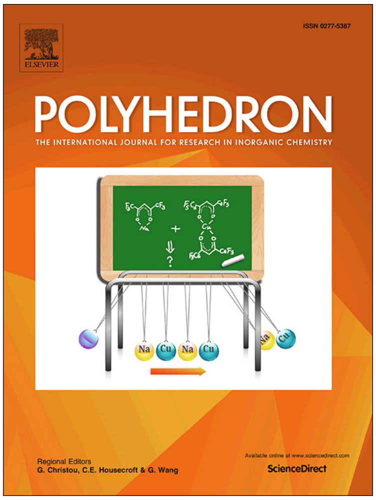

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SO_3H-Dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H): synthesis, characterization and its application as a novel and heterogeneous catalyst for the one-pot synthesis of polyfunctionalized pyrans and polyhydroquinolines

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Abstract: In this research, the novel SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) were prepared and characterized by using FT-IR, X-ray diffraction patterns, scanning electron microscopy, transmission electron microscopy, thermogravimetry analysis, and energy-dispersive X-ray spectroscopy. The synthesized nanosized catalyst was successfully applied to the synthesis of highly substituted pyrans and polyhydroquinolines via a straightforward one-pot multicomponent condensation reaction. The key advantages are the short reaction time, high yields, simple workup, and purification of products by non-chromatographic methods, by simple recrystallization from ethanol.

Keywords: SO_3H-Dendrimer functionalized magnetic nanoparticles, Dendrimer, Pyrans, Polyhydroquinolines.

1. Introduction

Dendrimers, a unique class of polymers, are highly branched macromolecules, in which their size and shape can be precisely controlled. The well-defined structure, a monodisperse size distribution, surface functionalization capability, and stability are properties of dendrimers that make them attractive drug carrier candidates.[1] Dendrimers have been also utilized for several applications[2] including homogeneous catalysis.[3] Interestingly, in many cases, the soluble dendritic catalysts were found to be more efficient or selective than the traditional analogues of metal complexes. In recent years, dendrimers immobilized on silica or polymers have been investigated intensively and applied to several catalytic organic transformations.[4]

These new catalytic materials are sometimes highly efficient in terms of reactivity and selectivity and are easily recyclable.

Heterogeneous catalysis is noteworthy for both academic and industrial synthesis due to its advantages over homogeneous catalysis.[5-6] It is clear that green chemistry not only requires the use of environmentally benign reagents and solvents but also it is very crucial to recover and reuse the catalysts. One method to prove this target, is the immobilization of a catalytic homogeneous tag on a nanomagnetic hybrid solid material, to convert it to a heterogeneous catalyst with homogeneous action in chemical-based processes. In thes.e types of solids, the reactive centers are highly mobile similar to homogeneous catalysts and at the same time these species have the advantage of being recyclable in the same fashion as heterogeneous catalysts. In view of this issue, several types of solid sulfonic acid have been synthesized and applied as an alternative to traditional sulfonic acid resins and homogeneous acids in catalyzing chemical transformations.[7] Application of solid acids in organic transformation has an important role because of their wide range of advantages, such as, simplicity in handling, decreased reactor and plant corrosion problems, easy separation from products without the necessity of washing, and more environmentally safe disposal.

Among the four types of magnetic nanoparticles (MNPs), including metals, alloys, metal oxides, and ferrites, iron oxides are by far the most widely used supports of magnetically recoverable catalysts. This is due to their low cost, easy preparation, biocompatibility properties [SPIONs (superparamagnetic iron oxide nanoparticles) are also much used for biomedical applications], stability, and ease of their surfaces functionalizing with other metal particle fragments (Au, Pd, Pt, Cu, Ni, Ir), inorganic and organometallic catalysts, organocatalysts, and enzymes.[8]

Compounds bearing a pyran framework are significant intermediates in organic synthesis and display several physiological properties and pharmacological activities, for example antibacterial,[9] antitumor,[10] anti-inflammatory,[11] anti-HIV, analgesic and myorelaxant[12] activities. In recent years, syntheses of these type of molecules have been studied, with reagents such as, nano-structured diphosphate ($Na_2CaP_2O_7$),[13] silica-coated magnetic $NiFe_2O_4$ nanoparticle-supported Preyssler heteropolyacid (H_{14} [$NaP_5W_{30}O_{110}$]),[14] silica-coated magnetic $NiFe_2O_4$ nanoparticles-supported $H_3PW_{12}O_{40}$,[15] nano α-Al_2O_3 supported ammonium dihydrogen phosphate (NH_4 H_2PO_4/Al_2O_3),[16] nano ZnO,[17] Fe_3O_4@D-NH_2-HPA,[18] sodium selenite,[19] and 1-butyl-3-methyl imidazolium hydroxide ([bmim]OH),[20] and ammonium acetate.[21] Fe_3O_4@PEO-SO_3H,[22] $CuFe_2O_4$/chitosan,[23] L-proline,[24] diacetoxyiodobenzene, [25] nano MgO,[26] and SO_3H–functionalized nano-MGO-D-NH_2.[27]

There is a continuing well-known importance in the synthesis of polyhydroquinolines due to the diverse biological properties associated with this system. Current studies reveal that polyhydroquinolines exhibit several medicinal applications which include neuroprotectant,[28] platelet antiaggregatory activity,[29] cerebral antischemic activity in treatment of alzheimer's diasease,[30] and chemo sensitizer acting in tumor therapy.[31] Polyhydroquinolines derivatives are commonly synthesized by one-pot four-component reaction of aldehyde, cyclic 1,3-dicarbonyl compounds, ethyl acetoacetate and ammonium acetate using numerous catalysts such as poly(AMPS-co-AA),[32] $SbCl_3$-SiO_2,[33] 1,3-Di (bromo or chloro)-5,5-dimethylhydantoin,[34] silica sulfuric acid,[35] $K_7[PW_{11}CoO_{40}]$,[36] sulfamic acid,[37] tetraethylammonium 2-(carbamoyl)benzoate.[38] γ-Fe_2O_3/Cu@cellulose,[39] Fe_3O_4/SiO_2-OSO_3H,[40] Fe_3O_4@PEO-SO_3H,[41] Fe_3O_4@SiO_2@PPh_3@[CrO_3Br],[42] SBA15@AMPD-Co,[43] Fe_3O_4@SiO_2@PPh_3@$Cr_2O_7^{2-}$,[44] cerium (IV) sulfate tetrahydrate,[45], and melamine trisulfonic acid.[46]

In this work, we have reported the synthesis and characterization of SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) as a novel and heterogeneous catalyst for the one-pot synthesis of highly substituted pyrans and polyhydroquinolines.

2. Experimental section

2.1. Preparation of dendrimer PAMAM

A solution of 1 g diethylenetriamine in 5 ml of dried methanol was added dropwise to a solution of 10 g methyl acrylate in 25 ml of dried methanol. The resulting reaction's mixture was stirred for 5 days at 25 °C under inert atmosphere. After evaporation of all volatiles in oil-pump vacuum, the first generation with 5-OCH_3 terminated groups (G0.5) was obtained. To this, 20 mL of dried methanol and 40 mL of ethylenediamine (0.5 mol) was added in one portion and kept for stirring under inert atmosphere for 5 days at 25 °C. The unreacted ethylenediamine and excess of methanol were removed under liquid N_2 in vacuum. The first generation dendrimer bearing 5-NH_2 end-grafted groups (G1) was obtained, which was purified till all the traces of organic volatiles were completely removed. To grow the obtained dendrimer to the next generation, 6.74 g (0.01 mol) of the first generation dendrimer and 30 mL (0.36 mol) of methyl acrylate was added in a single portion and again kept for stirring for 7 days at 25 °C. A thick yellowish liquid of the 10-arm-OCH_3 terminated dendrimer (G1.5) was obtained, which was again purified under liquid N_2 in vacuum to remove excess of methyl acrylate and methanol. To this thick yellow liquid, 60 mL ethylenediamine (in excess) was added and kept for stirring for 10 days under inert atmosphere at 25 °C. The reaction solution was then purified and thus, the desired second generation dendrimer with 10-NH_2 terminal groups (G2) (Scheme 2) was obtained as pale yellow oily substance.

