# **RESEARCH ARTICLE**



Magnetite Nanoparticles-Supported APTES as a Powerful and Recoverable Nanocatalyst for the Preparation of 2-Amino-5,10-dihydro-5,10-dioxo-4*H*-benzo[g]chromenes and Tetrahydrobenzo[g]quinoline-5,10-diones



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**Abstract:** *Aim and Objective:* This study introduces a green and effective approach for the preparation of biologically-active heterocyclic compounds including 2-amino-5,10-dihydro-5,10-dioxo-4*H*-benzo[*g*]chromenes and tetrahydrobenzo[*g*]quinoline-5,10-diones using one-pot multi-component reactions in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanocomposite. The preparation and use of amino-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> as a powerful and reusable nanocatalyst is described. The catalyst was characterized by spectral techniques including FT-IR, SEM, XRD, EDX and VSM analysis. This method offers the advantages of high yields, short reaction times, comfortable work-up and reusability of the catalyst.

ARTICLE HISTORY

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DOI: 10.2174/1386207319666161 223121612 *Material and Method*: The amino-functionalization silica-coated magnetite nanocomposite was prepared by three step method and the structure elucidation of the nanocatalyst has been done using various spectroscopic analyses. Then, the  $Fe_3O_4@SiO_2-NH_2$  nanocomposite was used in the multi-component synthesis of 2-amino-5,10-dihydro-5,10-dioxo-4*H*-benzo[*g*]chromenes and tetrahydrobenzo[*g*]quinoline-5,10-diones under reflux conditions. All of the products were analyzed with m.p., <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR spectroscopy techniques. The study on the recoverability of the nanocatalyst showed the recovered  $Fe_3O_4@SiO_2-NH_2$  nanocomposite could be reused sixth consecutive times with a little-decreased activity.

**Results:** Amino-functionalized SiO<sub>2</sub> coated Fe<sub>3</sub>O<sub>4</sub> nanocomposite exhibited superparamagnetic behavior and strong magnetization at room temperature. The average crystallite sizes of the catalyst was about 50-60 nm. The obtained magnetic nanocomposite showed excellent catalytic activity as a new heterogeneous magnetic catalyst for the synthesis of some benzo[g]chromenes and tetrahydrobenzo[g]quinoline-5,10-diones. We propose that NH<sub>2</sub> groups on the surfaces of nanocomposite act as the Brønsted base and cause to dehydrogenation of substrates to promote the reactions.

**Conclusion:** It was found that  $Fe_3O_4@SiO_2-NH_2$  nanocomposite act as an eco-friendly and efficient catalyst for one-pot synthesis of three/four component condensation reactions. In this research, amino-functionalized  $Fe_3O_4@SiO_2$  was used as recoverable catalyst for the synthesis of 2-amino-5,10-dihydro-5,10-dioxo-4*H*-benzo[*g*]chromenes and tetrahydrobenzo[*g*]quinoline-5,10-diones under reflux conditions. The significant advantages of this method are the reasonably simple work-up, little catalyst loading, short reaction times, excellent yields, non-hygroscopic quality and reusability of the nanocatalyst which is in good agreement with green chemistry disciplines.

**Keywords:**  $Fe_3O_4@SiO_2-NH_2$ , nanocomposite, multi-component reaction, core-shell, benzo[g]chromene, tetrahydrobenzo[g] quinoline-5,10-dione.

# **1. INTRODUCTION**

In recent decades, the use of nanotechnology as an efficient field has been of interest to scientists. The surface atoms of nanoparticles can be replaced by adjacent atoms, this process is accompanied by the exchange of energy which specified the reactivity and selectivity of the nanocatalyst [1].

 $Fe_3O_4$  nanoparticles have been expansively studied because of their inimitable magnetic properties and executive specific abilities such as magnetic hyperthermia, targeted drug delivery, ferrofluids, etc [2, 3].

 ${\rm Fe_3O_4}$  NPs have the ability to aggregate, and they are also known as hard dispersion nanoparticles in the organic

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conditions, therefore, the surface coating of  $Fe_3O_4$  NPs is very significant [4-7].

