

# Piperidine-functionalized Fe<sub>3</sub>O<sub>4</sub> supported graphene quantum dots as an efficient catalyst for the synthesis of 2-aminochromenes under solvent-free conditions

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**Abstract:** Fe<sub>3</sub>O<sub>4</sub> supported graphene quantum dots (GQDs) (Fe<sub>3</sub>O<sub>4</sub>@GQDs) was prepared under microwave irradiation. Piperidine was bound to Fe<sub>3</sub>O<sub>4</sub>@GQDs via its reaction with 3-piperidinopropyltrimethoxysilane and piperidine-functionalized Lewis basic nano-catalyst (Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip) was prepared. This freshly prepared catalyst was evaluated as a heterogeneous magnetic reusable catalyst for the one-pot synthesis of 2-aminochromenes under MW-assisted solvent-free conditions. Two composite particles, Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip were characterized by FT-IR, XRD, SEM, TGA and VSM analytical methods. The catalyst could be easily recovered by magnetic separation and recycled for 5 times without significant loss of its catalytic activity.

**Keywords:** Heterogeneous nano-catalyst; chromene; magnetic graphene quantum dots; piperidine ©2019 ACG Publications. All right reserved.

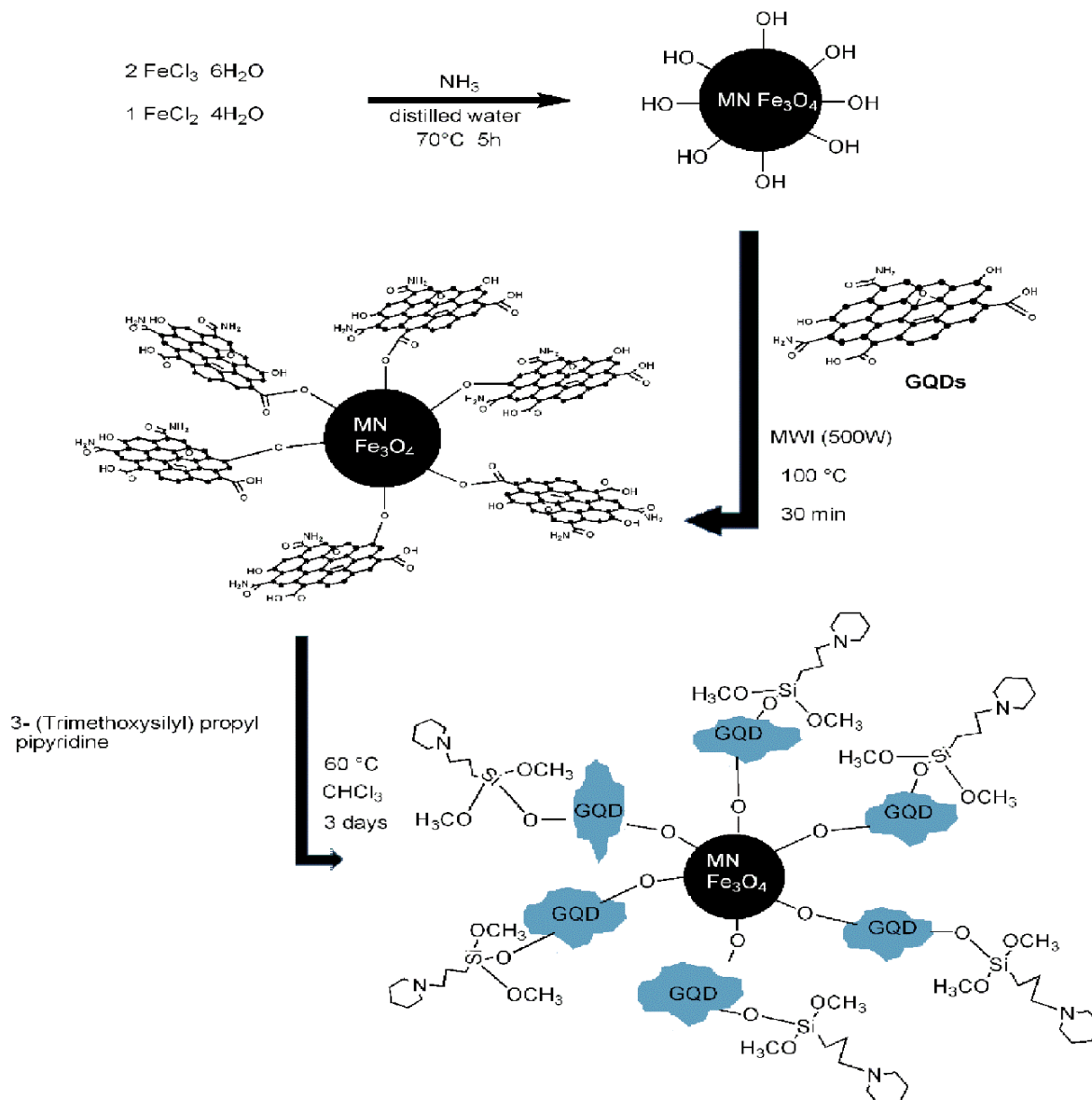
## 1. Introduction

In recent years, magnetic nanoparticles have been extensively investigated because of their potential applications in many fields such as: solar cells,<sup>1</sup> drug delivery,<sup>2</sup> heterogeneous catalysis,<sup>3</sup> biological labeling,<sup>4</sup> magnetic separation,<sup>5</sup> magnetic resonance imaging (MRI),<sup>6</sup> tissue engineering.<sup>7</sup> Additionally, the activity and selectivity of these compounds have been manipulated by their surface modification.<sup>8-9</sup> These compounds with large specific surface area can be readily removed from the reaction vessel by an external magnetic field.