2.2. Preparation of nano- Fe_3O_4

Nano-Fe_3O_4 was prepared according to the reported procedure in the literature.[47] For this reason, $FeCl_3.6H_2O$ (2 mol) and $FeCl_2.4H_2O$ (1 mol) were dissolved in 20 mL of deionized water. Under vigorous magnetic stirring (600 rpm), gradually the pH was raising by addition (dropwise for 2 minute) of 25% NH_3 solution (5 ml) to around 10 and the mixed solution was stirred at room temperature for 60 min. The resultant magnetite nanoparticles were collected by an external magnetic field and washed several times with ethanol (10 ml) and deionized water (10 ml). Then, the product was dried under vacuum at 50 °C for 6 h.

2.3. Preparation of dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH_2)

The initially prepared Fe_3O_4 nanoparticles (2.5 g) were ultrasonically dispersed into 50 mL deionized water at 20-50 °C for 20 min. Dendrimer PAMAM (7 mL) dissolved in 10 mL of deionized water was added to this solution and again sonicated at 80 °C for 5 h. The resulting Fe_3O_4@D-NH_2 nanoparticles were isolated by an external magnetic field, washed with deionized water (10 mL) and methanol (10 mL), and dried under vacuum at 50 °C for 6h.

2.4. Preparation of SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H)

2.5 g of Fe_3O_4@D-NH_2 nanoparticles were ultrasonically dispersed into 50 mL toluene at 20-50°C for 30 min. Then, 2.5 mL of 1,4-butane sultone was added dropwise to the mixture and again sonicated at 80 °C for 5 h. The resulting Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H nanoparticles were isolated by an external magnetic field, washed with deionized water (20 mL) and methanol (20 mL), and dried under vacuum at 50 °C for 6h.

2.5. One-pot synthesis of tetrahydrobenzo[b]pyrans and 2-amino-3-cyano-4H-pyrans

Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.05 g) was added to a mixture of the aldehydes **1** (1 mmol), malononitrile **2** (0.08 g, 1.2 mmol), and 1,3-cyclohexandione **3** or ethyl acetoacetate **5** (1 mmol), and 5 ml of ethanol in a 20 ml round bottom flask fitted with a reflux condenser. The resulting mixture was heated to reflux (an oil bath) for the appropriate time (*see Table 2*) with stirring (spin bar). After the completion of the reaction (monitoring by TLC; hexane-ethyl acetate, 4:1), the nanomagnetic catalyst was separated from the reaction mixture by use of an external magnetic field. The resulting crude product was poured onto crushed ice, and the solid product which separated was isolated by filtration and recrystallized from ethanol (5 ml) to afford tetrahydrobenzo[b]pyrans (**4a-o**), and 2-amino-3-cyano-4H-pyrans (**6a-e**).

2.6. One-pot synthesis of polyhydroquinolines

A mixture of aldehydes (**1b**, 1mmol), 1,3-cyclohexandione (**2**, 1 mmol), ethyl acetoacetate (**3**, 1 mmol), ammonium acetate (4 mmol) and Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.05 g), was heated on an oil bath at 120 °C for the appropriate time (*see Table 2*) with stirring (spin bar). Completion of the reaction was indicated by TLC (hexane:ethyl acetate, 2:1), after completion, appropriate amount of EtOH (96%) was added and the mixture stirred for 2 min. The catalyst was then separated by use of an external magnetic field. The filtrate was poured onto crushed ice and the solid product, which separated was filtered and recrystallized from ethanol to afford pure polyhydroquinolines (**7a-c**).

3. Results and discussion

In continuation of our previous researches on the design and application of heterogeneous and reusable solid catalysts in organic synthesis and multi-component reactions,[48] here we report an efficient, eco-friendly, safe, green, and practical method for the synthesis of polyfunctionalized pyrans (tetrahydrobenzo[b]pyrans, 2-amino-3-cyano-4H-pyrans) and polyhydroquinolines using SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) as a catalyst (*Scheme 1*).

Scheme 1

In this work, the novel SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) have been designed for the first time. We used this heterogeneous catalyst as a highly efficient and novel catalyst for the one-pot synthesis of polyfunctionalized pyrans and polyhydroquinolines. The synthesis of the second-generation dendrimer used in the present work was reported in previous works.[49] Michael addition method was used as a starting point from a multifunctional core (diethylenetriamine) with branching monomers. The procedure is based on the consecutive condensation of ethylenediamine with methyl acrylate to give the corresponding dendrimer (Scheme 2).

Scheme 2

Then, nano magnetic Fe_3O_4 was prepared using a co-precipitation technique.[33] In order to prepare the dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH_2), the synthesized dendrimer was mixed with nano magnetic Fe_3O_4 to give the corresponding Fe_3O_4@D-NH_2 (Scheme 3). Finally, the reaction of Fe_3O_4@D-NH_2 with 1,4-butane sultone produced SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) (*Scheme 4*).

Scheme 3

Scheme 4

In order to confirm the SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H), we employed different characterization techniques such as X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), energy-dispersive X-ray spectroscopy (EDS), Scanning electron spectroscopy (SEM), elemental analytical and thermal gravimetric analysis (TGA).

Fig. 1 shows the XRD patterns of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) with peaks of their crystalline structure at 30.18°, 35.41 °, 43.18 °, 57.12 °, 62.74 ° 2θ which is very close to the standard patterns of the crystalline magnetite and the diffraction peaks could be well indexed with the inverse spinel cubic Fe_3O_4 structure by the ICDD (Reference code: 00-019-0629) as well as present that the functionalizing process does not affect the crystal structure of the Fe_3O_4 particles and there is no other phase, such as Fe_2O_3 or FeO.

Figure 1

Anchoring of dendrimer PAMAM on the surface of magnetic nanoparticles was examined by FT-IR spectroscopy (Fig. 2). FT-IR spectral analysis of Fe_3O_4@D-NH_2 (Fig. 2b) shows a broad band at 3425 cm^{-1} due to N-H stretching. Absorptions at 2923 cm^{-1} is due to the alkyl chain stretching. There is also a strong vibration at 1634 cm^{-1}. The presence of vibration bands of the dendrimer along with a noticeable change in the intensities of the peaks at different wave numbers indicates effective stabilization of the Fe_3O_4 nanoparticles. A strong absorption band at 580 cm^{-1} is due to the Fe-O stretching vibration of the nanoparticles and the weak absorption at 3425 cm^{-1} can be assigned to the O-H stretching indicating a small amount of water in the sample.

The existence of sulfonic acid group (SO_3H) in the samples was further confirmed by the presence of an intense and broad absorption band from 2400 to 3400 cm^{-1} which corresponds to S–OH stretching vibration, and the appearance of two important peaks at 1037 and 1169 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations of S═O, respectively (Figure 2c) Thus, the FT-IR spectra confirm the successful of ring opening of 1,4-butanesultone by NH_2 groups of Fe_3O_4@D-NH_2. We have characterized the recycled nanocatalyst by FT-IR spectroscopy which showed suitable retention of its structure and morphology and there was no considerable deformation or leaching after five times reusing.

Figure 2

TGA study of the Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) and Fe_3O_4 was performed from room temperature to 700 °C in the N_2 atmosphere at heating rate of 10 °C/min. For Fe_3O_4 a continuous weight loss was observed from the first to final temperature and TGA curve for Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) indicates organic degradation of the catalyst at 200°C and the complete decomposition continues up to 700°C. The thermal decomposition of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) shifts towards higher temperatures in comparison with Fe_3O_4 which shows adsorption of polymer chain on the surface of magnetite, in the other words high level of dendrimer PAMAM had been immobilized on the Fe_3O_4 (Fig. 3).

