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Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride: A novel catalyst for the synthesis of coumarin containing 1,4 dihydropyridines

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ABSTRACT

Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride, as a novel and efficient nanomagnetic catalyst bearing urea linkers, was designed, synthesized and then fully characterized by using various techniques. To investigate the catalytic activity of the described catalyst, it was used for the synthesis of coumarin containing 1,4-dihydropyridines (DHPs), through a condensation reaction of aromatic aldehydes, 4-hydroxycoumarin, and ammonium acetate under solvent-free conditions. This procedure includes important aspects like simple procedure, simplicity of product isolation using water, decreasing the temperature of reaction, disuse of solvent, high to excellent yields, environmentally benign reaction conditions and short reaction times. Also, the presented catalyst was recycled and reused for at least five times with only a negligible decrease in its catalytic activity. The applied catalyst has both acidic and H-bond donor-acceptor sites so that it can use as a dual role catalytic system.

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1. Introduction

Over the years, among the heterocyclic compounds containing the oxygen atoms, coumarin derivatives due to their diverse pharmacological and biological properties, have attracted main attentions [1]. These compounds display a broad range of biological activities including anticancer [2], anti-HIV [3], anti-tuberculosis [4], anti-influenza [5], anti-Alzheimer [6], antioxidant [7], anticoagulant [8], antibacterial [9], anti-dyslipidemic [10], antimicrobial [11] and anti-inflammatory activity [12].

Polycyclic 1,4-dihydropyridines (1,4-DHPs) are an important class of heterocyclic compounds containing nitrogen atoms with intriguing molecular structures. They have been showed remarkable pharmacological activities. Some of the 1,4-dihydropyridines have been emerged as opening potassium channels [13], blocking calcium channel [14], anticonvulsant, analgesic, anti-inflammatory [15], treating Alzheimer's disease [16], anti-tumor [17], antimicrobial [18] and antimalarial [19] agents. Although, various procedures are reported for the synthesis of fused dihydropyridines [20,21], most of these methodologies have disadvantages such as use of microwave irradiation, utilization of costly and environmentally poisonous catalysts, long reaction times, low yields of the products, tedious workup protocols, high temperature and utilization of solvents. So, the development of simple, efficient and eco-friendly methods for the preparation of 1, 4-dihydropyridines under green conditions are desirable. Chemical structure of some natural products and synthetic drugs bearing DHP core are presented in Scheme 1.

From the perspective of green chemistry, high activity of catalysts and their reusability are two important factors in the most of modern catalytic processes. In this respect, magnetic nanoparticles (MNPs) have been emerged as one of the most useful heterogeneous catalysts due to their numerous applications in the chemical processes as well as organic synthesis. They are robust, inexpensive and recyclable by an external magnet for several runs without considerable loss of their selectivity and activity [22,23]. Good biocompatibility and biodegradability, as well as basic magnetic characteristics could be denoted for functional organic materials grafted to MNPs [24,25].

The compounds with urea moiety are interesting structures with biological properties which presented in numerous fields such as resin precursors, agriculture industry, dyes, pharmaceutical ingredients and additives to petroleum compounds and polymers [26]. In addition to, they were utilized as acidic and basic catalysts, chiral acid catalysts, coupling with metals as catalyst, coupling with ionic liquids, urea anions catalysts, urea polymer catalysts and urea based supported catalysts. Recently, we have reviewed the performance of biological urea based catalysts in the chemical reactions [27].

With regard to green chemistry, the construction of complex functionalized molecules through multi-component reactions

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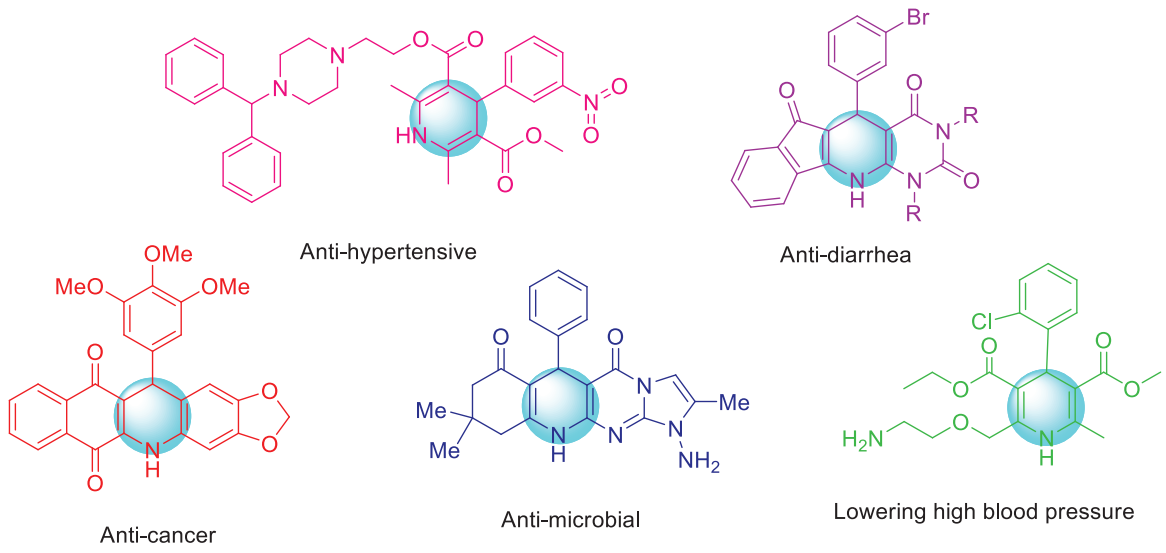
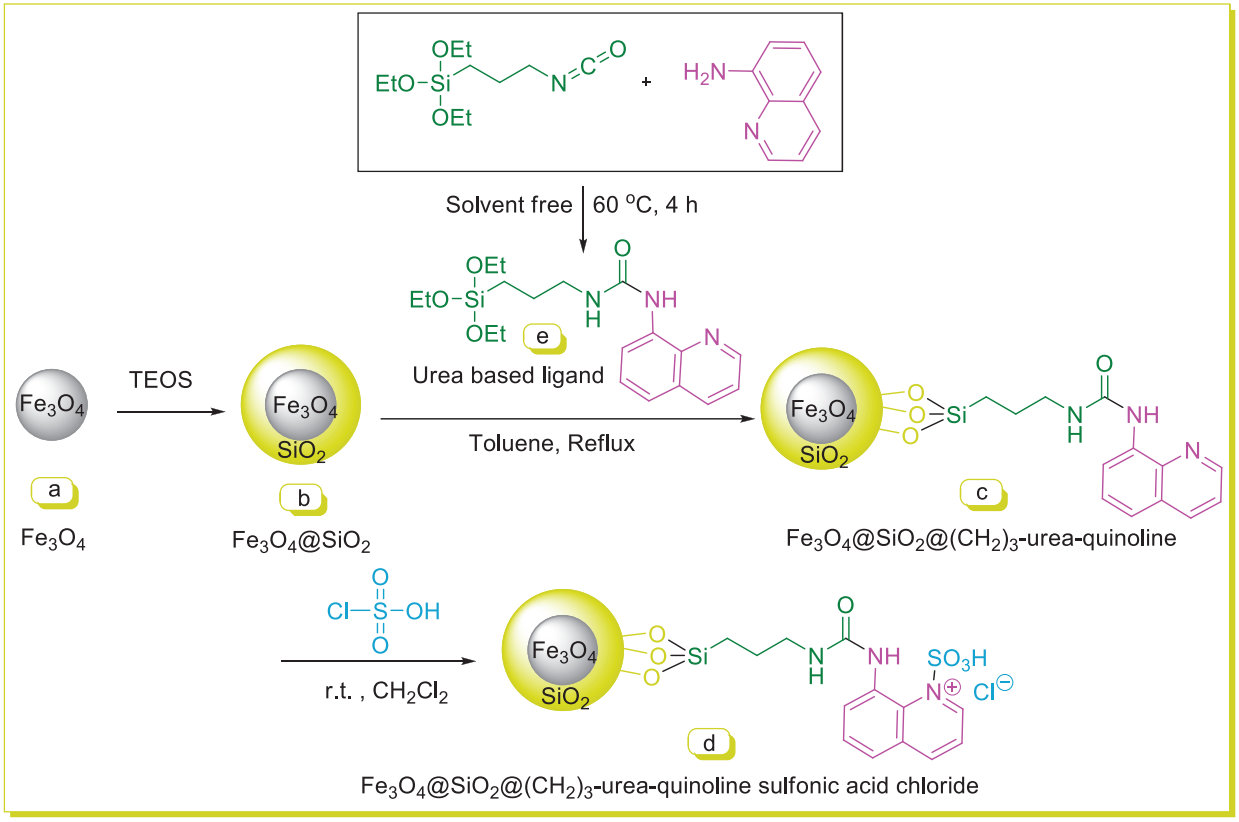


