different solvents

Entry	Solvent	Time (min)	Temperature (°C)	Yield (%) ^{a,b}
1	EtOH (3 mL)	110	80	55
2	H ₂ O;EtOH(1:2) (3 mL)	90	80	70
3	H ₂ O;EtOH(1:1) (3 mL)	80	80	77
4	H ₂ O;EtOH(2:1) (3 mL)	75	80	82
5	H ₂ O (3 mL)	60	80	90
6	Solvent-free	120	80	71

^aReaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), and 2'-hydroxyacetophenone (1 mmol) with Fe₃O₄@SiO₂@Sulfated boric acid catalyst.

^bYield refers to isolated pure products.

in water as a solvent (Table 2, Entry 5). The formation of hydrogen bonds between starting reactants and nanocatalyst in water show a greater effect on the reaction. Moreover, the rate of reaction was drastically decreased with further increase of the volume ratio of ethanol to water (Table 2, Entries 2,3,4).

To find optimum conditions of the amount of the nanocatalyst and selecting the best temperature for the preparation of 5-amino-2-phenyl-3H-chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile in aqueous media, the reaction of benzaldehyde (1 mmol), malononitrile (2 mmol), and 2'hydroxyacetophenone (1 mmol) in the presence Fe₃O₄@SiO₂@Sulfated boric acid nanoparticles as а nanocatalyst in water (3 mL) as a solvent was carried out in different temperatures and also with varying concentrations of the nanocatalyst (3-6 mg). Table 3 shows that using 4 mg of Fe₃O₄@SiO₂@Sulfated boric acid in the reaction mixture is sufficient for achieving the best yield. To find the optimum temperature, the reaction was performed at different temperatures (Table 3), such as 25, 60, 70, 80, and 90°C, by using

TABLE 3 Optimization conditions of the amount of the nanocatalyst and the best temperature for the preparation of 5-amino-2-phenyl-3*H*-chromeno [4,3,2-*de*][1,6] naphthyridine-4-carbonitrile in aqueous media

Entry	Catalyst (g)	Temperature (°C)	Time (min)	Yield (%) ^{a,b}
1	0.003	80	85	81
2	0.004	80	60	90
3	0.005	80	55	82
4	0.006	80	50	78
5	0.004	25	960	30
6	0.004	60	120	65
7	0.004	70	90	77
8	0.004	90	55	87

^a*Reaction conditions*: benzaldehyde (1 mmol), malononitrile (2 mmol), and 2'-hydroxyacetophenone (1 mmol) in water (3 mL) as solvent.

^bYield refers to isolated pure products.

 $Fe_3O_4@SiO_2@Sulfated boric acid (4 mg) in water, and the best result was obtained at 80°C (Table 3, Entry 2).$

According to optimal considered conditions, 5-amino-2-aryl-3H-chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile derivatives were synthesized using this methodology, and the results are shown in Table 4.

The proposed mechanism for the formation of the product is shown in Scheme 3. First, intermediate (I) was formed through condensation between 2'-hydroxyacetophenone (1) and aryl aldehyde (2). Next, intermediate (II) was obtained from the condensation of (I) with malononitrile (3). The intramolecular nucleophilic attack by the OH group (II) led to the formation of intermediate (III). In the following condensation between (III) and another malononitrile (3), intermediate (IV) was formed. Then, the intramolecular cyclization of (IV) led to the formation of the final product.

The recyclability of $Fe_3O_4@SiO_2@Sulfated$ boric acid was examined in the one-pot *pseudo* four-component synthesis of 5-amino-2-phenyl-3*H*-chromeno[4,3,2-de][1,6] naphthyridine-4-carbonitrile (Reaction model). After completion of the reaction, the reaction mixture was cooled to room temperature, and the water was separated from the crude product and the catalyst by simple filtration; ethanol was added to the solid mixture and heated to separate $Fe_3O_4@SiO_2@Sulfated$ boric acid using an external magnet. The catalyst was washed with ethanol thrice and dried. As was shown in Figure 2, even after six runs, the catalytic activity and product yield had no significant loss. Thus, this catalyst can endure reaction conditions and remain stable.