Figure 3

The SEM image of the synthesized Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H nanoparticle is shown in Figure 4, which indicates well-dispersed spherical particles.

Figure 4

Further characterization of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H was performed by transmission electron microscopy (TEM) image. The TEM image of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H showed well-defined spherical Fe_3O_4 nanoparticles dispersed in a dendrimer matrix (Figure 5). Also, the TEM image was used to confirm the core/shell morphology in the nanostructure including Fe_3O_4 as dark core and dendrimer light shell.

Figure 5

The EDX results for Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H, shown in Figure 6, clearly showed the presence of Fe, C, N, O and S in Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H.

Figure 6

To verify the immobilization of modified Fe_3O_4, CHNS elemental analysis of the catalyst (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) was conducted. The result confirms (C, 8.32%; H, 1.64%, N, 2.30%; S, 2.46%) that a large amount of organic groups was loaded onto the Fe_3O_4.

After complete characterization of SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H), we investigated the application of this catalyst for synthesis of polyfunctionalized pyrans (tetrahydrobenzo[b]pyrans, 2-amino-3-cyano-4H-pyrans) and polyhydroquinolines. For initiating optimization of the reaction conditions, we carried out one-pot three-component condensation of malononitrile, benzaldehyde and 1,3-cyclohexanedione in the presence of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H. The results are listed in Table 1. It was observed that 0.05 g of catalyst was enough to catalyze the reaction to produce high yields of 2–amino–3–cyano–4-(phenyl)-5–oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (**4a**). As can be seen in Table 1, the results showed that the efficiency and the yield of the reaction in EtOH was higher than those obtained in other solvents, such as H_2O, MeOH, and CH_3CN, or under solvent-free conditions. Increasing the amounts of the catalyst did not improve the yield of the reaction (entry 7). As indicated in Table 1, to compare the efficiency of this new nanocatalyst, we carried out a model reaction in the presence of various catalysts. Fe_3O_4, Fe_3O_4@SiOD-NH_2 and D-NH_2 (entries 8, 9, 10) needed longer reaction times than Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H under reflux in EtOH. To illustrate the need of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H for these reactions, an experiment was conducted in the absence of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (entry 11). The yield in this case was trace after 20 min. Obviously, Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H is an important component of the reaction.

Table 1

After optimization, a variety of other aldehydes and 1,3-dicarbonyl compounds (1,3-cyclohexanedione and ethyl acetoacetate) were shown to undergo the reaction smoothly, giving the desired tetrahydrobenzo[b]pyrans and 2-amino-3-cyano-4H-pyrans in good to high yields. The results are summarized in Table 2. All products were fully characterized by spectroscopic methods (IR, ^{1}H and ^{13}C NMR, Mass and elemental analysis) and compared with authentic spectra (*see supporting information*).

In another assay, the applicability of the Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H catalyst was explored for the synthetic reaction of 2-amino-3-cyano-4H-pyran and polyhydroquinoline derivatives. Initially, to find the optimal reaction conditions for the synthesis, the reaction of benzaldehyde, malononitrile and ethyl acetoacetate was chosen as a model reaction. The resulting data demonstrate that the best conditions occur when the reaction was performed under reflux conditions in the presence of 0.5 g of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H catalyst. Afterwards, the versatility and the generality of the optimized reaction conditions were checked for the synthesis of various 2-amino-3-cyano-4H-pyrans and polyhydroquinolines (Table 2).

Table 2

With due attention to the importance of recovery of the used catalyst in green synthetic processes, we considered the recyclying capability of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H through synthesis reactions leading highly substituted pyrans and polyhydroquinolines production. When the reaction was complete, the catalyst was recovered nearly quantitatively from the reaction flask by an external magnet and was subsequently reused in several runs. The obtained Results displayed in Table 3 approve that the magnetically separable Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H could be reused and recycled for five runs without any remarkable loss of its initial catalytic activity.

Table 3

A proposed mechanism for this reaction is shown in Scheme 5. In first step, Knoevenagal condensation between aldehydes and malononitrile produced 2-benzylidenemalononitrile. Second, Michael addition of 2-benzylidenemalononitrile with 1,3-cyclohexanedione or ethyl acetoacetate accour, and finally followed cyclization and tautomerization afforded the corresponding products (tetrahydrobenzo[b]pyrans, 2-amino-3-cyano-4H-pyrans). Also, in a similar mechanism, the corresponding polyhydroquinolines can be produced. In this process, Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H with H^+ could play a remarkable role in increasing of reaction rate.

Scheme 5

In order to show the efficiency of our procedure, a comparison was done between the present work and others earlier reports for the one-pot synthesis of polyfunctionalized pyrans and polyhydroquinolines. The results summarized in Table 4 clearly demonstrate the superiority of the present work in catalyst amount, time of reaction, high yields of the products and the reusability of the nanocatalyst.

Table 4

4. Conclusion

In conclusion, we have developed an easy, convenient, inexpensive and friendly environmental synthetic approach for the preparation of polyfunctionalized pyrans (tetrahydrobenzo[b]pyrans, 2-amino-3-cyano-4H-pyrans) and polyhydroquinolines catalyzed by Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H. The method is associated with several advantages such as high yields, operational simplicity, non-toxic catalyst and solvents, utilization of a heterogeneous catalyst, short reaction time and minimum pollution of the environment, which makes it a useful and attractive process for the preparation of these compounds.

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Figure and scheme legends

Scheme 1 One-pot synthesis of polyfunctionalized pyrans and polyhydroquinolines

Scheme 2 Preparation of dendrimer PAMAM

Scheme 3 Preparation of dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH_2)

Scheme 4 Preparation of SO_3H-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H)

Scheme 5 Proposed mechanism for multicomponent synthesis of polyfunctionalized pyrans (tetrahydrobenzo[b]pyrans, 2-amino-3-cyano-4H-pyrans) and polyhydroquinolines

Figure 1 X-Ray diffraction pattern for the Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H)