Scheme 1. Some natural products and synthetic drugs bearing DHP moieties.



Scheme 2. Synthesis of Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride.

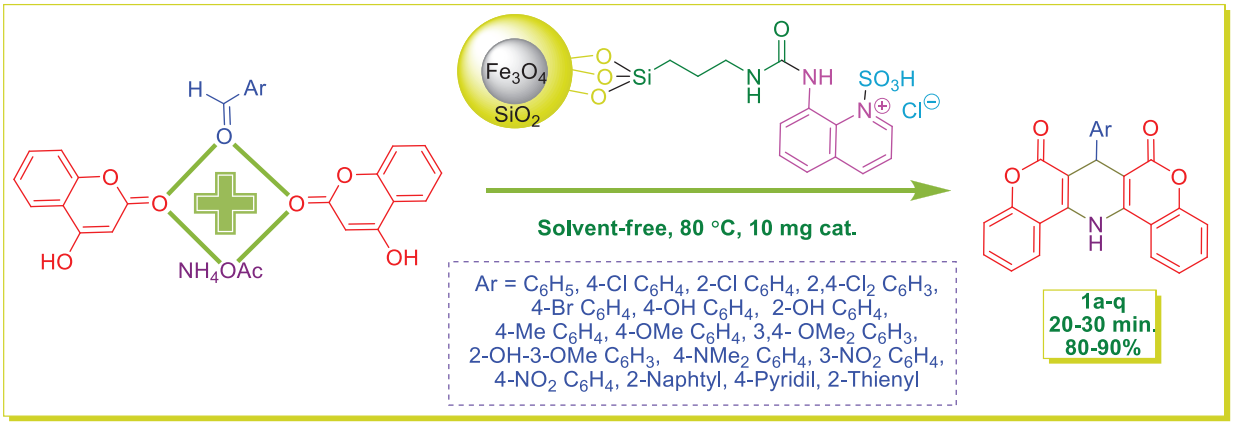
(MCRs) become increasingly important to both pharmaceuticals and organic chemists due to their merit features such as higher atom economy, convenient reaction design, simplicity of operation and purification, and minimization of costs, time, energy, solvents, and waste production compared to classical multi-step synthesis. MCRs lead to interesting heterocyclic building blocks by the introduction of several diversity elements in a single chemical event [28,29].

In continuation of our two decades studies on the chemistry of 1,4-DHPs [30,31] and efforts to develop catalysts bearing urea moiety [27,32], this exploration describes the preparation of novel nanomagnetic catalyst namely Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride and it's catalytic application in one pot synthesis of coumarin with 1,4-DHPs moieties (Schemes 2 and 3).

2. Experimental

2.1. General procedure for the synthesis of urea-based ligand

At first, urea-based ligand was prepared by the reaction of triethoxy(3-isocyanatopropyl)silane (5 mmol, 1.237 g) and 8-aminoquinoline (5 mmol, 0.720 g) under solvent free conditions at



Scheme 3. Catalytic synthesis of coumarin containing 1,4-DHPs.

60 °C for 4 h. Afterwards, the obtained product washed with the mixture of *n*-hexane and dichloromethane (3 × 10 mL) to afford the desired urea-based ligand (Scheme 2).

2.2. General procedure for the synthesis of Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid

Initially, Fe_3O_4 nano particles were prepared on the basis of the previously reported procedure [33]. In the next step, Fe_3O_4@SiO_2, was prepared through the reaction of Fe_3O_4 nano particles with tetraethyl orthosilicate (TEOS). Afterwards, the obtained Fe_3O_4@SiO_2 (1 g) was functionalized by the reaction with urea-based ligand (2 mmol, 0.782 g) under refluxing toluene for 48 h. In the next step, the obtained Fe_3O_4@SiO_2@$(CH_2)_3$-urea- quinoline (1 g), at ice bath subjected to the reaction with chlorosulfuric acid (2 mmol, 0.233 g) in dichloromethane as solvent for 2 h. In the final step, the Fe_3O_4@SiO_2@$(CH_2)_3$-urea- quinoline sulfonic acid chloride was washed thoroughly (dichloromethane (3 × 15 mL)) and air dried (Scheme 2).

2.3. General procedure for the synthesis of coumarin containing 1,4-DHPs catalyzed by Fe_3O_4@SiO_2@$(CH_2)_3$-urea- quinoline sulfonic acid chloride

A round-bottomed flask was charged with arylaldehyde derivatives (0.5 mmol), 4-hydroxycoumarin (0.162 g, 1 mmol), NH_4OAc (0.154 g, 2 mmol), and Fe_3O_4@SiO_2@$(CH_2)_3$-urea- quinoline sulfonic acid chloride (10 mg) were stirred vigorously at 80 °C under solvent free conditions for appropriate times (Table 2). Reaction progress was monitored by TLC (using *n*-hexane and ethyl acetate as eluent). After the reaction completion, hot ethanol was added to the mixture. The catalyst was insoluble in hot ethanol and easily separated by an external magnet bar. After evaporation of solvent, the precipitate was collected, filtered and washed with water to afford the pure product **1a–q** with the range of yields from 80 to 90%.

2.4. Selected spectral data

2.4.1. 1-(Quinolin-8-yl)–3-(3-(triethoxysilyl)propyl)urea (Urea-based ligand)

Brown solid, M.p.: 121–123 °C.

FT-IR (KBr, ν, cm^{-1}): 3298, 3273, 3093, 2974, 1693, 1642, 1558, 1518, 1103, 1079, 788.