Graphene quantum dots (GQDs) is zero-dimensional material which has characteristics of both graphene and carbon dots.<sup>10</sup> GQDs has excellent properties such as high photostability, high solubility in various solvents, biocompatibility and low toxicity.<sup>10</sup> These properties make it suitable for many important applications such as bioimaging,<sup>11</sup> sensors,<sup>12</sup> environmental monitoring,<sup>13</sup> photoluminescent material.<sup>14</sup>

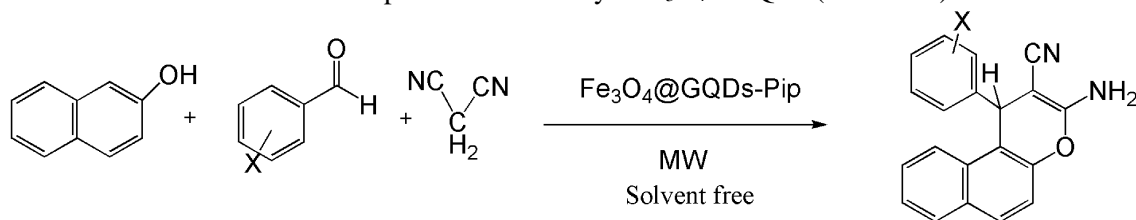
Chromene derivatives especially pyranochromenes have attracted great interest due to their biological and pharmaceutical activities<sup>15</sup> such as antimicrobial,<sup>16</sup> anticancer,<sup>17</sup> anti-HIV<sup>18</sup> antitumor agents.<sup>19</sup> Moreover, these compounds can be used in cosmetic materials and pigments.<sup>20</sup> Recently, the heterogeneous catalysts based on magnetic nanoparticles were attracted much attention of scientists due to economic and environmental aspects.<sup>21</sup> Iron is most interesting material due to its low cost, affluence, environmentally benign and nontoxic nature.<sup>22</sup> Our interest in employing ionic liquid immobilized nano-silica and functionalized GQDs as an effective catalyst and or reagent for organic transformations,<sup>23-25</sup> provided the impetus to prepare and employ the new heterogeneous magnetic nano-catalyst via the coating of magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles with GQDs (Fe<sub>3</sub>O<sub>4</sub>@GQDs) (Scheme 1).

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**Scheme 1.** Synthesis of the nano-catalysts: Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip

To achieve Lewis basicity, piperidine was bound to Fe<sub>3</sub>O<sub>4</sub>@GQDs via the reaction with 1-(3-trimethoxysilylpropyl) piperidine and a new heterogeneous magnetic catalyst (Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip) was prepared (Scheme 1). This modified catalyst was examined for the synthesis of 2-aminochromenes and better results were obtained in comparison with catalyst Fe<sub>3</sub>O<sub>4</sub>@GQDs (Scheme 2).



X: -H, 2-NO<sub>2</sub>, 3-NO<sub>2</sub>, 4-NO<sub>2</sub>, 4-Cl, 4-OCH<sub>3</sub>, 4-CH<sub>3</sub>, 4-F, 4-Br, 3-Cl, 3-OCH<sub>3</sub>. **4a:** X=H

**Scheme 2.** Synthesis of chromene derivatives **4a-4k** using catalyst Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip

## 2. Experimental

### 2.1. General information

All chemical materials and solvents were obtained from Merck Company and were used without further purification. Infrared spectra (FT-IR) were obtained with KBr pellets on a Perkin-Elmer FT-IR spectrometer. Melting points were determined using the capillary tube method with Stuart melting point apparatus and are uncorrected. The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded in DMSO- $d_6$  on a Bruker Spectro Spin-400MHz instrument spectrometer using TMS as an internal standard. Catalyst nanostructures were characterized by X-ray diffractometry using Siemens/Bruker D5000 (XRD) diffractometer. SEM images were taken using (FESEM; KYKY-EM3200) instrument. Thermal gravimetric analysis (TGA) were recorded on a Mettler Toledo TGA-DTA STAR SW.8.10 system at a heating rate of 10 °C/min in a nitrogen atmosphere. The magnetic measurement was carried out in a vibrating sample magnetometer (VSM, Model MDKF) at room temperature. Microwave experiments were conducted in a Milestone Micro Synth apparatus.

### 2.2. Preparation of catalyst

#### 2.2.1. Synthesis of magnetite nanoparticles (MNPs)

$\text{FeCl}_3$  (10 gr) was dissolved into a 200 mL distilled water and after a few minute,  $\text{FeCl}_2$  (5 gr) was added to the mixture while stirring. The reaction mixture was heated up to 70°C for 10 min. Then ammonia solution (25%) was added to the mixture reaction until black colored particles of iron oxide were observed. After completion of the reaction, these particles were separated from the solution by using a strong magnet and then were washed for many times with distilled water. The black precipitated magnetite nanoparticles were dried in hot air oven at 100°C for overnight.<sup>26</sup>

#### 2.2.2. Synthesis of graphene quantum dots (GQDs)

Ammonia solution (2 mL, 25%) and citric acid (15 gr) were added into the closed vessel. Then the reaction mixture was heated at 145°C with full power MWI (1000W) for 30 min. After this, the reaction mixture was placed under vacuum at 70°C for 15 min to produce crude GQDs.

#### 2.2.3. Preparation of $\text{Fe}_3\text{O}_4$ @GQDs nanoparticles

GQDs (5 gr) and  $\text{Fe}_3\text{O}_4$  nanoparticles (0.1 gr) were placed into the microwave vessel and the mixture was heated at 100°C with full power MWI (500W) for 30min. After cooling the mixture, the resulted black suspension was washed with deionized water for several times. Then,  $\text{Fe}_3\text{O}_4$ @GQDs nanoparticles was magnetically separated from the mixture by applying a permanent external magnet and dried under vacuum at 60°C for 12 h.