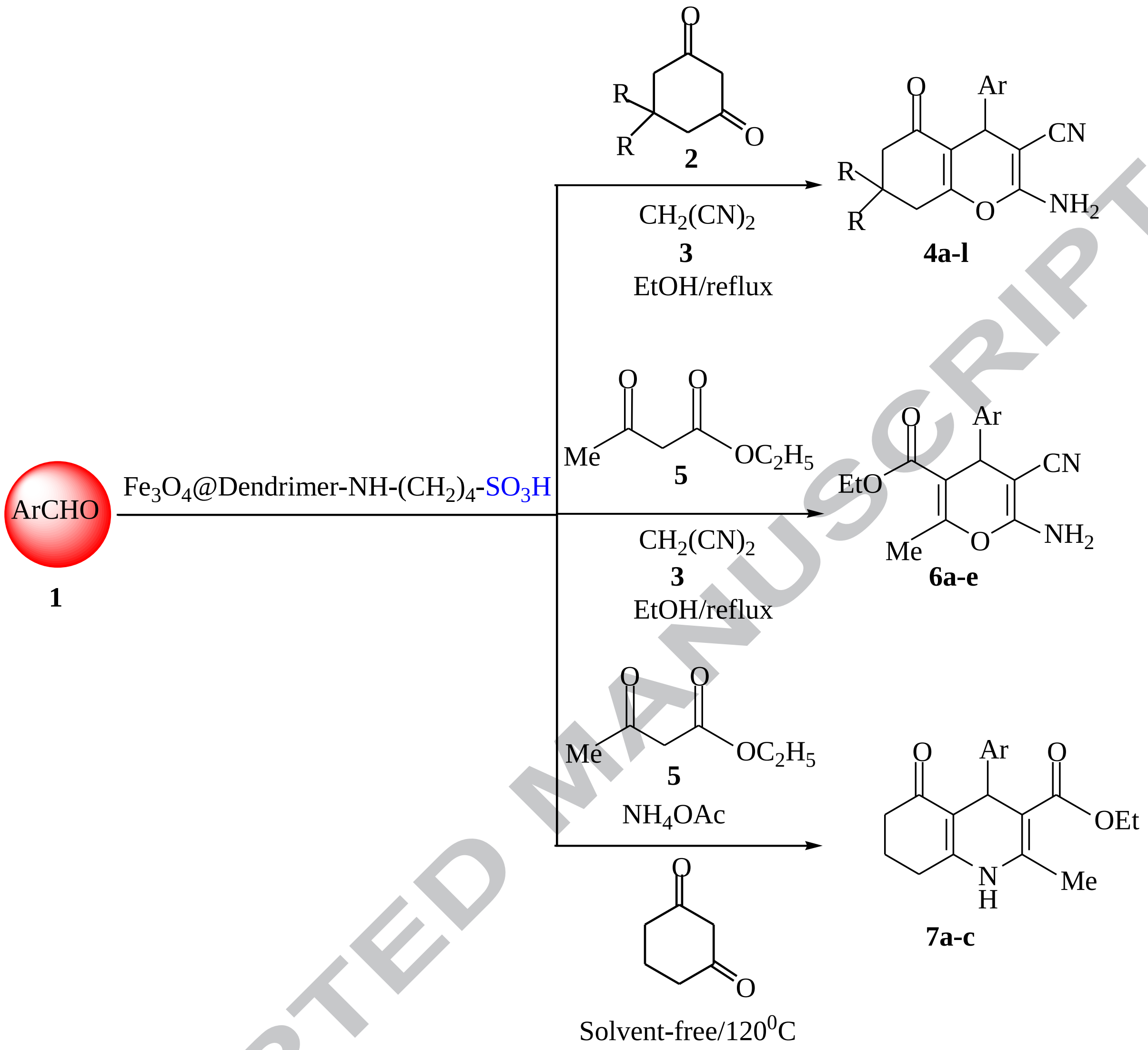
Figure 2 FT-IR spectra for (a) Fe_3O_4 (b) Fe_3O_4@D-NH_2 (c) Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H)

Figure 3 TGA of nano Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H vs Fe_3O_4

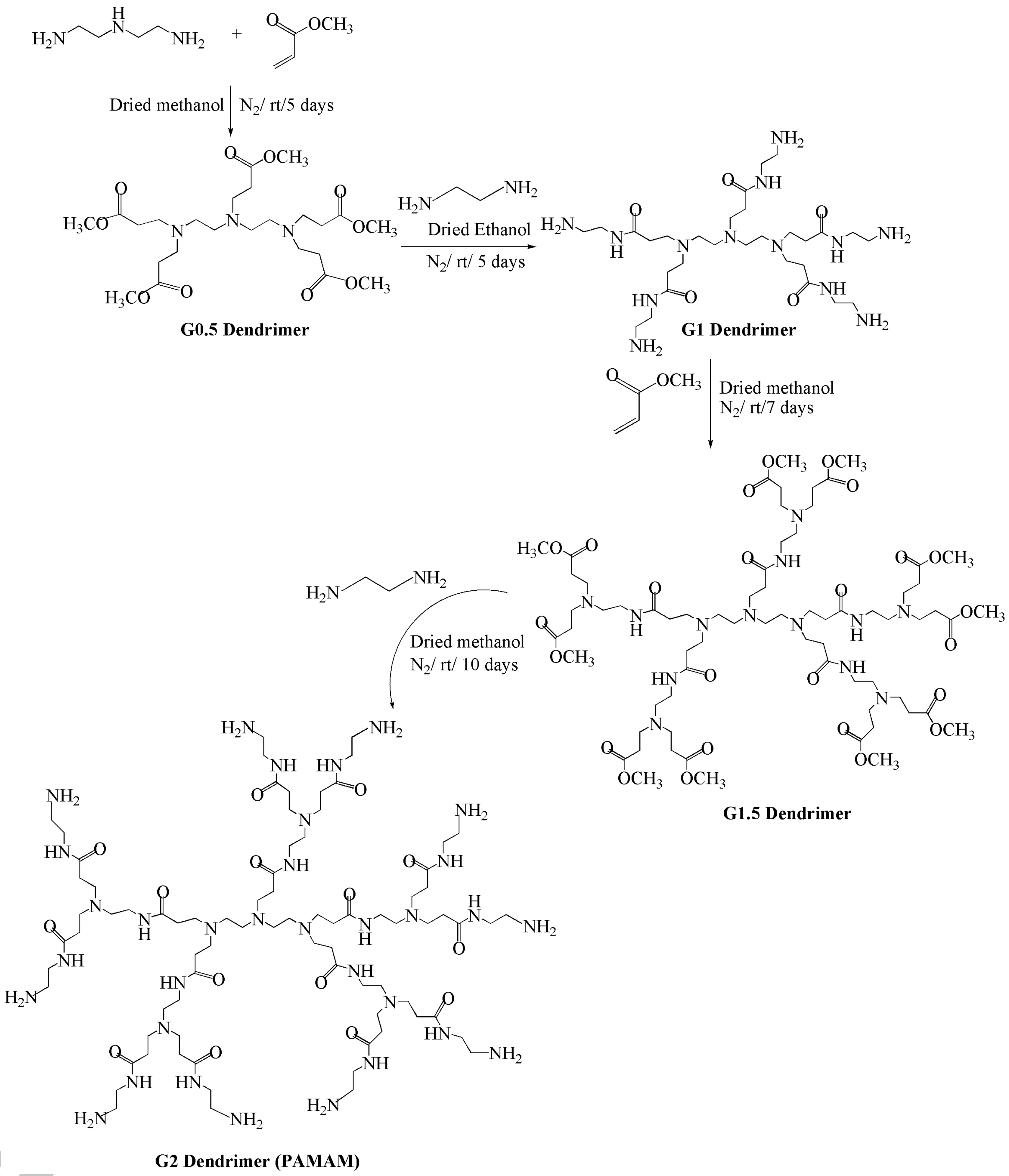
Figure 4 SEM image of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H nanoparticles.