To show the merit of the present work in comparison with reported results in the literature, we compared the results of $Fe_3O_4@SiO_2@Sulfated$ boric acid with other reported catalysts in the synthesis of 5-amino-2-phenyl-3*H*-chromeno

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Yield (%)^{a,b} Aromatic aldehydes Products Time(min) **Observed M.p.** (°C) Lit. M.p. (°C), reference Entry >300, [25] 1 60 90 >300 റ ΪI N 4a NC ΝH₂ 4a >300, ^[25] 2 C 80 CI 86 >300 0 Н Ň 4b NC $\dot{N}H_2$ 4b >300, [25] 3 65 89 >300 CI CI || N 4c NC ΝH₂ 4c >300, [25] 4 CI 75 93 >300 Ň C 4d NC ΝH₂ 4d 7 OCH₃O OCH₃ 80 94 294-296 295–296, [25] `| N 4e NC ΝH₂ 4e 278-280, [26] 8 OCH₃ 92 65 280-282 H₃CO Ν 4f NC NH₂ 4f

TABLE 4 Synthesis of 5-amino-2-aryl-3*H*-chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile derivatives by $Fe_3O_4@SiO_2@sulfated$ boric acid (4 mg) as a nanocatalyst at 80°C in water (3 mL) as a green solvent

TABLE 4 (Continued)

Entry	Aromatic aldehydes	Products	Time(min)	Yield (%) ^{a,b}	Observed M.p. (°C)	Lit. M.p. (°C), reference
9	H ₃ CO	H ₃ CO N N N N N H ₂ 4g	75	96	>300	>300, ^[25]
10	H ₃ CO H ₃ O H	$\begin{array}{c} OCH_3\\ \bullet\\ OCH_3\\ H\\ NC\\ NC\\ NH_2\\ H \end{array}$	100	73	285–287	288–290, ^[25]
	О F	F N NC NH_2 $4i$	70	87	>300	>300, ^[25]
	F	$ \begin{matrix} F \\ N \\ N \\ N \\ N \\ N \\ H_2 \\ H_2 \\ H_2 \end{matrix} $	80	90	>300	>300, ^[25]
11	H ₃ C	H ₃ C N NC NH ₂ 4k	40	94	>300	>300, ^[25]
12	Br	Br NC NC NH ₂ 41	65	94	>300	>300, ^[25]



TABLE 4 (Continued)



^a*Reaction conditions*: aryl aldehyde (1 mmol), malononitrile (2 mmol), and 2'-hydroxyacetophenone (1 mmol) in water (3 mL) as solvent. ^bYields refers to isolated pure products.



SCHEME 3 Mechanism for the synthesis of 5-amino-2-aryl-3Hchromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile derivatives in the presence of Fe₃O₄@SiO₂@sulfated boric acid as a nanocatalyst



FIGURE 2 Reusability of Fe₃O₄@SiO₂@sulfated boric acid as nanocatalyst

[4,3,2-de][1,6]naphthyridine-4-carbonitrile (Reaction model). As shown in Table 5, Fe₃O₄@SiO₂@Sulfated boric acid can act as an effective catalyst with respect to reaction times and yields of the obtained products. Thus, the present protocol with the Fe₃O₄@SiO₂@Sulfated boric acid catalyst is convincingly superior to the reported catalytic methods.

3 | EXPERIMENTAL

3.1 | Preparation of $Fe_3O_4@SiO_2@sulfated$ boric acid

 $Fe_3O_4@SiO_2@Sulfated$ boric acid as a nanocatalyst was synthesized based on the following procedure (Scheme 4).^[28]

Entry	Catalyst	Catalyst amount	Temperature (°C)	Time (min)	Yield (%)	References
1	Fe ₃ O ₄ NPs	5 mol%	70 (MW)	25	88	[26]
2	Fe ₃ O ₄ NPs	5 mol%	70 (conventional)	90	48	[26]
3	SiO_2	0.03 g	80	120	78	[25]
4	Fe ₃ O ₄ @SiO ₂ @sulfated boric acid	0.004 g	80	60	90	This work





SCHEME 4 Synthesis of $Fe_3O_4@SiO_2-O-B(OSO_3H)_2$ as a nanocatalyst

First, superparamagnetic Fe₃O₄ nanoparticles were facilely prepared using a chemical coprecipitating method.^[28] Second, Fe₃O₄ was coated with tetraethyl orthosilicate, (TEOS), becoming Fe₃O₄@SiO₂. Then, the reaction of thionyl chloride with Fe₃O₄@SiO₂ formed FE₃O₄@SiO₂–Cl; following this, Fe₃O₄@SiO₂–O-B(OH)₂ was formed from the reaction of Fe₃O₄@SiO₂–Cl with boric acid. Finally, Fe₃O₄@SiO₂-O-B(OH)₂ nanoparticles in 40 mL chloroform was ultrasonicated for 30 min, Then, chlorosulfonic acid was added dropwise, and the resulting reaction mixture was stirred for 4 hr at room temperature. The resulted brown powder was separated using an external magnet, washed with ethanol several times to remove the remaining acid, and dried for 12 hr at 60°C to form a superparamagnetic silica-encapsulated $Fe_3O_4@SiO_2-O-B$ (OSO₃H)₂ as the nanocatalyst