^{1}H NMR (301 MHz, DMSO, δ, ppm): 9.38 (s. 1H, NH), 8.86 (d, 1H, J = 3 Hz, Aromatic) 8.58 (d, 1H, J = 9 Hz, Aromatic), 8.32 (d, 1H, J = 9 Hz, Aromatic), 7.58- 7.43 (m, 4H, Aromatic, NH), 3.75 (q, 6H, J = 6 Hz, CH_2O), 3.17(q, 2H, J = 6 Hz, CH_2N, 1.56 (quint, 2H, J = 6 Hz, CH_2), 1.15 (t, 9H, J = 6 Hz, CH_3), 0.61- 0.66 (m, 2H, CH_2Si).

^{13}C NMR (76 MHz, DMSO, δ, ppm): 155.6, 148.3, 138.1, 137.2, 136.9, 128.4, 127.6, 122.1, 119.2, 114.3, 58.2, 42.3, 23.7, 18.6, 7.8.

2.4.2. 7-p-Tolyldichromeno[4,3-b:3′,4′-e]pyridine-6,8(7H,14H)–dione (1i)

Cream solid, M.p.: 256–258 °C.

FT-IR (KBr, ν, cm^{-1}): 3377, 3183, 1675, 1618, 1534, 1407, 757.

^{1}H NMR (301 MHz, DMSO, δ, ppm): 9.55 (br, 1H, NH), 7.95- 7.07 (m. 12 H, Aromatic), 6.39 (s, 1H, CH), 2.27 (s. 3H, Me).

^{13}C NMR (76 MHz, DMSO, δ, ppm): 165.4, 152.6, 136.9, 135.0, 132.5, 129.2, 127.1, 124.4, 118.2, 116.5, 104.81, 36.1, 21.1.

2.4.3. 7-(4-Methoxyphenyl)dichromeno[4,3-b:3′,4′-e]pyridine-6,8(7H,14H)–dione (1j)

Cream solid, M.p.: 230–232 °C.

FT-IR (KBr, ν, cm^{-1}): 3216, 3069, 2930, 1662, 1604, 1509, 758.

^{1}H NMR (301 MHz, DMSO, δ, ppm): 7.91- 6.81 (m, 13 H, Aromatic, NH), 6.30 (s, 1H, CH), 3.72 (s, 3H, OMe).

^{13}C NMR (76 MHz, DMSO, δ, ppm): 166.0, 165.2, 157.7, 152.7, 132.2, 128.2, 124.4, 124.1, 118.7, 116.3, 113.9, 104.8, 55.4, 35.8.

2.4.4. 7-(3,4-Dimethoxyphenyl)dichromeno[4,3-b:3′,4′-e]pyridine-6,8(7H,14H)–dione (1k)

Cream solid, M.p.: 264–266 °C.

FT-IR (KBr, ν, cm^{-1}): 3417, 3207, 3078, 2995, 1651, 1613, 1533, 1405, 754.

^{1}H NMR (301 MHz, DMSO, δ, ppm): 7.9- 6.7 (m, 12 H, Aromatic, NH), 6.3 (s, 1H, CH), 3.7 (s, 3H, OMe), 3.6 (s, 3H, OMe).

^{13}C NMR (76 MHz, DMSO,):165.9, 165.2, 152.7, 149.0, 147.6, 133.0, 132.2, 124.4, 124.1, 119.4, 118.6, 116.38, 112.2, 111.9, 104.8, 56.1, 56.0, 36.2.

2.4.5. 7-(2-Hydroxy-3-methoxyphenyl)dichromeno[4,3-b:3′,4′-e]pyridine-6,8(7H,14H)–dione (1l)

Cream solid, M.p.: 209–211 °C.

FT-IR (KBr, ν, cm^{-1}): 3393, 3073, 2982, 1665, 1616, 1566, 1513, 763.

^{1}H NMR (301 MHz, DMSO, δ, ppm): 7.91- 6.58 (m, 13 H, Aromatic, NH, OH), 6.25 (s, 1H, CH), 3.59 (s, 3H, OMe).

^{13}C NMR (76 MHz, DMSO, δ, ppm): 166.4, 165.2, 152.7, 147.7, 145.0, 131.9, 124.4, 123.9, 119.7, 119.1, 116.2, 115.5, 112.2, 104.7, 56.2, 36.1.

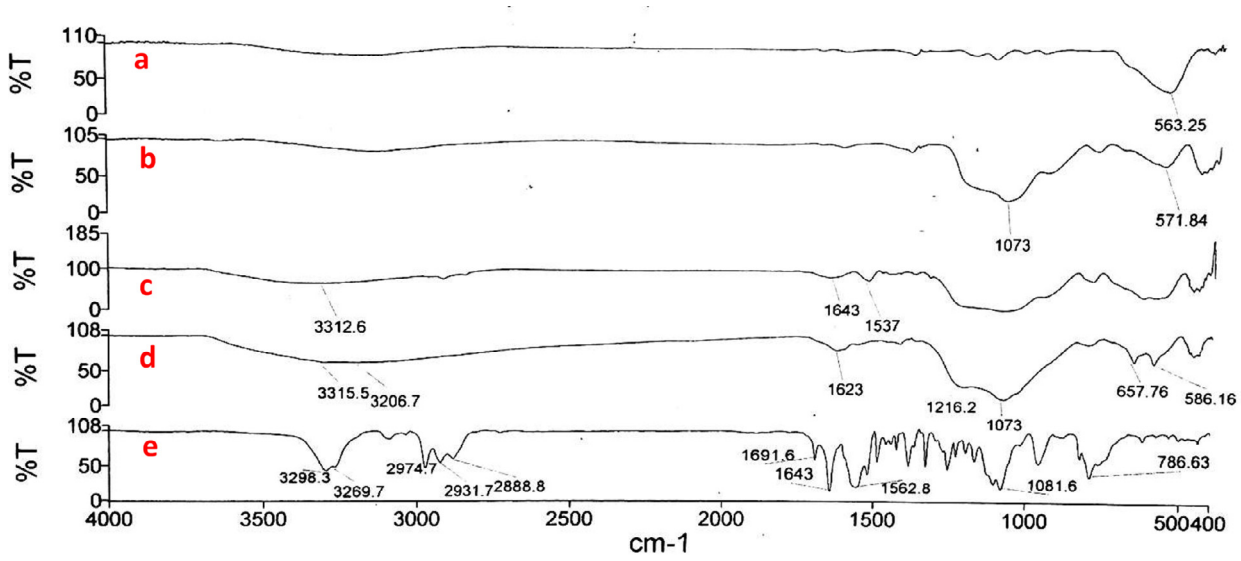


Fig. 1. Comparative study of FT-IR spectra of Fe_3O_4 (a), Fe_3O_4@SiO_2 (b), Fe_3O_4@SiO_2@$(CH_2)_3$-urea-aminoquinoline (c) and Fe_3O_4@SiO_2@$(CH_2)_3$-urea- aminoquinoline sulfonic acid chloride (d), urea based ligand (e).