#### 2.2.4. Synthesis of 1-(3-trimethoxysilylpropyl)piperidine

1-Chloro-3-trimethoxysilylpropane (20 mmol), piperidine (21 mmol) were refluxed at 80°C for 24 h in the presence of MgO under solvent-free conditions. Completion of the reaction was indicated by TLC monitoring. The reaction mixture was cooled to ambient temperature and the crude product was separated by flash chromatography using n-hexan/ethylacetate (5/1) to afford 1-(3-trimethoxysilylpropyl) piperidine in 89% yield. The product was characterized by FT-IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopies.

FTIR (KBr,  $\text{cm}^{-1}$ ): 2936, 2854, 20763, 1468, 1443, 1376, 1351, 1309, 1270, 1121, 1038, 767, 696, 466.  
 $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 0.68 (t, 2 H,  $J$  = 7.32 Hz), 1.60-1.64 (m, 2 H), 1.98-2.30 (m, 6 H), 2.87-

2.92 (m, 4 H), 3.00 (t, 2 H,  $J = 7.32$  Hz), 3.80 (s, 9 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 8.10, 25.70, 27.9, 56.8, 58.4, 58.68, 59.76$ .

### 2.2.5. Preparation of Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip

Fe<sub>3</sub>O<sub>4</sub>@GQDs nanoparticles (10 gr) and 1-(3-trimethoxysilylpropyl) piperidine (10.50 gr) were mixed and added into a vessel containing CHCl<sub>3</sub> (100 mL). The mixture was refluxed at 60°C for 72h while continuous stirring. After completion of the reaction, the solvent was evaporated and the residue was washed with deionized water for several times. Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip nanoparticles were magnetically separated from the mixture by a magnetic field and washed with CHCl<sub>3</sub> for several times and left to dry under vacuum at 60°C for 12h.

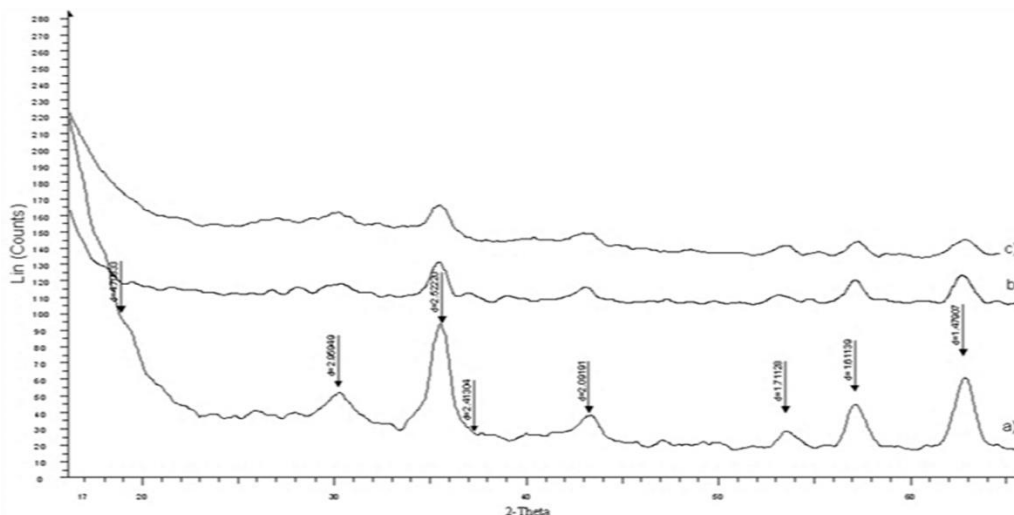
### 2.3. General procedure for the synthesis of chromene derivatives

A mixture of  $\beta$ -naphthol (1 mmol), malononitrile (1 mmol), aldehyde (1 mmol) and catalyst (0.07 gr) was heated under microwave irradiation (500 W) for the appropriate time as shown in Table 1. After completion of the reaction indicated by TLC, the mixture was cooled and ethylacetate (15 mL) was added into the reaction mixture and the catalyst was removed from the mixture by external magnetic field. After evaporation of the solvent, crude product was recrystallized from hot ethanol and the pure products were produced in high to excellent yields.