Figure 5 TEM image of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H

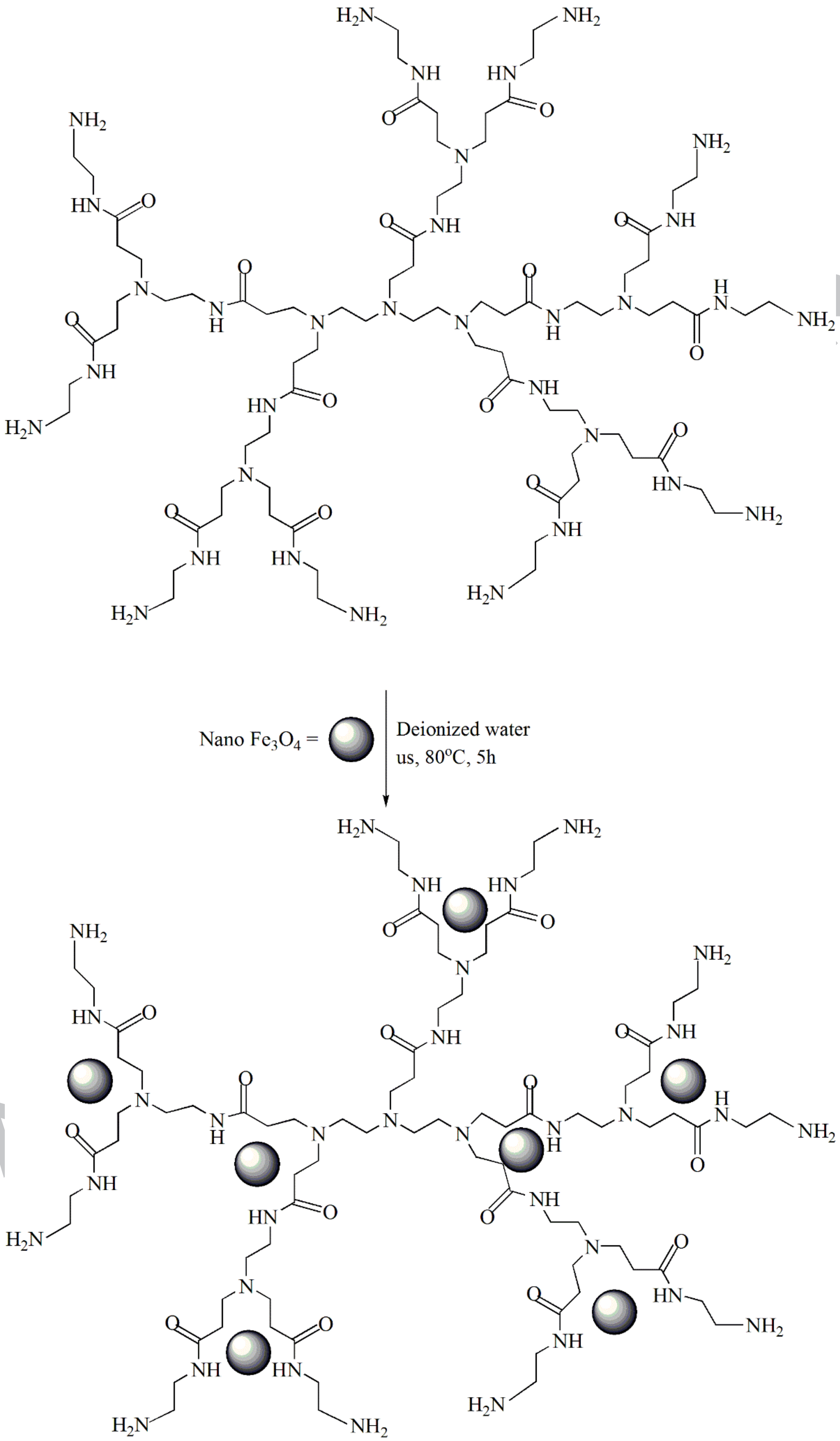
Figure 6 EDX image of nano Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H



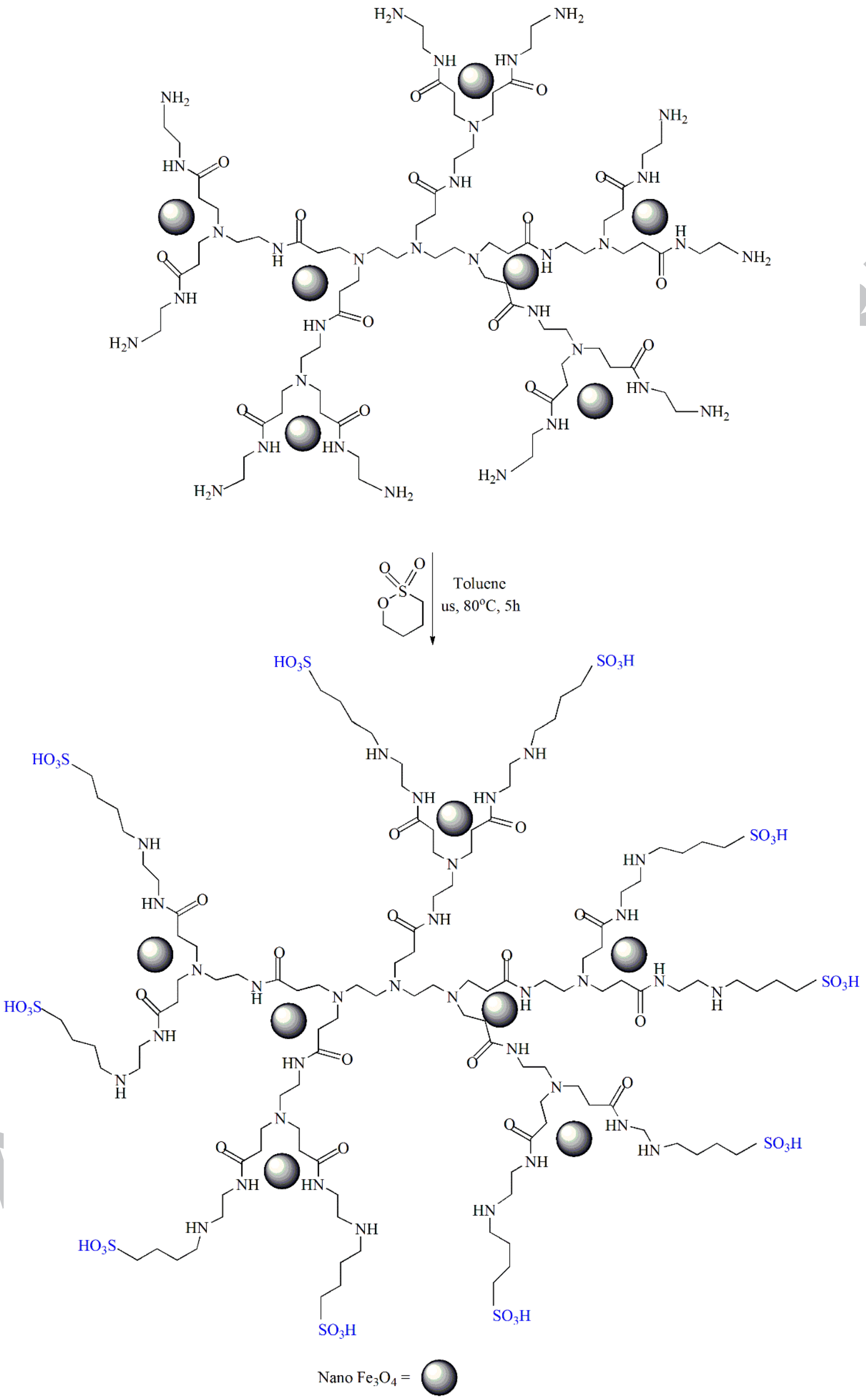
Scheme 1 One-pot synthesis of polyfunctionalized pyrans and polyhydroquinolines