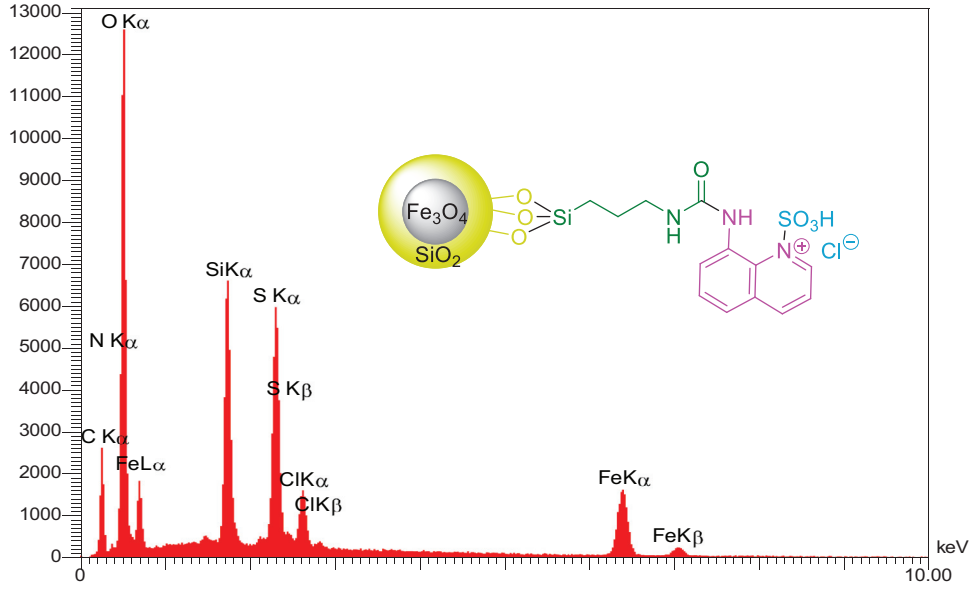


Fig. 2. EDX analysis of the Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride.

3. Result and discussion

Arthur Rudolf Hantzsch had been reported the synthesis of 1,4-DHPs in 1882. The chemistry of 1,4-DHPs comprehensively have been reviewed [34]. Although this old one-pot multi-component reaction (MCR) is a well-known name reaction in organic chemistry but the synthesis of new organic molecules which have 1,4-DHPs moieties are a great demand due to their remarkable pharmacological activities. On the basis of the mentioned facts, herein we wish to report a new methodology for the synthesis coumarin with 1,4-DHPs moieties.

3.1. Characterization of the novel catalyst

Firstly, characterization of Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride as a recoverable nanomagnetic catalyst was performed using FT-IR, TGA, DTG, VSM, FESEM, Mapping and TEM analysis. The outcomes of all applied analysis were discussed below in details.

In a comparative style, as shown in the Fig. 1, the FT-IR spectra of different intermediates and desired catalyst were investigated in the range 400–4000 cm^{-1}. Addition of each layer to the previous one, leads to observation of characteristic peaks of new added functional groups in the spectrum which proves the formation of a new layer. The FT-IR spectrum of the final catalyst (d) shows all predictable functional groups at their related positions. The broad peak from about 2700–3700 cm^{-1} confirms the existence of acidic OH and NH functional groups within the structure of the catalyst. Also, amidic $C = O$ (urea moiety) and $S = O$ (sulfonic acid) functional groups verified by their characteristic peaks at 1627 cm^{-1} and 1216 cm^{-1}, respectively.

In order to explore the elemental composition of the catalyst Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride, energy-dispersive spectroscopy (EDX) and elemental mapping analysis were conducted (Figs. 2 and 3). The obtained data from these anal-

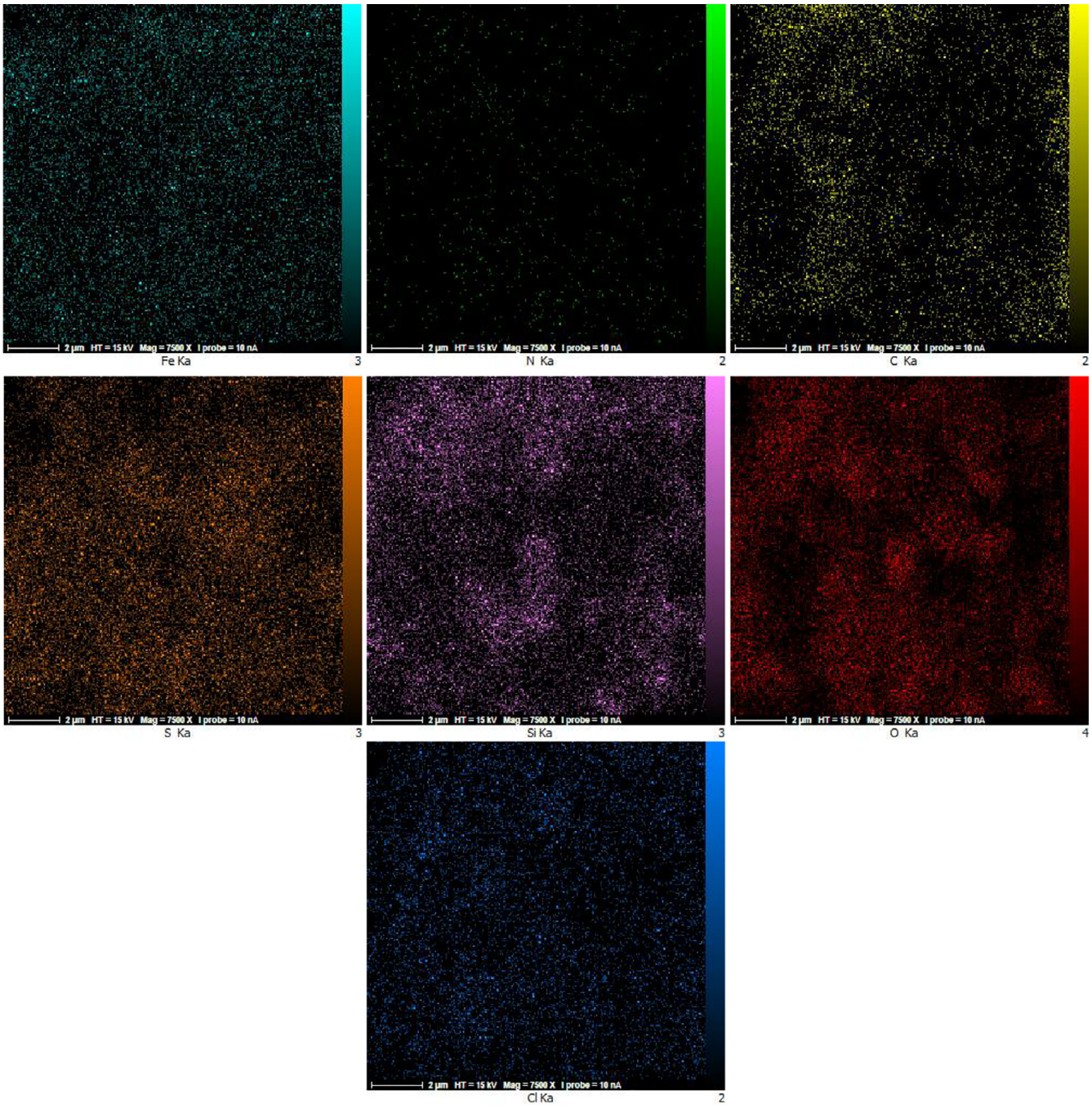


Fig. 3. Elemental mapping analysis of the Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride.

yses approve of each other well. Achieved data from both EDX and elemental mapping (Figs. 2 and 3), approved the presence of Fe, O, Si, C, N, S and Cl in the catalyst with a suitable dispersity.