## 3. Results and Discussion

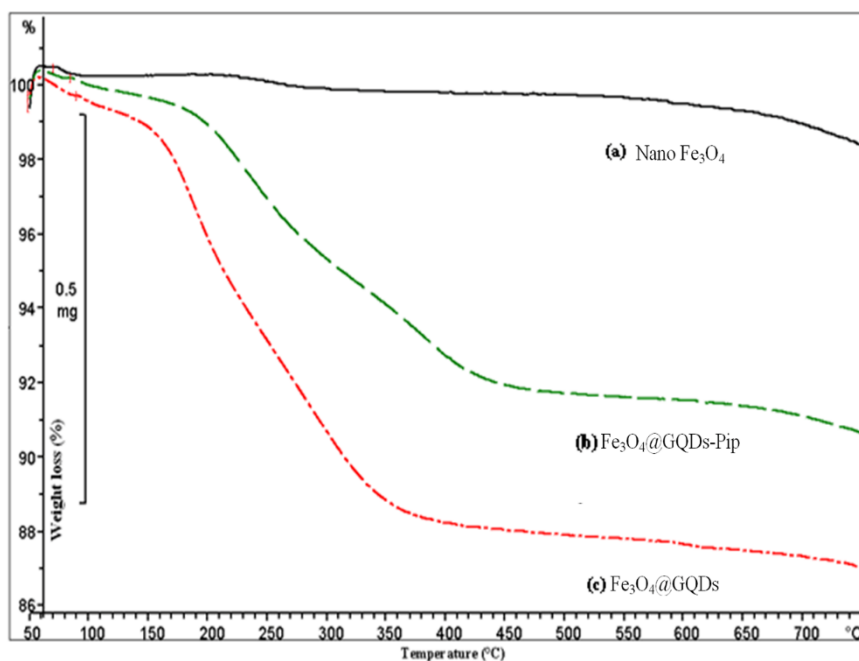
Catalyst Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip was prepared following the procedure shown in Scheme 1. Magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were easily prepared by a promising reported method and was subsequently coated with graphene under MWI to produce Fe<sub>3</sub>O<sub>4</sub>@GQDs catalyst. Then, the freshly prepared Fe<sub>3</sub>O<sub>4</sub>@GQDs was reacted with 1-(3-trimethoxysilylpropyl)piperidine under reflux conditions to obtain the catalyst Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip. The structure of the two catalysts was characterized by FT-IR, XRD, TGA, SEM and VSM analyses. The FT-IR spectra of GQDs, Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip are shown in Figure S1. As it can be seen from the FT-IR spectrum of GQDs, the signals of stretching vibrations of C=O, O-H and C-O were appeared in 1708 cm<sup>-1</sup>, 3456 cm<sup>-1</sup> and 1222 cm<sup>-1</sup> respectively. The presence of magnetite nanoparticles in Fe<sub>3</sub>O<sub>4</sub>@GQDs can be confirmed by the Fe-O stretching vibration at 562 cm<sup>-1</sup>, O-H stretching vibration at 3422 cm<sup>-1</sup> and O-H deformed vibration at 1636 cm<sup>-1</sup>. Peaks at 1245 cm<sup>-1</sup>(C-N) and 2938 cm<sup>-1</sup> (C-H) are attributed to the piperidine functionalized surface of Fe<sub>3</sub>O<sub>4</sub>@GQDs.

X-ray powder diffraction patterns (XRD) of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip were shown in Figure 1. The X-ray diffraction spectroscopy of Fe<sub>3</sub>O<sub>4</sub> nanoparticles show diffraction peaks at  $2\theta = 18.4^\circ, 30.1^\circ, 35.6^\circ, 37.1^\circ, 43.1^\circ, 53.6^\circ, 57.3^\circ$  and  $62.7^\circ$  that were related to the (111), (220), (311), (222), (400), (422), (511) and (440) planes of Fe<sub>3</sub>O<sub>4</sub>, respectively. These data indicate that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles have a cubic face-centered (fcc) lattice. As it can be seen, XRD patterns of Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip show the same peaks as for Fe<sub>3</sub>O<sub>4</sub> nanoparticles. This proves that after immobilization of the Fe<sub>3</sub>O<sub>4</sub> to prepare Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip, the XRD profile is not changed sensible and suggesting that the crystalline structure of the support remained almost unchanged. These results further indicate that catalysts were prepared successfully.



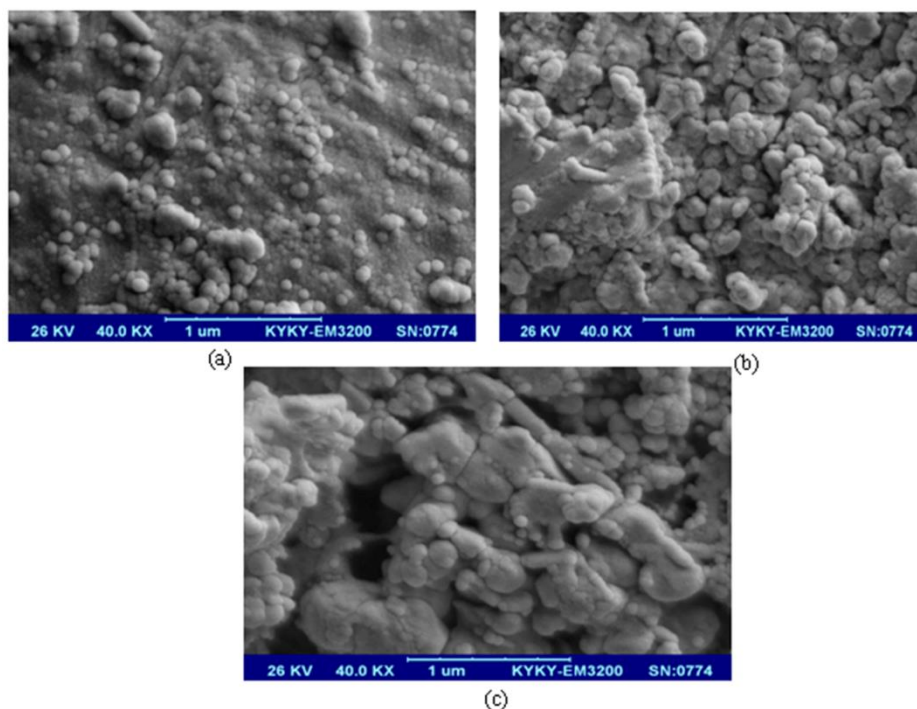
**Figure 1.** XRD patterns: a)  $\text{Fe}_3\text{O}_4$  nanoparticles, b)  $\text{Fe}_3\text{O}_4$ @GQDs and c)  $\text{Fe}_3\text{O}_4$ @GQDs-Pip

Figure 2 shows the TGA curves of  $\text{Fe}_3\text{O}_4$  nanoparticles,  $\text{Fe}_3\text{O}_4$ @GQDs and  $\text{Fe}_3\text{O}_4$ @GQDs-Pip. Two weight-loss steps are observed for  $\text{Fe}_3\text{O}_4$ @GQD. First weight-loss related to desorption of water from the catalyst which is observed between 110–150 °C and the second weight-loss step between 180 °C and 330 °C is due to the decomposition of GQDs. The TGA curve of  $\text{Fe}_3\text{O}_4$ @GQDs-Pip shows that the main weight loss process occurs at 190–420 °C which has lower decomposition rate compared to  $\text{Fe}_3\text{O}_4$ @GQDs. This confirms the presence of 1-(3-trimethoxysilylpropyl)piperidine on the surface of  $\text{Fe}_3\text{O}_4$ @GQDs.