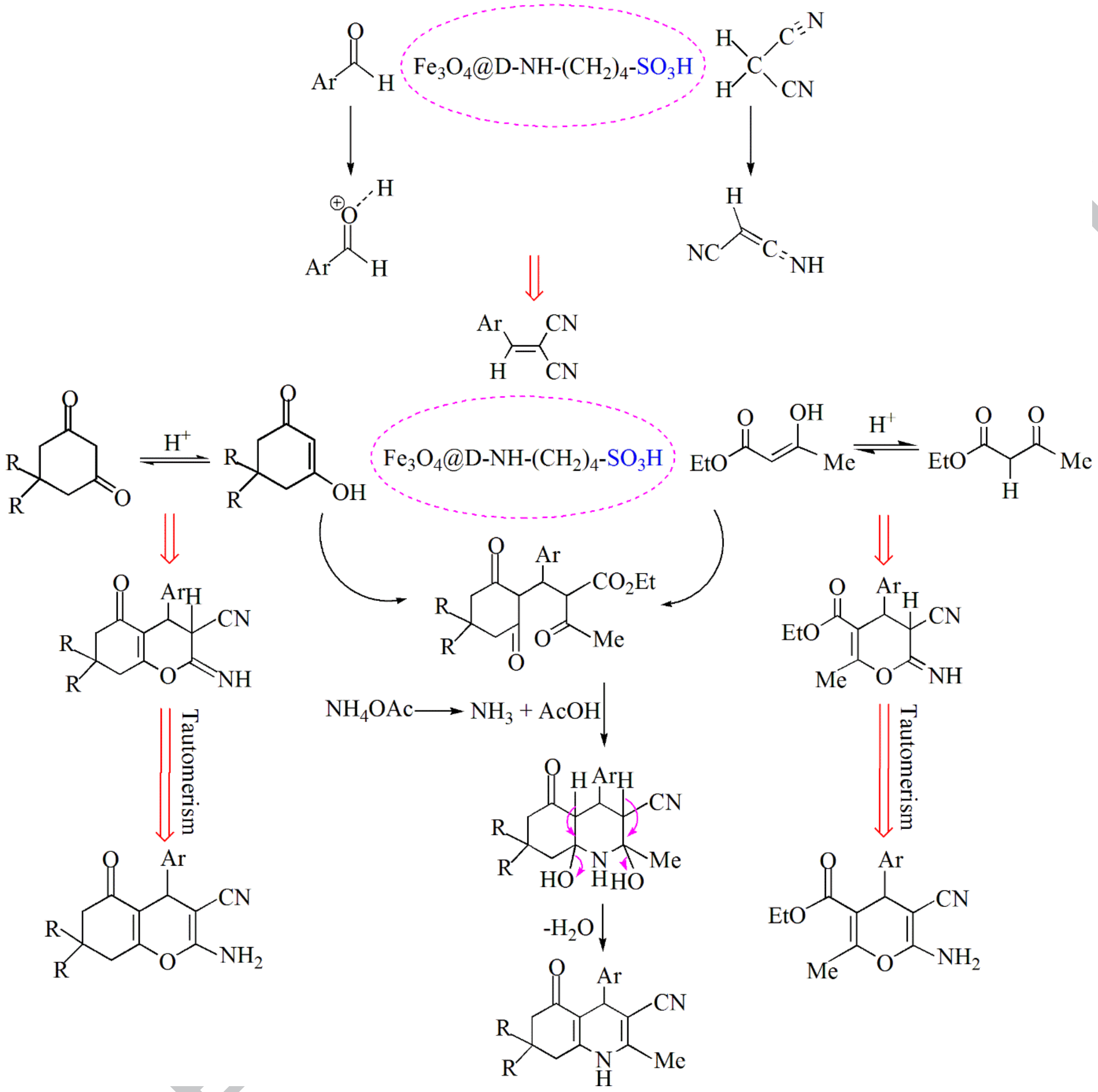
Scheme 2 Preparation of dendrimer PAMAM



Scheme 3 Preparation of dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH_2)



Scheme 4 Preparation of SO$_3$H-dendrimer functionalized magnetic nanoparticles (Fe$_3$O$_4$@D-NH-(CH$_2$)$_4$-SO$_3$H)



Scheme 5 Proposed mechanism for multicomponent synthesis of polyfunctionalized pyrans (tetrahydrobenzo[b]pyrans, 2-amino-3-cyano-4H-pyrans) and polyhydroquinolines

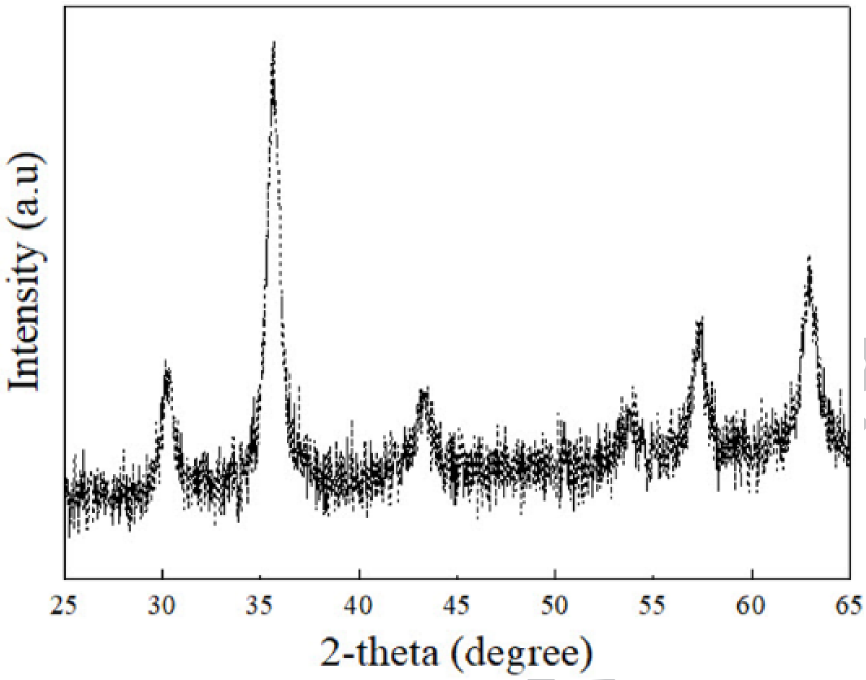


Figure 1 X-Ray diffraction pattern for the Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H)

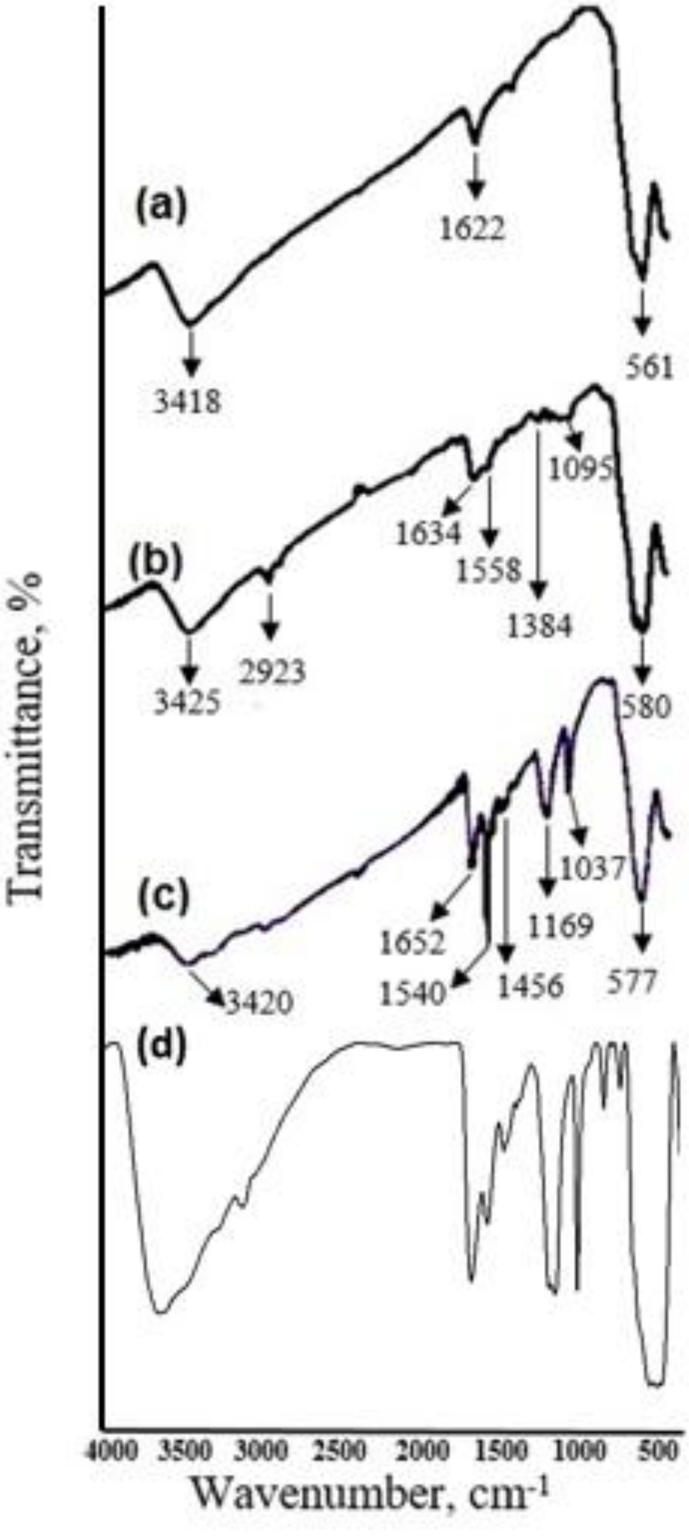


Figure 2 FT-IR spectra for (a) Fe_3O_4; (b) Fe_3O_4@D-NH_2; (c) Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H) and (d) recycled Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H)