In attempting to investigate the surface morphological characteristics and particle size of the prepared catalyst, SEM images were recorded and are shown in the Fig. 4. The SEM images show that the size of the catalyst particles is in the nano meter range (10–15 nm) with sphere-like structure. These observations verified with the achieved data from TEM images (Fig. 5).

TGA/DTG analysis was applied to study the thermal stability of Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride (Fig. 6). The weight loss upon heating from room temperature to about 180 °C can be attributed to the evaporation of the solvents which were employed during the course of catalyst preparation. Also, the weight loss from 180 to 520 °C can be ascribed to the decomposition of organic layer connected to Fe_3O_4@SiO_2 particles (weight loss of about 35.3%). The mass residue above 600 °C can be attributed to the inorganic parts of the catalyst including Fe_3O_4 or Fe_3O_4@SiO_2 particles. On the basis of the achieved results, the presented nanomagnetic catalyst well modified with active organic parts and shows proper thermal behavior upon the investigated reaction.

As illustrated in Fig. 7, the magnetic behavior of Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride was also investigated using VSM and compared to that of Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline as intermediates in the synthetic pathway. As expected, decrease saturation magnetization from about 40 emu/g to about 20 emu/g, is related to the new coated layer and confirmed

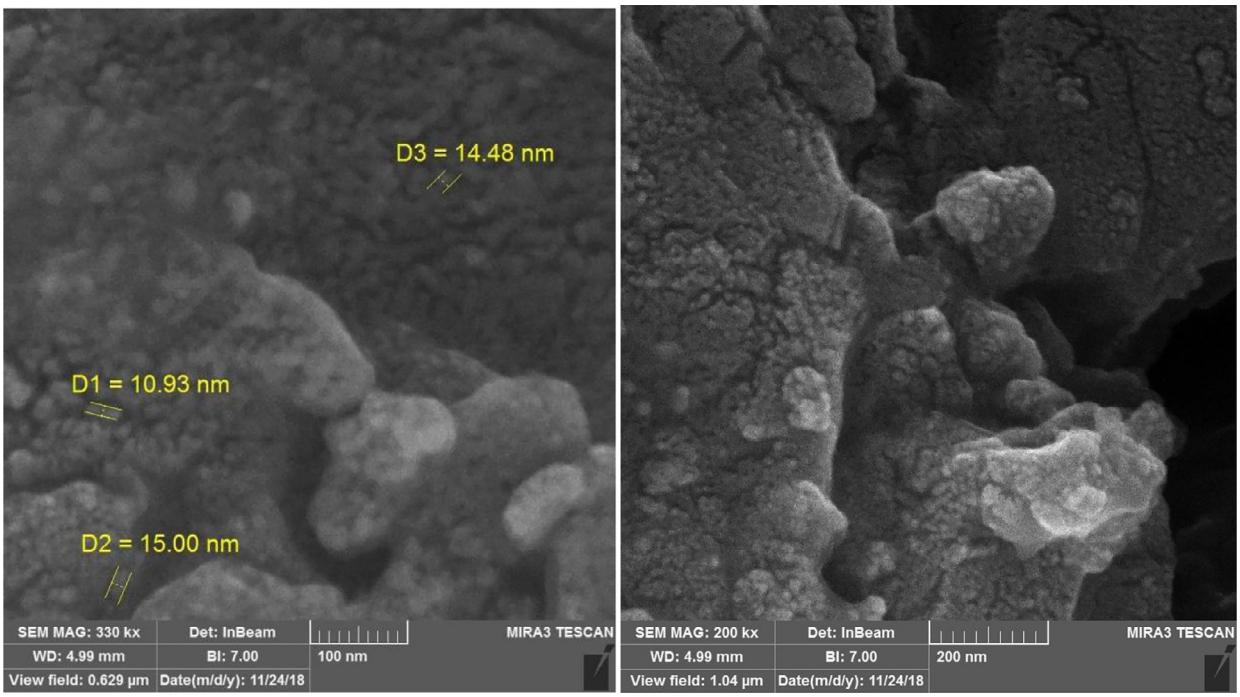


Fig. 4. SEM micrographs of the $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride.

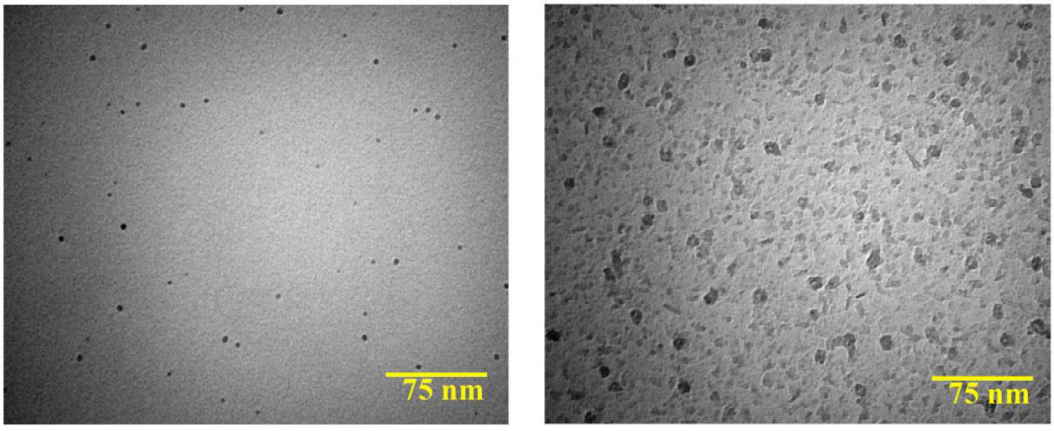


Fig. 5. TEM images of the $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride.

the successful formation of desired catalyst. Also, this data verified the capability of a simple external magnet for separation of the catalyst from the reaction mixture.

3.2. Catalytic application of $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride for the synthesis of coumarin containing DHPs

After preparation and full characterization of the novel $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride, its catalytic activation was also investigated over a multi component reaction between arylaldehydes, 4-hydroxycoumarins and ammonium acetate to produce pyridine derivatives (**2a-q**) as favorite products. Due to these compounds could be a puzzle piece of our research interest in expanding of our new established term entitled "cooperative vinylogous anomeric based oxidation mechanism" [35,36]. In contrast of our expected product, the obtained spectral data showed that the reaction proceed towards the synthesis of dihydropyridine derivatives (**1a-q**) (Scheme 4). Since these compounds show remarkable pharmacological activities, we determine to complete the study and present an efficient method for their synthesis.

At first, for achieving the optimal reaction parameters, the influence of temperature, catalyst loading and different solvents over the reaction of 4-methyl benzaldehyde, 4-hydroxycoumarine, and ammonium acetate as a model reaction, were investigated. On the basis of our achieved experimental results, using 10 mg of the $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride at 80 °C under solvent free conditions supplied the best results. Elevating the operational reaction temperature and increasing the amount of catalyst did not lead to more favorable results. All obtained data are summarized in Table 1.