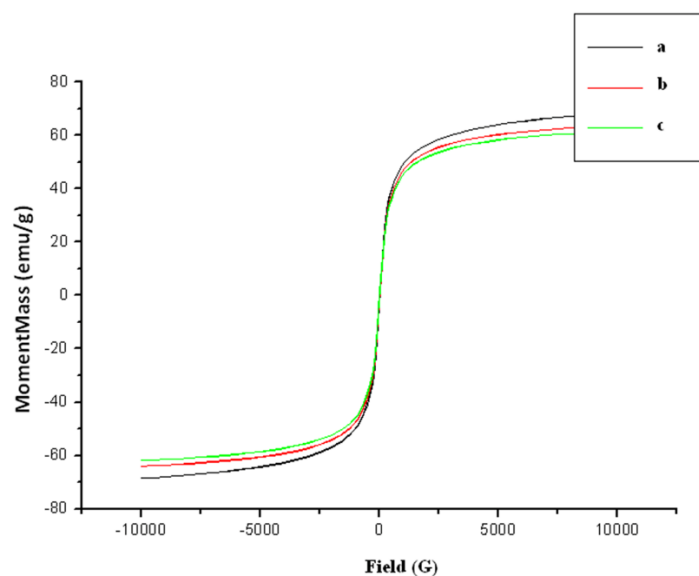
**Figure 2.** TGA curves: a)  $\text{Fe}_3\text{O}_4$  nanoparticles, b)  $\text{Fe}_3\text{O}_4$ @GQDs-Pip and c)  $\text{Fe}_3\text{O}_4$ @GQDs

The particle size distributions and morphologies of  $\text{Fe}_3\text{O}_4$  nanoparticles,  $\text{Fe}_3\text{O}_4$ @GQDs and  $\text{Fe}_3\text{O}_4$ @GQDs-Pip are studied by SEM images (Figure 3). Figure 4a shows the SEM image for magnetic nanoparticles of  $\text{Fe}_3\text{O}_4$  that have spherical shape with average size around 15 nm. In this Figure aggregation of the particles is clearly observed. As it can be seen from Figure 4b, the morphology and size of the  $\text{Fe}_3\text{O}_4$ @GQDs particles were changed and the average diameter of particles is higher than 50 nm. According to Figure 4c,  $\text{Fe}_3\text{O}_4$ @GQDs-Pip have nano dimensions ranging from 65 to 117 nm.



**Figure 3.** SEM images: (a) Fe<sub>3</sub>O<sub>4</sub> nanoparticles, (b) Fe<sub>3</sub>O<sub>4</sub>@GQDs and (c) Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip

The magnetic properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip were analyzed by vibrating sample magnetometer (VSM) at room temperature and the results are shown in Figure 4. The saturation magnetization (*M<sub>s</sub>*) values of these compounds are shown at 68.48, 63.74 and 62.13 emu/g, respectively. The outcome of the VSM analysis approve that these compounds have super paramagnetic behavior. The room temperature magnetization curves show that the saturation magnetization of the Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip is less than Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The diamagnetic contributions of the GQDs and 1-(3-silylpropyl)piperidine cause the decreasing of the magnetic ability of the related compounds. In spite of the small saturation magnetization, Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip catalyst is easily separated from the reaction mixture using the external magnetic field.



**Figure 4.** Magnetization curves: a) Fe<sub>3</sub>O<sub>4</sub> nanoparticles, b) Fe<sub>3</sub>O<sub>4</sub>@GQDs and c) Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip

To investigate the effect of catalysts, the well-known three-component reaction of  $\beta$ -naphthol, benzaldehyde and malononitrile for the synthesis of related 2-aminochromene (**4a**) was carried out in the presence of freshly prepared catalysts. A variety of catalysts such as poly(4-vinylpyridine), [bmim][PF<sub>6</sub>], [EMIM][OH], SiO<sub>2</sub>-Pr-SO<sub>3</sub>H were also examined for the typical reaction for comparison. The results are shown in Table 1.

**Table 1.** Synthesis of the product **4a** using different catalysts.

Entry	Catalyst	Time (min)	Yield <sup>Ref.</sup> (%)	T (°C)	Solvent
1	Poly(4-vinylpyridine)	10	93 <sup>27</sup>	80	Solvent free
2	[BMIM][PF <sub>6</sub> ]	120	86 <sup>28</sup>	80	[bmim][PF <sub>6</sub> ]
3	[EMIM][OH]	3	84 <sup>29</sup>	r.t	H <sub>2</sub> O
4	SiO <sub>2</sub> -Pr-SO <sub>3</sub> H	330	97 <sup>30</sup>	100	H <sub>2</sub> O
5	Fe <sub>3</sub> O <sub>4</sub> @GQDs-Pip	4	98	100	Solvent free

The reaction in the presence of Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip required lower microwave power and reaction time in comparison with other catalysts. Synthesis of 2-aminochromenes (**4a**, **4b**, **4c**, **4d** and **4e**) were examined using two catalysts Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip and the results are gathered in Table 2. As it can be seen, Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip promoted the reactions more effectively under mild reaction conditions in comparison with Fe<sub>3</sub>O<sub>4</sub>@GQDs and it could be considered as one of the best environmentally benign and user-friendly catalyst for the synthesis of 2-aminochromenes.