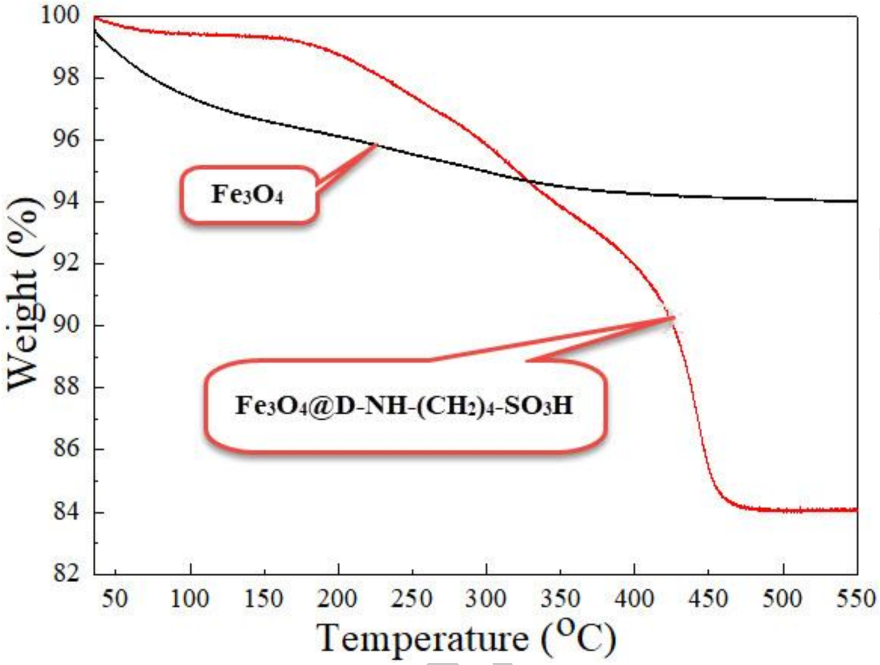


Figure 3 TGA of nano Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H vs Fe_3O_4

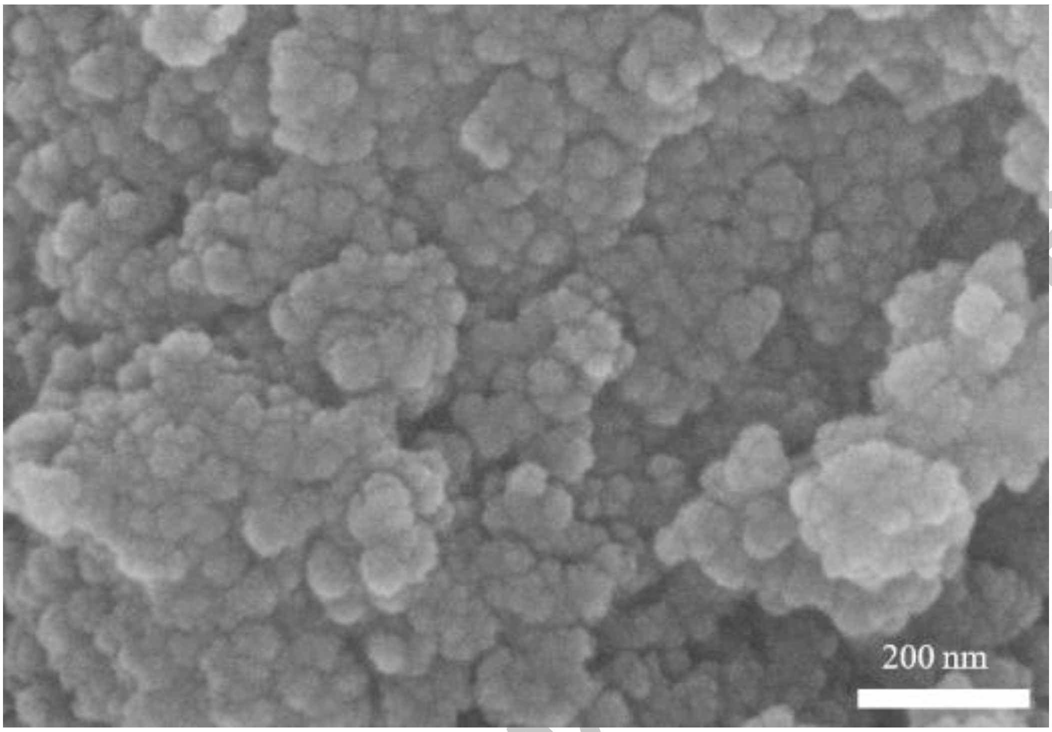


Figure 4 SEM image of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H nanoparticles.