Also, we performed the model reaction in the presence of related intermediates of the $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride at 80 °C under solvent free conditions for 20 min. The achieved data as inserted in Table 2 shows no satisfactory results compare with $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride.

Afterwards, scope and generality of the presented method was investigated by examining the reaction of structurally diverse aromatic aldehydes, 4-hydroxycoumarin and ammonium acetate in the presence a catalytic amount of described nanomagnetic cat-

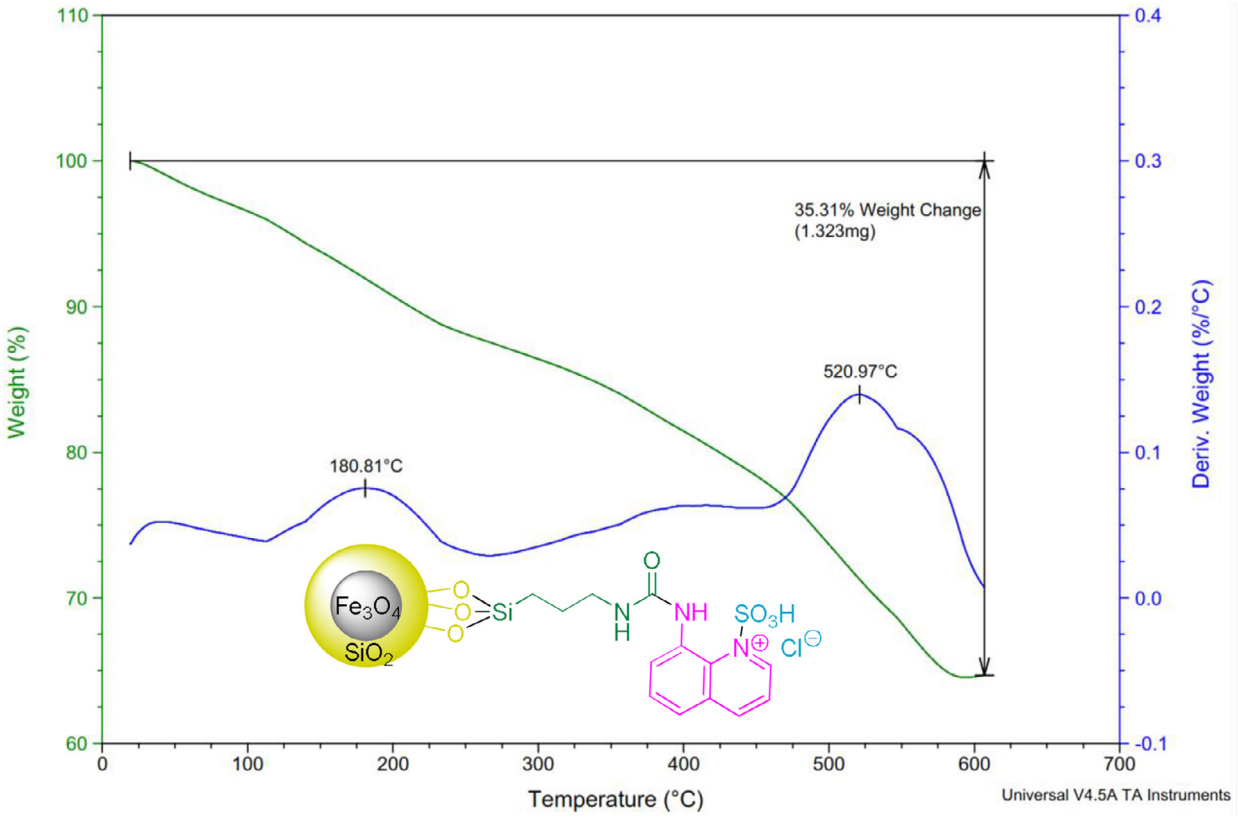


Fig. 6. TGA and DTG analysis curves of the $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride.

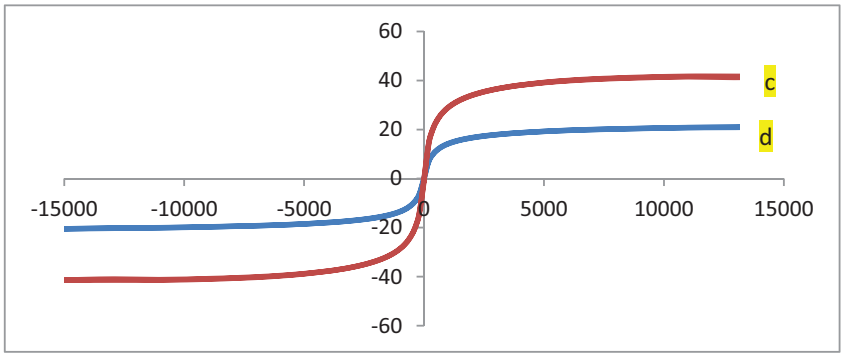
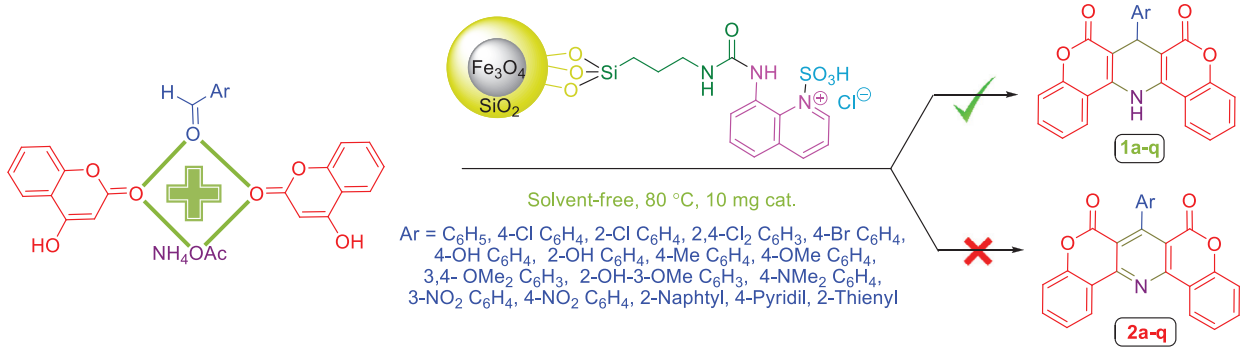
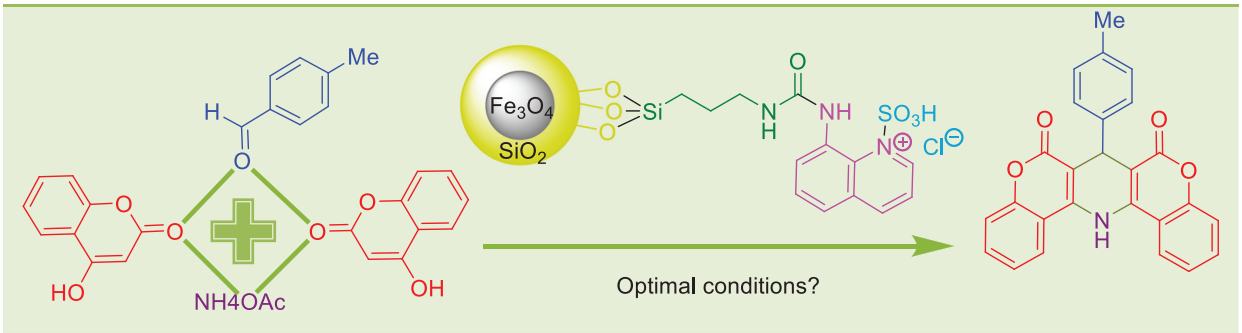


Fig. 7. VSM curves of (c) $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline and (d) $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride.