**Table 2.** Fe<sub>3</sub>O<sub>4</sub>@GQDs and Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip as a catalyst for the synthesis of chromenes **4a-4e**.

Entry	Product	Fe <sub>3</sub> O <sub>4</sub> @GQDs		Fe <sub>3</sub> O <sub>4</sub> @GQDs-Pip	
		Time (min)	Yield <sup>a</sup> (%)	Time (min)	Yield <sup>a</sup> (%)
1	<b>4a</b>	6	85	4	98
2	<b>4b</b>	5	84	4	98
3	<b>4c</b>	6	80	5	90
4	<b>4d</b>	5	86	4	96
5	<b>4e</b>	6	80	4	99

<sup>a</sup>Isolated yields.

The effect of the catalyst amount (g) on the yield of the product **4a** was also examined by using different amounts of Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip (Table 3). It was observed that while the amount of the catalyst was increased from 0.02 to 0.07g, the yield was increased to 96%, which is probably due to the availability of more piperidine sites. The results showed that the further increasing of Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip had no significant effect on the yield.

**Table 3.** The effect of the catalyst amount (g) on the yield of **4a**.

Entry	Fe <sub>3</sub> O <sub>4</sub> @GQDs-Pip (g)	T (°C)	Time (min)	Yield <sup>a</sup> (%)
1	0.020	60	1	10
2	0.020	80	1	15
3	0.020	100	1	18
4	0.030	80	1	25
5	0.030	100	2	40
6	0.030	120	2	40
7	0.040	80	1	50
8	0.040	100	1	55
9	0.040	100	2	70
10	0.070	80	1	60
11	0.070	100	2	80
12	0.070	100	4	98
13	0.070	120	4	98
14	0.10	100	2	98

<sup>a</sup>Isolated yield.

The catalyst, Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip can be readily isolated from the reaction mixture using an external magnetic field. We also studied the reusability of Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip in this reaction. The isolated catalyst was used for the synthesis of **4a** under the same reaction conditions. The results showed that the catalyst could be efficiently used for five runs (Table 4).

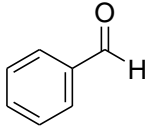
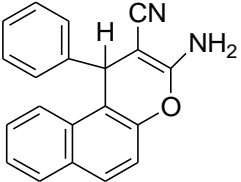
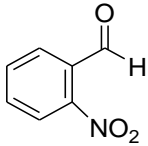
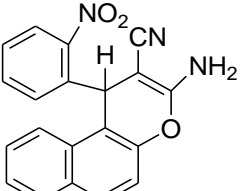
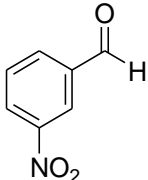
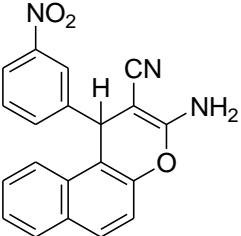
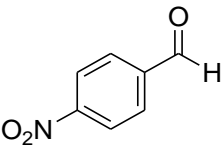
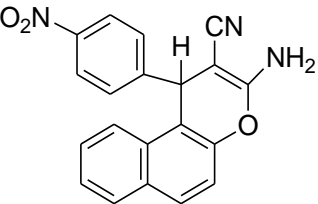
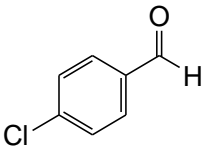
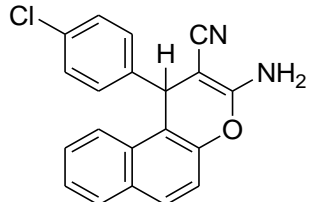
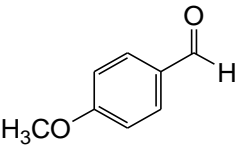
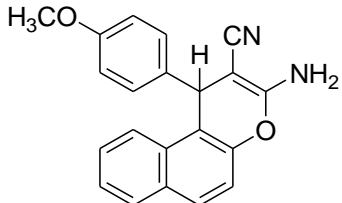
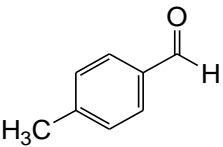
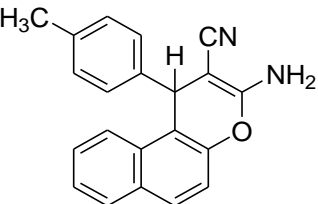
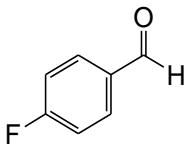
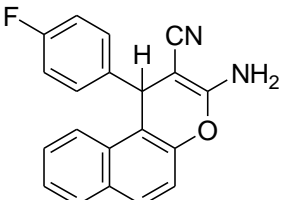
**Table 4.** Recyclability of the catalyst.