Silica due to its large surface and the ability to compromise with other substances is a substantial shellforming material [8, 9]. The process of nanoparticles' coating by silica improves their stability and develops sites for more surface functionalization using different groups such as silica sulfuric acid [10], proline [11], (3aminopropyl)- triethoxysilane [12], guanidine [13] and sulfamic [14]. The reaction acid of 3aminopropyltriethyloxysilane and nanoparticles leads to the formation of Si-O bonds. The Brønsted basic (-NH<sub>2</sub>) functionalized Fe<sub>3</sub>O<sub>4</sub> core has an important catalytic effect in the described transformation. The isolation of APTES coreshell nanocomposite can be used by applying an external magnetic field with a comfortable work up.

Multi-component reactions (MCRs) are exceedingly important due to their wide scope of applications in the organic synthesis and pharmaceutical chemistry [15]. Heterocyclic compounds containing nitrogen which are abundant in nature, have important and various applications in agrochemicals, activated biological pharmaceuticals and functional compounds [16-18]. The benzo[g]quinoline-5,10diones with interesting biological attributes act as a structural element in natural substances. For instance, dielsiquinone I is a strong cytotoxic natural compound for anthracyclines that is demonstrated as secure anticancer drugs [19] and Phomazarin II is achieved from the phomaterrestris Hansen [20]; Fig. 1 shows the vitro cytotoxic activity [21]. The procedure for the synthesis of tetrahydrobenzo[g]quinoline-5,10-dione derivatives mainly are classified via annulations reactions [22, 23], aza-Diels–Alder cycloaddition of an  $\alpha$ , $\beta$ unsaturated hydrazone to a quinone [24], hetero Diels-Alder reaction [25] and regioselective synthesis [26].



**Fig. (1).** Some heterocyclic compounds containing benzo[g]quinoline-5,10-dione moiety.

The synthesis of benzo[g]chromenes achieved great interest due to their wide range of biological activities

including: antimalarial [27, 28], anti-inflammatory [29], anticancer activities [30], besides demonstrating efficacy in pesticide activities [31] and cytotoxic activities [32, 33]. 2amino-3-cyano-4-(3-nitrophenyl)-4H-benzo[h]chromene III, is used for cartilage destruction associated with various degenerative illness of the articular joint such as rheumatoid arthritis [34]. Furthermore, 4H-chromen-4- yl-cyanoacetate IV as disincentive of Bcl-2 protein and apoptosis inducer [35] and benzopyrane V have been known for anticancer remedies (Fig. 2) [36]. Recently, the multi component synthesis of 2-amino-4H-chromene derivatives has been developed using different catalysts including triethylbenzylammonium chloride (TEBA) [37], triethylammonium hydrogen sulfate ([Et<sub>3</sub>NH][HSO<sub>4</sub>]) [38], potassium phthalimide-N-oxy (POPINO) [39] and triethylamine [40].



Fig. (2). Three kinds of 2-amino-4*H*-chromenes with diverse biological properties.

Due to the significant role of multi-component reactions especially in heterocyclic synthesis and in order to complete this study analysing the performance of nanocatalysts in MCRs [41-44], an efficient one-pot synthesis of tetrahydrobenzo[g]quinoline and 2-amino-4*H*-chromene derivatives was used using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanocomposite as a powerful and recoverable nanocatalyst under reflux conditions (Scheme 1).

#### 2. EXPERIMENTAL

Chemicals were purchased from the Sigma–Aldrich and Merck in high purity. All of the materials were of commercial reagent grade and were used without further purification. All melting points were uncorrected and determined by the capillary tubes on a Boetius melting point microscope. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Bruker 400MHz spectrometer with CDCl<sub>3</sub> and DMSO- $d_6$  as solvents using tetramethylsilane as an internal standard;



Scheme 1. Preparation of 2-amino-5,10-dihydro-5,10-dioxo-4H-benzo[g]chromenes and tetrahydrobenzo[g]quinoline-5,10-diones.

the chemical shift values were in  $\delta$ . Fourier transforminfrared spectrum was recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm<sup>-1</sup>. The elemental analyses (C, H, N) were performed by a Carlo ERBA Model EA 1108 analyzer. Powder XRD was carried out on a Philips diffractometer of X'pert Company with monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5406$ Å). Microscopic morphology of products was visualized by SEM (LEO 1455VP). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV. Magnetic properties were obtained by a BHV-55 vibrating sample magnetometer (VSM) made by MDK-I.R.Iran. The compositional analysis was done by energy dispersive analysis of X-ray.

#### 2.1. Preparation of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles

 $Fe_3O_4$  nanoparticles were synthesized on the basis of the procedure provided by Zhang *et al.* [45].