Scheme 4. Synthesis of coumarin containing DHPs in the presence of $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride.

Table 1
Optimization of reaction conditions upon the synthesis of molecule 1i in the presence of Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride as a novel catalyst[a] .



Entry	Solvent	Temperature (°C)	Catalyst (mg)	Time (min.)	Yield (%)[b]
1	–	90	–	90	30
2[c]	–	90	5	30	80
3	–	90	10	20	86
4	–	90	15	20	85
5	–	100	10	20	81
6	–	80	10	20	85
7	–	60	10	30	70
8	H_2O	Reflux	10	30	85
9	EtOH	Reflux	10	45	75
10	EtOAc	Reflux	10	90	20
11	CH_2Cl_2	Reflux	10	90	Trace
12	*n*-Hexane	Reflux	10	90	Trace

[a] Reaction conditions: 4-Methylbenzaldehyde (0.5 mmol, 0.06 g), 4-hydroxycoumarine (1 mmol, 0.162 g) and ammonium acetate (2 mmol, 0.154 g).
[b] Isolated yields.

Table 2
Screening the model reaction in the presence of desired catalyst and its related intermediates[a].

Entry	**Catalyst**	Yield (%)[b]
1	Fe_3O_4	40
2	Fe_3O_4@SiO_2	40
3	Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline	65
4	Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride	85

[a] Reaction conditions: 4-Methylbenzaldehyde (0.5 mmol, 0.06 g), 4-hydroxycoumarine (1 mmol, 0.162 g) and ammonium acetate (2 mmol, 0.154 g), catalyst: 10 mg.
[b] Isolated yields.

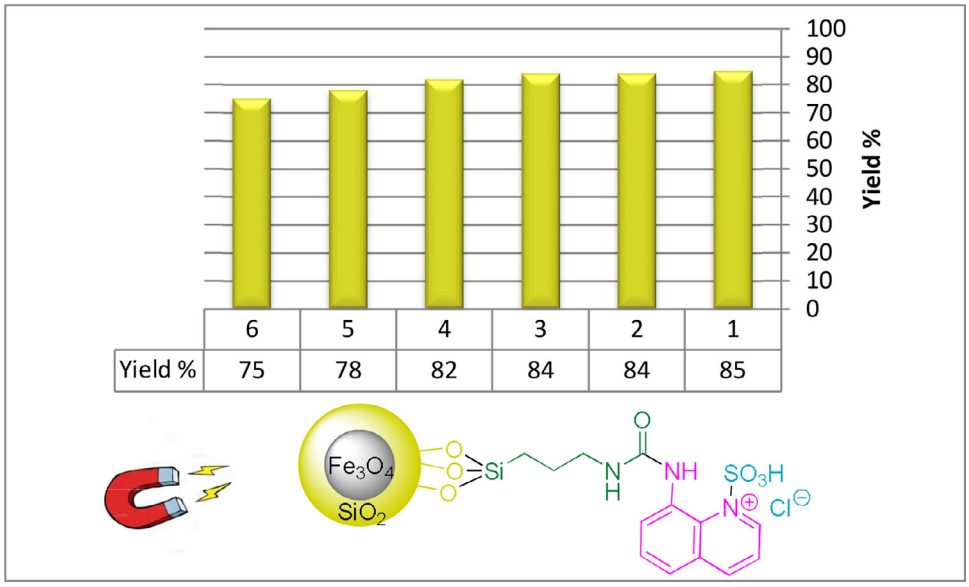
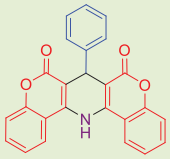
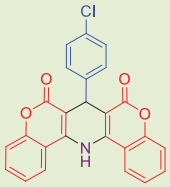
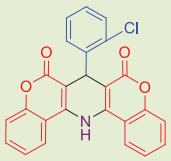
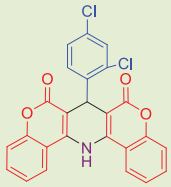
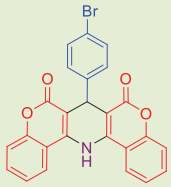
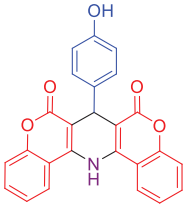
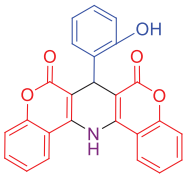
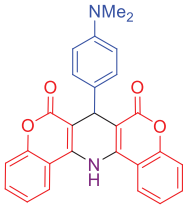
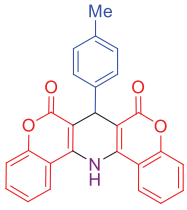
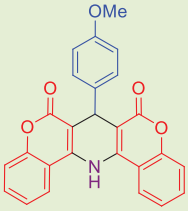
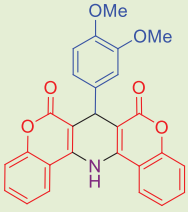
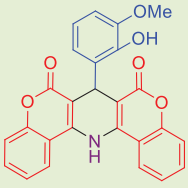
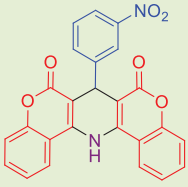
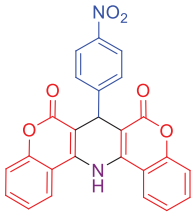
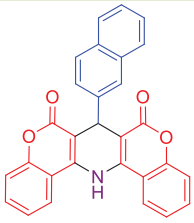
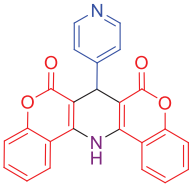
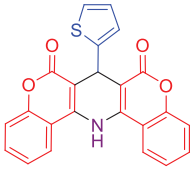


Fig. 8. Successful reusing test of Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride at the synthesis of target molecules **1i**.

Table 3
Catalytic Synthesis of target molecules 1a-q in the presence of $Fe_3O_4@SiO_2@(CH_2)_3$- urea-quinoline sulfonic acid chloride[a].