3.2 | General procedure for the direct synthesis of 5-amino-2-aryl-3*H*-chromeno [4,3,2-*de*] [1,6]naphthyridine-4-carbonitrile derivatives using Fe₃O₄@SiO₂@Sulfated boric acid nanoparticles

Fe₃O₄@SiO₂@Sulfated boric acid MNPs (4 mg) were added to a mixture of aromatic aldehyde (1 mmol), malononitrile (2 mmol), and 2'-hydroxyacetophenone (1 mmol) in water (3 mL). The reaction mixture was stirred at 80°C in an oil bath. The reaction was monitored by thin layer chromatography (TLC); after completion of the reaction, the reaction mixture was cooled to room temperature, and the water was separated from the crude product and the catalyst by filtration. Ethanol was added to the solid mixture and heated to separate Fe₃O₄@SiO₂@Sulfated boric acid using an external magnet. The catalyst was washed with ethanol thrice and dried. The warm ethanoic solution containing crude product was cooled until the precipitated pure product was formed. The known pure products were characterized and their physical data compared with those of known compounds. The new unknown products are characterized as follows:

5-amino-2-*meta*-tolyl-3*H*-chromeno[4,3,2-*de*][1,6]naphthyridine-4-carbonitrile (**4m**). Yellow solid; mp > 300°C. IR (KBr) (ν max/cm⁻¹): 3,482, 3,306, 2,209, 1,599, 1,510, 1,356, 758, 1,558, 1,573, 756; ¹HNMR (300 MHz, DMSO*d*₆): (δ , ppm): 2.47 (s, 3H, CH₃), 7.40 (s, 1H, Ar-H), 7.45 (s, 2H, NH₂), 7.47–7.52 (m, 3H, Ar-H), 7.69 (t, *J* = 7.2 Hz, 1H, Ar-H), 8.20–8.31 (m, 2H, Ar-H), 8.58 (d, *J* = 7.2 Hz, 1H, Ar-H), ¹³CNMR (75.6 MHz, DMSO-*d*₆): δ = 21.6, 76.1, 102.9, 105.2, 116.9, 117.7, 118.4, 125.4, 125.6, 128.6, 129.1, 131.8, 133.5, 138.2, 138.4, 138.9, 152.2, 155.9, 159.6, 162.2, 162.7 ppm.

5-amino-2-(3-hydroxyphenyl)-3H-chromeno[4,3,2-de] [1,6]naphthyridine-4-carbonitrile (**4n**).Yellow solid; mp > 300°C. IR (KBr) (ν max/cm⁻¹): 3,373, 3,472, 2,221, 1,558, 1,573, 1,356, 756; ¹HNMR (300 MHz, DMSO-*d*₆): (δ , ppm): 6.98 (d, *J* = 6.9 Hz, 1H, Ar-H), 7.37 (s, 2H, NH₂), 7.40–7.49 (m, 3H, Ar-H), 7.66 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.81 (d, J = 9.0 Hz, 2H, Ar-H), 8.20 (s, 1H, Ar-H), 8.51 (d, J = 7.5 Hz, 1H, Ar-H), 9.76 (s, 1H, OH).; ¹³CNMR (75.6 MHz, DMSO- d_6): $\delta = 76.1$, 102.9, 105.3, 115.0, 117.0, 117.6, 118.2, 118.3, 119.2, 125.6, 130.1, 133.4, 138.8, 139.8, 152.1, 155.8, 158.2, 159.5, 162.2, 162.8 ppm. The spectra of new compounds are presented in the supporting information.

4 | CONCLUSIONS

 $Fe_3O_4@SiO_2@Sulfated$ boric acid as a heterogeneous nanomagnetic catalyst has been successfully used for the *pseudo* four-component preparation of 5-amino-2-aryl-3*H*chromeno [4,3,2-de][1,6]naphthyridine-4-carbonitrile derivatives under green conditions in aqueous media. Easy reaction conditions, simple work-up or purification, excellent yields, high purity of the desired product, and short reaction times are some advantages of this protocol. The superparamagnetic nanocatalyst is separable and stable in the reaction conditions without detectable activity loss

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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