#### 2.2. Preparation of Fe<sub>3</sub>O<sub>4</sub> @SiO<sub>2</sub> Nanoparticles

In this research, the  $Fe_3O_4@SiO_2$  core-shell microspheres were prepared according to the method reported in the previous literature [46].

#### 2.3. Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>MNPs was prepared according to the slightly modified previously reported method by Jiahong Wang et al [47]. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles (2 g) were added to the three-necked flask and ultrasonically dispersed for 15 min in dry toluene (50 mL). Then, 1 ml of 3-aminopropyltriethoxysilane (APTES) was added into the flask, and the reaction mixture was refluxed at 110 °C for 10 h with stirring under nitrogen atmosphere. When the reaction was completed, the prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> was gathered by centrifugation and then washed several times with water and ethanol, which was then dried at 50 °C under vacuum for 12 h.

In the preliminary experiments, nanostructured  $Fe_3O_4@SiO_2-NH_2$  was prepared and characterized by EDX, FE-SEM, XRD, FT-IR and VSM analysis.

To evaluate the size and morphology of the nanostructures, the scanning electron microscopy (SEM) of the nanocatalysts are given in Fig. **3**. As can be seen in Fig. 3a, the Fe<sub>3</sub>O<sub>4</sub> NPs have a cubic shape and the diameter of the particles is around 15 nm. The structure and morphology of the Fe<sub>3</sub>O<sub>4</sub> NPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocomposite were nearly similar, but the smoother surface area of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocomposite was observed because of the coating by silica shell (Fig. **3a** and Fig. **3b**). The micrograph of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-



Fig. (3). SEM images of Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (c) NPs.



Fig. (4). FT-IR spectra of  $Fe_3O_4$  (a),  $Fe_3O_4@SiO_2$  (b) and  $Fe_3O_4@SiO_2$ -NH<sub>2</sub> (c) NPs.



Fig. (5). X-ray diffraction for Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (c) NPs.

 $NH_2$  nanocomposite indicated a star-like shape with an average size about 50-60 nm (Fig. **3c**). This observation is the result of self-poly condensation of aminopropylsilane groups.

The comparison of FT-IR spectra of the three kinds of nanocatalyst (Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>–NH<sub>2</sub> nanostructures) is shown in Fig. **4**. In all cases, the absorption peak at 500-600 cm<sup>-1</sup> belonged to the Fe–O vibration [48]. The stretching vibrations of SiO<sub>2</sub> groups were observed at 1072 cm<sup>-1</sup> due to silica coating on the Fe<sub>3</sub>O<sub>4</sub> core for both of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>. The evidence for the amino-functionalization was the absorption bands at 1498 (C–H bending) and 3361cm<sup>-1</sup> (N–H stretching) [49]. The C–H stretching vibrations overlapped with the vibration band of N–H at about 3025-2800 cm<sup>-1</sup>. Stretching vibration of C–N bond was appeared at about 1385 cm<sup>-1</sup> [50].

The crystalline structures of the nanostructures were identified with XRD (Fig. 5). The XRD pattern of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with crystalline cubic spinel structure showed reflections at  $2\theta$ = 30.2 °, 36.4 °, 43.7 °, 53.5 °, 56.3 °, 62.3°, and 73.8° [51]. Also, the characteristic peaks of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> were completely similar to crystalline Fe<sub>3</sub>O<sub>4</sub> phase that indicated the stability of the Fe<sub>3</sub>O<sub>4</sub> during functionalization. The crystalline structures of the nanostructures were identified with XRD (Fig. 5).

Fig. **6** shows the room-temperature magnetization curve of the nanostructures including  $Fe_3O_4$ ,  $Fe_3O_4$ @SiO<sub>2</sub>, and  $Fe_3O_4$ @SiO<sub>2</sub>-NH<sub>2</sub> recorded by a VSM, without any hysteresis in the magnetization. It was found that the three nanostructures were super-paramagnetic due to coercivity and remanence. The saturation magnetization value of  $Fe_3O_4$ obtained was 47.1 emu/g, of  $Fe_3O_4$ @SiO<sub>2</sub> about 41.2 emu/g and finally for  $Fe_3O_4$ @SiO<sub>2</sub>-NH<sub>2</sub>, it was equal to 32.4 emu/g. As shown in Fig. 6 the saturation magnetization of pristine  $Fe_3O_4$  nanoparticles was higher than silica-coated  $Fe_3O_4NPs$ and saturation magnetization of  $Fe_3O_4$ @SiO<sub>2</sub>-NH<sub>2</sub> was lower than  $Fe_3O_4$ @SiO<sub>2</sub>. The surface including a magnetically inactive layer (NH<sub>2</sub>/SiO<sub>2</sub> shell) decreased saturation magnetization in the coated nanostructures.