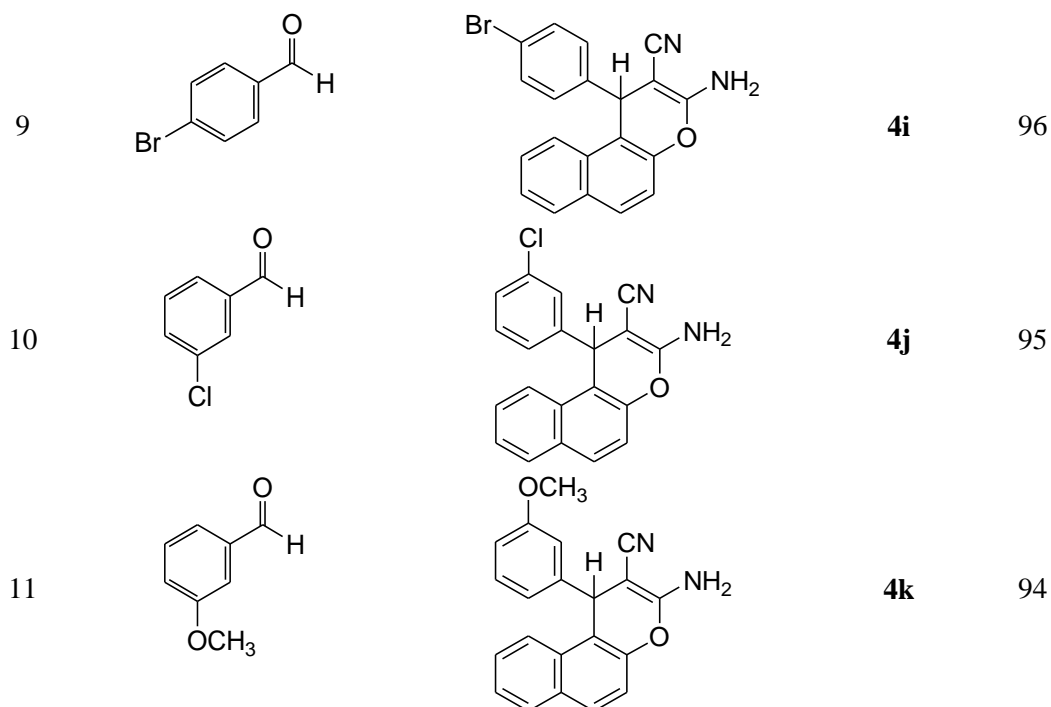
Run	1	2	3	4	5
Yield (%)	98	94	93	91	90

Reactions of various arylaldehydes was investigated in the presence of Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip under optimized reaction conditions for the synthesis of related chromenes **4a-k** (Table 5). In all cases, the three-component reaction proceeded smoothly to give the corresponding chromens in good to excellent yields. Aromatic aldehydes carrying electron-withdrawing or electron-donating groups gave the corresponding products in good yields and high purity in this procedure.



**Table 5.** Synthesis of a variety of 2-aminochromenes using Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip.

Entry	Arylaldehyde	Product	Product Number	Yield <sup>a</sup> (%)
1			<b>4a</b>	98
2			<b>4b</b>	98
3			<b>4c</b>	90
4			<b>4d</b>	96
5			<b>4e</b>	99
6			<b>4f</b>	91
7			<b>4g</b>	92
8			<b>4h</b>	97



<sup>a</sup>Isolated yield.

#### 4. Conclusion

In summary, we successfully synthesized a magnetic core-shell Fe<sub>3</sub>O<sub>4</sub>@GQDs-Pip Lewis basic catalyst and used for the efficient synthesis of aminochromenes under MW-assisted solvent-free conditions. High catalytic activity under mild reaction conditions, easy separation of the catalyst after reaction by an external magnet, and reusability of the catalyst for several times without any significant loss in the yield of the reaction make it attractive for the large scale synthesis of biologically active chromene derivatives. Moreover, we have developed a facile, convenient and environmentally benign method for the synthesis of 2-minochromenes.

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#### Supporting Information

Supporting information accompanies this paper on <http://www.acgpubs.org/journal/organic-communications>

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#### References

- [1] Lee, J.H.; Huh, Y.M.; Jun, Y.; Seo, J.; Jang, J.; Song, H.T.; Kim, S.; Cho, E.J.; Yoon, H.G.; Suh, J.S.; Cheon, J. Artificially engineered magnetic nanoparticles for ultra-sensitive molecular imaging. *Nat. Med.* **2007**, *13*, 95.