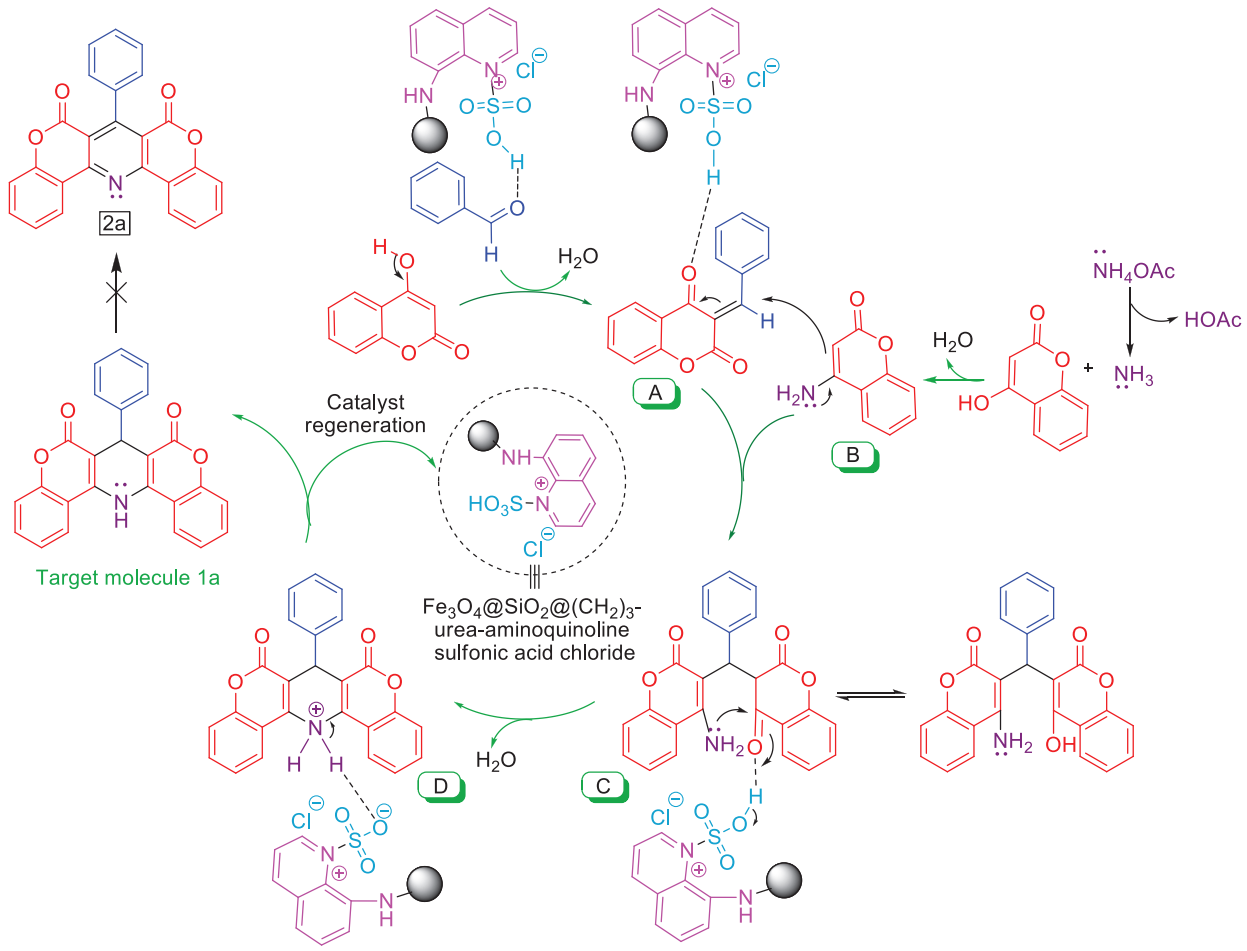
 **1a** 20 min., 87% MP (°C)= 218-220 Rep. [208-210][21a]	 **1b** 20 min., 90% MP (°C)= 268-270 Rep. [274-276][21a]	 **1c** 25 min., 85% MP (°C)= 210-212 Rep. [215-217][21b]	 **1d** 25 min., 86% MP (°C)= 218-220 Rep. [221-223][21a]	 **1e** 25 min., 87% MP (°C)= 246-248 Rep. [257-259][21c]
 **1f** 20 min., 82% MP (°C)= 194-197 Rep. [172-174][21b]	 **1g** 25 min., 80% MP (°C)= 180-182 Rep. [176-178][21d]	 **1h** 25 min., 82% MP (°C)= 200-202 Rep. [190-191][21d]	 **1i** 20 min., 85% MP (°C)= 256-258 Rep. [257-259][21a]	
 **1j** 20 min., 87% MP (°C)= 230-232 Rep. [234-235][21c]	 **1k** 25 min., 86% MP (°C)= 264-266 Rep. [287-289][21e]	 **1l** 25 min., 82% MP (°C)= 209-211 New	 **1m** 15 min., 85% MP (°C)= 219-221 Rep. [217-219][21a]	
 **1n** 15 min., 85% MP (°C)= 235-238 Rep. [240-242][21a]	 **1o** 30 min., 80% MP (°C)= 298-300 Rep. [>290][21c]	 **1p** 30 min., 81% MP (°C)= 253-255 Rep. [282-285][21c]	 **1q** 30 min., 84% MP (°C)= 181-183 Rep. [184-186][21d]	

[a]Reaction conditions: Arylaldehyde (0.5 mmol), 4-hydroxycoumarine (1 mmol, 0.162 g) and ammonium acetate (2 mmol, 0.154 g), catalyst: 10 mg, Isolated yields.

alyst at the optimized reaction conditions. The obtained results were illustrated in Table 3. All desired molecules were furnished in short reaction times with high to excellent yields.

3–3. Recycling of $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride

In order to examine the green and economic aspects of $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride, we also explored reusability of prepared catalyst in the synthesis of molecule **1i** using condensation of 4-methyl benzaldehyde, 4-hydroxycoumarine, and ammonium acetate under optimal conditions for 20 min. After completion of each run, hot EtOH was added to the reaction mixture. The desired product and unreacted starting materials dissolve in hot EtOH, but the nanomagnetic catalyst is not soluble, thus it can be separated from the reaction mixture using an external magnet. Then, the recovered catalyst washed well with ethanol, dried and then applied for next runs. As illustrated in Fig. 8, the reusing test of $Fe_3O_4@SiO_2@(CH_2)_3$-urea-



Scheme 5. A reasonable mechanistic pathway for the synthesis of molecule **1a**.

quinoline sulfonic acid chloride was successful over five continuous runs with only a marginal decreasing of its catalytic activity.

Also, we suggested a plausible mechanistic pathway for the synthesis of target molecule **1a** in the presence of $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride (Scheme 5). At first, benzaldehyde is activated with nanomagnetic catalyst and attacked by one molecule of 4-hydroxycoumarin to obtained intermediate **A** and releasing one molecule of H_2O. Second molecule of 4-hydroxycoumarin reacted with ammonium acetate as a nitrogen source to yield β-aminobenzopyran-2-one (**B**). The reaction is followed *via* a Michael-type additionof β-aminobenzopyran-2-one to intermediate **A**. Subsequently, cyclization followed by dehydration of intermediate **C**, yield the desired molecule **1a**. As above mentioned, in contrast of our prediction, "anomeric based oxidation" (ABO) did not occur in the course of reactions [35-36].

4. Conclusion

As a conclusion, a novel nanomagnetic catalyst with urea linkers was prepared and fully characterized using various techniques. The applied catalyst has both acidic and H-bond donor-acceptor sites so that it can use as a dual role catalytic system. Afterward, $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride as an efficient and recoverable catalyst was used for the preparation of coumarine containing DHPs moieties under solvent-free conditions. Simple and mild procedure, high to excellent yields of products, short reaction times, disuse of solvent, lower temperature rather than previous works, easy work-up using water and facile separation and recyclability of catalyst are the most attractive features of presented protocol.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129294.

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