Fig. (6). VSM magnetization curves of the  $Fe_3O_4$  (a),  $Fe_3O_4@SiO_2$  (b) and  $Fe_3O_4@SiO_2-NH_2$  (c) NPs.

To study the purity of the three prepared nanocatalyst, the energy dispersive X-ray spectroscopy (EDX) was investigated as shown in Fig. 7. For the bare  $Fe_3O_4$  NPs, the only elements were O and Fe. The EDX spectra of  $Fe_3O_4@SiO_2$  (Fig. **7b**) and  $Fe_3O_4@SiO_2$ -NH<sub>2</sub> (Fig. **7c**) showed that the elemental compositions were (Fe, Si and O) and Fe, Si, C, O.

# 2.4. Generic Method for the Synthesis of 2-amino-5,10dihydro-5,10-dioxo-4H-benzo[g]chromenecatalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (4a-4n)

Aldehyde (1 mmol) and malononitrile (1.2 mmol) were dissolved in ethanol under stirring at an ambient temperature in the presence of  $Fe_3O_4@SiO_2-NH_2$  (0.02 g) as the catalyst followed by the addition of 2-hydroxynaphthalene-1,4-dione (1 mmol). Then, the reaction mixture was heated at 80°C under reflux conditions. Finally, n-hexane (10 mL) was added to the reaction mixture and the insoluble catalyst was separated by an external magnet. Evaporation of the solvent under reduced pressure afforded the solid residue which was recrystallized by ethanol.



Fig. (7). EDX spectra of  $Fe_3O_4$  (a),  $Fe_3O_4@SiO_2$  (b),  $Fe_3O_4@SiO_2$ -NH<sub>2</sub> (c) NPs.

All the products were analyzed with m.p., <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR spectroscopy techniques. Spectral data of the new products are given below.

#### Selected spectra of two products are given below:

# 2-Amino-3-cyano-4-(2,4-dichlorophenyl)-5,10-dioxo-5,10dihydro-4H-benzo[g] chromene (41)

Orange solid; FT-IR (KBr, cm<sup>-1</sup>): 3437, 2211, 1665, 1633, 1590, 1249, 1200.<sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  5.08 (1H, s, CH), 6.51 (2H, s, NH<sub>2</sub>), 7.21–7.46 (3H, m, ArH), 7.56–7.75 (4H, m, ArH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): 37.1, 55.9, 111.3, 119.4, 119.8, 121.4, 126.8, 127.1, 127.4, 129.7, 131.5, 131.4, 134.2, 137.1, 137.6, 137.9, 145.5, 156.1, 176.4, 185.5. Anal.Calcd. for C<sub>20</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub>: C 60.48, H 2.54, N 7.05. Found C 60.40, H 2.48, N 7.11.

# 2-Amino-3-cyano-4-(2-nitrophenyl)-5,10-dioxo-5,10dihydro-4H-benzo[g] chromene (4m)

Orange solid; FT-IR (KBr, cm<sup>-1</sup>): 3439, 2208, 1676, 1621.<sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  5.11 (1H, s, CH), 6.56 (2H, s, NH<sub>2</sub>), 7.33–7.66 (6H, m, ArH), 7.91–7.93 (2H, m, ArH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): 31.3, 55.2, 119.2, 121.6, 124.5, 126.3, 127.0, 128.9, 131.1, 131.4, 132.1, 134.3, 134.6, 134.1, 137.3, 149.2, 149.4, 159.3, 177.2, 183.2. Anal.Calcd. for C<sub>20</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub>: C 64.35, H 2.97, N 11.26. Found C 64.42, H 3.04, N 11.32.

# 2.5. General Method for the Preparation of Tetrahydrobenzo[g]quinoline-5,10-diones Catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (7a-7j)

A mixture of 2-hydroxy-1,4-naphthoquinone (1 mmol), ethyl acetoacetate (1 mmol) aromatic aldehyde (1 mmol), NH<sub>4</sub>OAc (2.5 mmol) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> NPs (0.05 g) was taken in a round bottom flask and the mixture was refluxed using 2.5 mL ethanol and 2.5 mL. After completion of the reaction, the mixture was diluted by CHCl<sub>3</sub> (10 mL) and the nanocatalyst was separated using an external magnet. Evaporation of the solvent under reduced the pressure afforded the corresponding products that purified using ethanol as solvent. The final products were determined by FT-IR and NMR spectroscopy.