- [2] Dobson, J. Magnetic nanoparticles for drug delivery. *Drug Dev. Res.* **2006**, *67*, 55–60.
- [3] Lu, A.H.; Schmidt, W.; Matoussevitch, N.; Bpnnermann, H.; Spliethoff, B.; Tesche, B.; Bill, E.; Kiefer, W.; Schüth, F. Nanoengineering of a magnetically separable hydrogenation catalyst. *Angew. Chem.* **2004**, *116*, 4403-4406.
- [4] Gupta, A.K.; Gupta, M. Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomaterials.* **2005**, *26*, 3995-4021.
- [5] Nuñez, L.; Kaminski, M.D. Transuranic separation using organophosphorus extractants adsorbed onto superparamagnetic carriers. *J. Magn. Magn. Mater.* **1999**, *194*, 102-107.
- [6] Weiss, W.; Ranke, W. Surface chemistry and catalysis on well-defined epitaxial iron-oxide layers. *Prog. Surf. Sci.* **2002**, *70*, 1.
- [7] Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Vander Elst, L.; Muller, R.N. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. *Chem. Rev.* **2008**, *108*, 2064-2110.
- [8] Baig, R.B.N.; Varma, R.S. Magnetically retrievable catalysts for organic synthesis, *Chem. Commun. Chem. Commun.* **2013**, *49*, 752.
- [9] Wang, X.J.; Tian, J.F.; Yang, T.Z.; Bao, L.H.; Hui, C.; Liu, F.; Shen, C.M.; Gu, C.Z.; Xu N.S.; and Gao, H. J. Single crystalline boron nanocones: Electric transport and field emission properties. *Adv. Mater.* **2007**, *19*, 4480.
- [10] Baig, R.B.N.; Varma, R.S. Magnetically retrievable catalysts for organic synthesis. *Chem. Commun.* **2013**, *49*, 752.
- [11] Li, L.; Gehui, W.; Guohai, Y.; Juan, P.; Jianwei Z.; and Jun-Jie, Z. Focusing on luminescent graphene quantum dots: current status and future perspectives. *Nanoscale.* **2013**, *5*, 4015-4039.
- [12] Zhao, J.; Guifang, C.; Li, Z.; and Genxi, L. Graphene quantum dots-based platform for the fabrication of electrochemical biosensors. *Electrochem. Commun.* **2011**, *13*, 31-33.
- [13] Dong, Y.; Li, G.; Zhou, N.; Wang, R.; Chi, Y.; Chen, G. Graphene quantum dot as a green and facile sensor for free chlorine in drinking water. *Anal. Chem.* **2012**, *84*, 8378-8382.
- [14] Wang, D.; Lei, W.; Xinyi, D.; Zhun, Sh.; and Jian, J. Chemically tailoring graphene oxides into fluorescent nanosheets for Fe<sup>3+</sup> ion detection. *Carbon.* **2012**, *50*, 2147-2154.
- [15] Bowers, R.S.; Ohta, T.; Cleere, J.S.; Marsella, P.A. Discovery of insect anti-juvenile hormones in plants. *Science.* **1976**, *193*, 542-547.
- [16] Chetan, B.S.; Nimesh, M.S.; Manish, P.P.; Ranjan, G.P. Microwave assisted synthesis of novel 4H-chromene derivatives bearing phenoxyprazole and their antimicrobial activity assess. *J. Serb. Chem. Soc.* **2012**, *77*, 1–17.
- [17] Kumar, A.; Siddharth, Sh.; Ram Maurya, A.; and Jayant, S. Diversity oriented synthesis of benzoxanthene and benzochromene libraries via one-pot, three-component reactions and their anti-proliferative activity *J. Comb. Chem.* **2009**, *12*, 20-24.
- [18] Denish, C.K.; Hetal, K.P.; Nilesh, K.G. Synthesis, characterization & anti-HIV activity of 4-Hydroxy-3-(5-methylisoxazol-3-yl) pyrano (3, 2-C) chromene-2, 5-dione. *AJBPR.* **2012**, *2*, 126- 130.
- [19] Bianchi, G.; Tava, A. Synthesis of (2 R)-(+)-2, 3-dihydro-2, 6-dimethyl-4 H-pyran-4-one, a homologue of pheromones of a species in the hepialidae family. *Agric. Biol. Chem.* **1987**, *51*, 2001.
- [20] Sofan, M.A.; El-Taweel, F.M.; Elagamey, A.G.A.; Elnagdi, M.H. Studies on cinnamonitriles: The reaction of cinnamonitriles with cyclopentanone. *Ann. Chem.* **1989**, *9*, 935–936.
- [21] Zeng, T.; Chen, W. -W.; Cirtiu, C.M.; Moores, A.; Song, G.; Li, C.-J. Fe<sub>3</sub>O<sub>4</sub> nanoparticles: a robust and magnetically recoverable catalyst for three-component coupling of aldehyde. *Green Chem.* **2010**, *12*, 570-573.
- [22] Kumar, N.U.; Reddy, B.S.; Reddy, V.P.; Bandichhor, R. Bandichhor, Iron triflate catalyzed reductive amination of aldehydes using sodium borohydride. *Tetrahedron. Lett.* **2012**, *53*, 4354-4356.
- [23] Valizadeh, H.; shomali, A.; Nourshargh, S.; Rezaei, R. M. Carboxyl and nitrite functionalized graphene quantum dots as a highly active reagent and catalyst for rapid diazotization reaction and synthesis of azo-dyes under solvent-free conditions. *Dyes Pigments.* **2015**, *113*, 522-528.
- [24] Valizadeh, H.; Ahmadi, M. A facile and efficient [bmim] N<sub>3</sub> catalyzed direct oxidative esterification of arylaldehydes with alcohols. *Compt. Rend. Chim.* **2012**, *15*, 1077-1080.
- [25] Valizadeh, H.; Amiri, M.; khalili, E. Task-specific nitrite and azide ionic liquids for the efficient one-pot synthesis of 1, 2, 3 -triazoles from the aniline derivatives. *Mol. Divers.* **2012**, *16*, 319-323.
- [26] Kulkarni, S.A.; Sawadh, P.S.; and Kokate, K.K. Synthesis and Characterization of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles for Engineering Applications. *IJCA.* **2012**, *2*, 17-18.
- [27] Albadi, J.; Mansournezhad, A.; Darvishi-Paduk, M. As a green, efficient and commercial available basic catalyst for the synthesis of chromene derivatives. *Chinese. Chemical. Letters.* **2013**, *24*, 208–210.

- [28] Rao, M.S.; Chhikara, B.S.; Tiwari, R.; Nasrolahi Shirazi, A.; Parang, K.; Kumar, A. A greener synthesis of 2-aminochromenes in ionic liquid and evaluation of their antiproliferative activities. *Chemistry & Biology Interface*. **2012**, *2*, 362-372.
- [29] Pagore, V.P.; Tekale, S.U.; Rupnar, B.D.; and Pawar, R.P. Efficient and green synthesis of 2-amino-4H-chromenes, *Journal of Chemical and Pharmaceutical Research*. *JCHPS*. **2015**, *7*, 1057-1061.
- [30] Mohammadzianari, Gh.; Badii, A.; Dashtianeh, Z.; Hajiabbasi, P. Hajiabbasi, Green one-pot syntheses of 1H-and 4H-Chromenes derivatives using SiO<sub>2</sub>-Pr-SO<sub>3</sub>H as catalyst. *Rev. Roum. Chim.* **2013**, *58*, 765-772.

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