#### The spectroscopic data of new compounds

# 4-(4-Fluorophenyl)-2-methyl-5,10-dioxo-1,4,5,10 tetrahydrobenzo[g]-quinoline-3-carboxylate(7e)

Red brown solid; FT-IR (KBr, cm<sup>-1</sup>): 3226, 1720, 1370, 1232.<sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  1.19 (3H, t, CH<sub>3</sub>), 2.41 (3H, s, CH<sub>3</sub>), 4.08 (2H, q, CH<sub>2</sub>), 4.86 (1H, s, CH), 7.08 (1H, bs, NH), 7.19-7.38 (4H, m, ArH ), 7.55-7.78 (4H, m, ArH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): 14.5, 20.5, 36.2, 62.1, 105.5, 119.5, 126.3, 126.7, 128.8, 129.5, 130.5, 132.4, 132.9, 134.3, 136.7, 142.8, 145.1, 166.5, 179.8, 181.3. Anal.Calcd. for C<sub>23</sub>H<sub>18</sub>FNO<sub>4</sub>: C 70.58, H 4.64, N 3.58. Found C 70.62, H 4.56, N 3.53.

# 4-(4-Thiomethylphenyl)-2-methyl-5,10-dioxo-1,4,5,10tetrahydrobenzo[g]-quinoline-3-carboxylate (7j)

Red brown solid; FT-IR (KBr, cm<sup>-1</sup>): 3215, 1725, 1410, 1240. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  1.21 (3H, t, CH<sub>3</sub>), 2.42 (3H, s, CH<sub>3</sub>), 2.53 (3H, s, SCH<sub>3</sub>), 4.12 (2H, q, CH<sub>2</sub>), 4.91 (1H, s, CH), 7.06 (1H, s, NH), 7.16-7.29 (4H, m, ArH), 7.44-7.68 (4H, m, Ar-H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): 14.2, 19.6, 20.9, 37.1, 59.9, 104.9, 119.4, 125.9, 126.3, 128.1, 129.1, 130.2, 132.4, 132.9, 134.5, 136.3, 136.8, 141.8, 143.3, 166.7, 180.0, 182.4. Anal.Calcd. for C<sub>24</sub>H<sub>21</sub>NO<sub>4</sub>S: C 68.79, H 5.05, N 3.38. Found C 68.72, H 5.01, N 3.31.

#### **3. RESULTS AND DISCUSSION**

The Fe<sub>3</sub>O<sub>4</sub> NPs were obtained from the reaction of iron (II,III) ions via co-precipitation method. The surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was coated using silica shell that was the result of tetraethyl orthosilicate (TEOS) addition.Then in order to equip reaction sites for thermal stability and more reactivity, the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was reacted with APTES to perform amino-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (Scheme **2**).

In order to optimize the reaction conditions, a principled experimental method with diverse influencing variables such as catalyst, solvent and temperature was investigated. The reaction of 2-hydroxy-1,4-dihydronaphthalene-1,4-dione (1), 4-chlorobenzaldehyde (2a) and malononitrile (3) was selected as a model reaction. The results are classified in Table 1.



Scheme 2. The preparation steps to the synthesis of nanocatalyst.

Table 1. The effect of catalyst, catalyst amounts, solvent and temperature in the preparation of benzo[g]chromene (4a)<sup>a</sup>.

$ \begin{array}{c}                                     $							
Entry	Catalyst	Catalyst loading (g)	Solvent	T (°C)	Time (min)	Yield (%) <sup>b</sup>	
1	None	-	Solvent-free	r.t	180	20	
2	None	-	Solvent-free	100 °C	180	25	
3	None	-	Water/EtOH	r.t	150	35	
4	None	-	Water/EtOH	Reflux	120	50	
5	ZnO	0.04	Water/EtOH	Reflux	70	70	
6	CuI	0.04	Water/EtOH	Reflux	75	65	
7	Fe <sub>3</sub> O <sub>4</sub>	0.04	Water/EtOH	Reflux	60	66	
8	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	0.04	Water/EtOH	Reflux	45	73	
9	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	0.04	Water/EtOH	Reflux	30	97	
10	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	0.02	Water/EtOH	Reflux	30	97	
11	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	0.01	Water/EtOH	Reflux	45	85	
12	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	0.02	EtOH	Reflux	75	60	
13	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	0.02	Water	Reflux	70	55	
14	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	0.02	CH <sub>2</sub> Cl <sub>2</sub>	Reflux	80	45	
15	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	0.02	Toluene	Reflux	100	35	

<sup>a</sup>General reaction conditions: 2-hydroxy-1,4-dihydronaphthalene- 1,4-dione (1) (1 mmol), 4 chlorobenzaldehyde (2a) (1 mmol), malononitrile (3) (1.2 mmol) <sup>b</sup> Isolated yields.

As shown in Table 1, in the absence of catalyst, just a trace amount of benzo[g]chromene (4a) was obtained under solvent-free conditions even at 100 °C (Table 1, entries 1,2). However, when the reaction was performed using H<sub>2</sub>O/EtOH as the solvent, we observed that the product yield was slightly increased (Table 1, entries 3, 4). Then the model reaction was carried out using different nanocatalysts such as CuI, Fe<sub>3</sub>O<sub>4</sub>, ZnO, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> in the ethanol/water as solvent under reflux conditions as indicated in Table 1. The comparison of various nanocatalysts based on yields and times of their corresponding reactions determined that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> is the best particle. It is likely that higher catalytic activity of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> NPs can be attributed to the better dispersion of nanocomposite and wider surface of nanoparticles (Table 1, entries 5-10).

In the next step, the influence of the amount of MNPs was studied (Table 1, entries 9-11). 0.02 g of the magnetic  $Fe_3O_4@SiO_2-NH_2$  NPs proved to be the best reaction condition. Decreasing the amount of MNPs led to the decline in the reaction time and yield.

According to the considerable results of the above experiments, we started to produce various 2-amino-5,10-dihydro-5,10-dioxo-4H-benzo[g]chromenes in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> NPs under the optimized reaction conditions (Table 2). A series of 2-amino-5,10-dihydro-5,10-dioxo-4H-benzo[g]chromene derivatives were prepared in excellent yields within short reaction times. The diverse aryl aldehydes with electron-withdrawing or electron-donating groups (4a-m), were obtained with high purity and efficiency. According to the data, the electronic nature of different aromatic aldehyde has no important effect on the





(Table 2) Contd....

Entry	Aldehyde	Product	Time (min)	Yield (%) <sup>b</sup>	mp (°C)	Lit. M.p. (°C)
7	F-CHO (2g)	(4g) F	35	93	242-245	244-246 <sup>39</sup>
8	O <sub>2</sub> N CHO (2h)	0 NH <sub>2</sub> CN (4h) NO <sub>2</sub>	35	92	248-250	247-250 <sup>38</sup>
9	он <sub>3</sub> с-Сно (2і)		40	90	245-248	246-248 <sup>38</sup>
10	Н <sub>3</sub> СО СНО (2 <b>ј</b> )		40	86	248-250	249-251 <sup>38</sup>
11	СІ СНО (2k)		50	87	235-238	235-237 <sup>38</sup>
12	СІ-СІ СІ-СНО (21)		55	85	286-288	288 <sup>38</sup>
13	NO <sub>2</sub> СНО (2m)	(4m)	50	85	240-243	241-243 <sup>38</sup>
14	С <sub>7</sub> Н <sub>15</sub> СНО ( <b>2n</b> )	-	-	24 h	-	-

<sup>a</sup> General reaction conditions: 2-hydroxy-1,4-dihydronaphthalene-1,4-dione (1) (1 mmol), Aldehyde (2a-n) (1 mmol), malononitrile (3) (1.2 mmol), Reflux, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (0.02 g). <sup>b</sup> Isolated yields.



Scheme 3. The synthesis of 2-ethyl-5,10-dioxo-4-(4-chlorophenyl)-1,4,5,10-tetrahydrobenzo[g]quinoline-3-carboxylates (7b) using  $Fe_3O_4$  (@SiO\_2-NH\_2 NPs.

 Table 3.
 Preparation of 2-ethyl-5,10-dioxo-4-(4-chlorophenyl)-1,4,5,10-tetrahydrobenzo[g]quinoline-3-carboxylate (7b) in different solvents<sup>a</sup>.

Entry	Solvent	T (°C)	Time (min)	Yield (%) <sup>b</sup>
1	EtOH	Reflux	160	70
2	Water	Reflux	180	60
3	CH <sub>2</sub> Cl <sub>2</sub>	Reflux	180	35
4	Toluene	Reflux	240	30
5	Water/EtOH	Reflux	150	95
6	Water/EtOH	25	200	55
7	Solvent-free	25	240	30
8	Solvent-free	100	180	35

<sup>a</sup><sup>2</sup>-hydroxy-1,4-dihydronaphthalene-1,4-dione (1) (1mmol), 4- chlorobenzaldehyde (2a) (1mmol), ethyl acetoacet (5)(1mmol), ammonium acetate (6) (2.5 mmol) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (0.1 g).

b Isolated yields.

rate or yield of reactions. In addition, the reaction of an aliphatic aldehyde was carried out without the synthesis of any significant product after 24 h (Table **2**, entry 14).

In continuation of our research, we encouraged to apply  $Fe_3O_4(a)SiO_2-NH_2$ NPs for the preparation of tetrahydrobenzo[g]quinoline-5,10-dione derivatives. On the basis of optimized reaction condition, the four component reaction of 2-hydroxy-1,4-dihydronaphthalene-1,4-dione (1), 4-chlorobenzaldehyde (2a), ethyl acetoacetate (5) and ammonium acetate (6) was chosen as the main synthetic model (Scheme 3). The conditions were optimized due to variable conditions such as catalyst, temperatures and solvent for the preparation of 2-ethyl-5,10-dioxo-4-(4chlorophenyl)-1,4,5,10 tetrahydrobenzo[g]quinoline-3carboxylates (7b).

Following this, we investigated the effect of solvent and also solvent free when the model reaction was carried out in the presence of  $Fe_3O_4@SiO_2-NH_2$  nanocomposite. As shown in table 3, the rate of reaction and the amount of product were increased under reflux conditions (**7b**) (95% yield, 150 min) (Table 3, entry 5).

The importance of our research was reflected in the comparison of the magnetite nanocomposite-supported APTES (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>) with other catalysts such as CuI, ZnO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. According to the collected results shown in Table 4, the best reaction time and high yield belonged to Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> MNPs.

Next, our research was preceded due to the use of various amounts of  $Fe_3O_4@SiO_2-NH_2$  nanocatalysts under reflux

conditions (Table 5). As shown in Table 5, the yield of product was traced in the absence of the nanocatalyst (Table 5, entry 1). The results showed that 0.05 g of the  $Fe_3O_4(a)SiO_2-NH_2$  was sufficient to promote the reaction.

Entry	Catalyst	Time (min)	Yield (%) <sup>b</sup>
1	Fe <sub>3</sub> O <sub>4</sub>	200	55
2	ZnO	240	45
3	CuI	220	55
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	150	95
5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	180	60

Table 4.The model synthesis of tetrahydrobenzo[g]quinoline-<br/>3-carboxylates (7b) by various catalysts<sup>a</sup>.

<sup>a</sup> Water/ethanol as solvent under reflux conditions

<sup>b</sup> Isolated yields

Finally, we investigated the one-pot synthesis of tetrahydrobenzo[g]quinoline-5,10-diones using  $Fe_3O_4(a)$  SiO<sub>2</sub>–NH<sub>2</sub> MNPs under reflux conditions. As shown in Table **6**, we observed that different aromatic aldehydes could be used to produce high yields of corresponding products. In addition, aromatic aldehyde bearing electron-withdrawing groups such as NO<sub>2</sub>, Cl and Br in *p*-position reacted very smoothly toward substances with electron-donating groups like OH and OME. However, the reaction of sterically hindered aldehydes was slow in comparison with unhindered aldehydes and required long reaction times (Table **6**).

Table 5.	Effect of the amounts of Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> NPs on				
	the preparation of tetrahydrobenzo[g]quinoline-3-				
	carboxvlates (7b). <sup>a</sup>				

Entry	Catalyst amount (g)	Time (min)	Yield (%) <sup>b</sup>
1	None	250	None
2	0. 01	220	30
3	0. 03	180	75
4	0.05	150	95
5	0.06	150	95

<sup>a</sup> Water/ethanol as solvent under reflux conditions

<sup>b</sup> Isolated yields

# 3.1. Recycling and Reusing of the Catalyst

The recoverability of  $Fe_3O_4$ @SiO<sub>2</sub>-NH<sub>2</sub> is very important because of their practical applications. When the reaction was complete, the catalyst separated magnetically and washed with methanol and chloroform and dried at 50°C for 8 h. According to the results, the MNPs could be reused for sixth consecutive times with a little-decreased activity. The results are summarized in Table 7.

# 3.2. Proposed Mechanism

A plausible mechanism for the preparation of 2-amino-5,10-dihydro-5,10-dioxo-4*H*-benzo[*g*]chromene using  $Fe_3O_4@SiO_2-NH_2$  NPs has been shown in Scheme 4. It is likely that NH<sub>2</sub> groups on the surfaces of nanocomposite act as the Brønsted base and lead to dehydrogenation of substrates. Firstly, the Knoevenagel condensation reaction of aldehyde and malononitrile afforded intermediate A in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> as the catalyst.

Next, the intermediate **C** was prepared by the nucleophilic attack of 2-hydroxynaphthalene-1,4-dione **B** to intermediate **A** using  $Fe_3O_4$ @SiO<sub>2</sub>-NH<sub>2</sub> nanocomposite. In the next step, the intermediate **D** was obtained by nucleophilic attack of the hydroxyl group on behalf of the CN, and then the intermediate **D** was tautomerized to product **4**. Moreover, the effect of the catalytic behavior of  $Fe_3O_4$ @SiO<sub>2</sub>-NH<sub>2</sub> NPs on the synthesis of 2-amino-5,10-dihydro-5,10-dioxo-4*H*-benzo[*g*]chromenes was the same as the above-mentioned mechanism for the preparation of tetrahydrobenzo[*g*]quinoline-5,10-dione derivatives.

# 4. CONCLUSION

In conclusion, we provided a green and facile protocol for the synthesis of some 2-amino-3-cyano-4-aryl-5,10dioxo-5,10-dihydro-4*H*-benzo[*g*]chromene and tetrahydrobenzo[*g*]quinoline-5,10-dione derivatives in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanocomposite as the catalyst. The significant advantages of this method using aminofunctionalization silica-coated magnetite nanocomposite as a strong Brønsted base included easy work up, clean reaction conditions, simple procedure, satisfactory yields, and reusability of the nanocatalyst.

### **CONFLICT OF INTEREST**

The authors have confirmed that they have no conflict of interest.

Entry	Ar	Product	Time (min)	Yield (%) <sup>b</sup>	М.р. (°С)	Lit. M.p. (°C)
1	$C_6H_5$	7a	180	92	230-232	232 <sup>26</sup>
2	$4-C1C_6H_4$	7b	150	95	207-210	209 <sup>26</sup>
3	3-BrC <sub>6</sub> H <sub>4</sub>	7c	170	92	186-190	189 <sup>26</sup>
4	$4-CH_3C_6H_4$	7d	180	90	219-222	222 <sup>26</sup>
5	$4-FC_6H_4$	7e	160	93	205-207°	
6	$4-O_2NC_6H_4$	7f	160	95	195-199	198 <sup>26</sup>
7	$2-C1C_6H_4$	7g	190	91	204-207	207 <sup>26</sup>
8	2,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	7h	200	90	180-183	182 <sup>26</sup>
9	4-(CH <sub>3</sub> ) <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub>	7i	210	88	160-165	165 <sup>26</sup>
10	4-MeSC <sub>6</sub> H <sub>4</sub>	7j	180	92	238-240 <sup>c</sup>	

 Table 6.
 Preparation of tetrahydrobenzo[g]quinoline-5,10-diones.<sup>a</sup>

<sup>a</sup>General reaction conditions: 2-hydroxy-1,4-dihydronaphthalene- 1,4-dione (1) (1 mmol), Aldehyde (7a-j) (1 mmol), ethyl acetoacetate (5) (1 mmol) and ammonium acetate (6) (2.5 mmol)), Water/ethanol at Reflux,  $Fe_3O_4@SiO_2-NH_2$  (0.05g).

<sup>b</sup>Isolated yields.

Table 7.	The reusability of the catalyst in the preparation	of 2-amino-5,10-dihydro-5,10-dioxo-4H-	benzo[g]chromene	and
	tetrahydrobenzo[g]quinoline-5,10-dione derivatives.			

Cycle	First	Second	Third	Fourth	Fifth	Sixth
Yield(%) <sup>a</sup>	95	95	91	90	88	85

<sup>a</sup> Yields refer to the isolated pure product



Scheme 4. Proposed reaction mechanism for preparation of 2-amino-5,10-dihydro-5,10-dioxo-4H-benzo[g]chromenes using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> NPs.

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