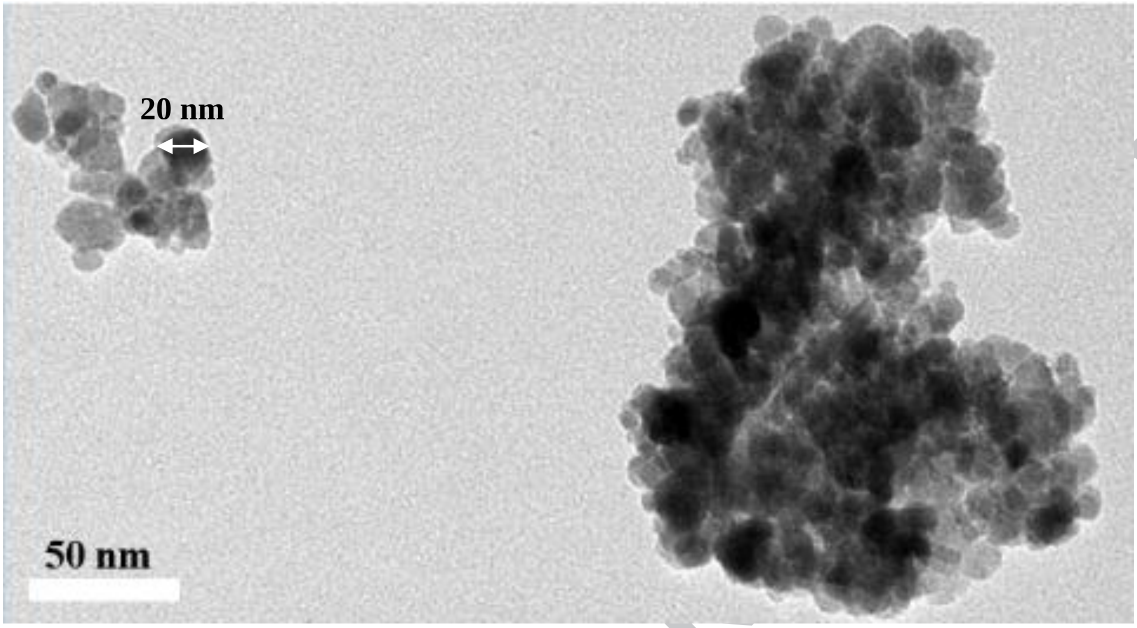


Figure 5 TEM image of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H

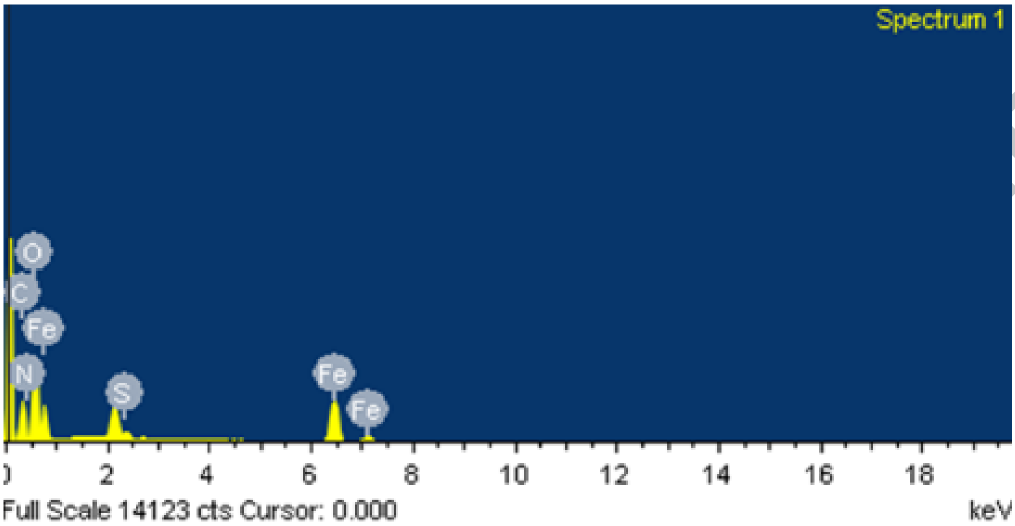


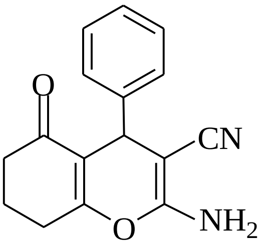
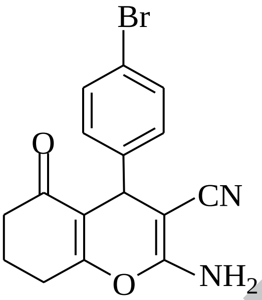
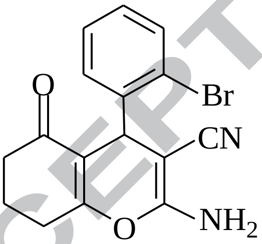
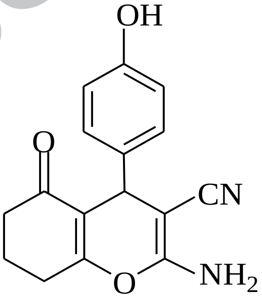
Figure 6 EDX image of nano Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H

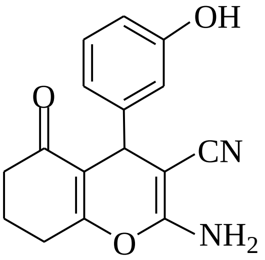
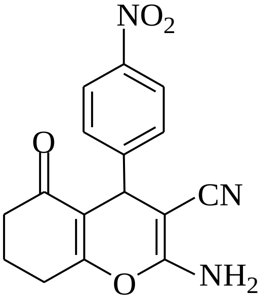
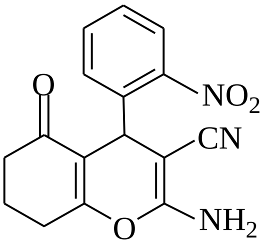
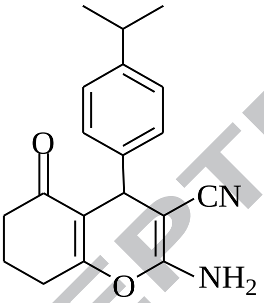
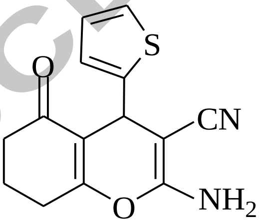
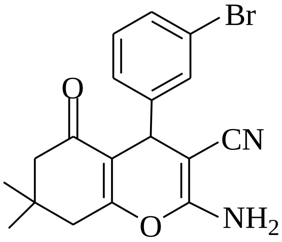
Table 1. Optimization of Reaction Conditions for **4a**

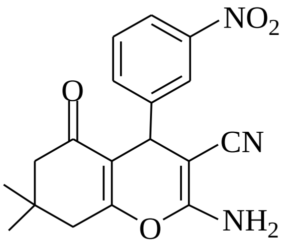
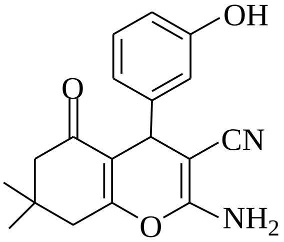
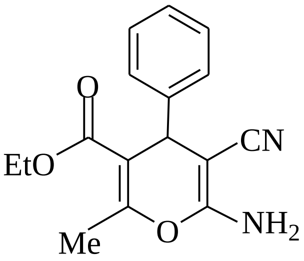
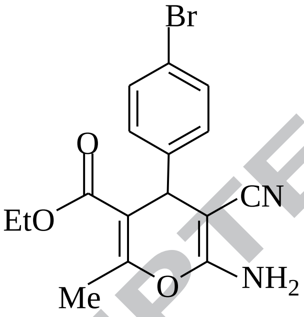
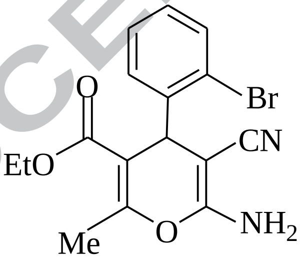
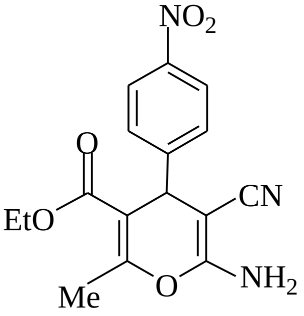
Entry	Catalyst (g)	Conditions	Time (min)	Yield[a] (%)
1	Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.05 g)	EtOH/reflux	20	84
2	Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.05 g)	H_2O/reflux	20	74
3	Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.05g)	MeOH/reflux	20	80
4	Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.05 g)	CH_3CN/reflux	20	62
5	Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.05 g)	Solvent-free/80^{0}C	20	63
6	Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.03 g)	EtOH/reflux	20	80
7	Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H (0.07 g)	EtOH/reflux	20	85
8	Fe_3O_4@D-NH_2 (0.05 g)	EtOH/reflux	60	42
9	Fe_3O_4 (0.05 g)	EtOH/reflux	60	32
10	D-NH_2 (0.05 g)	EtOH/reflux	60	36
11	--[b]	EtOH/reflux	20	trace

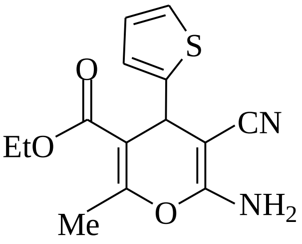
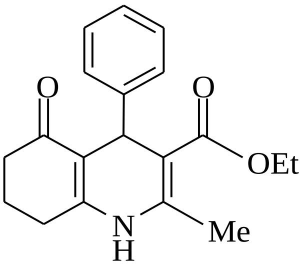
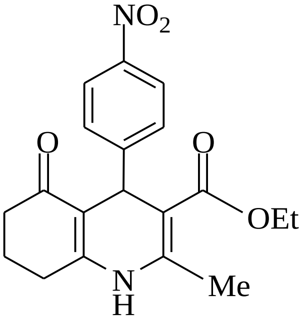
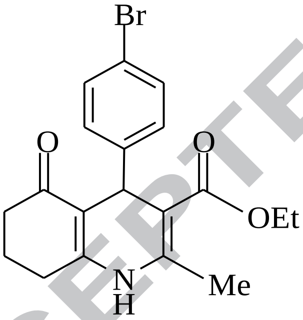
[a] Isolated yield. [b] This reaction was carried out in the absence of any catalyst.

Table 2. One-pot synthesis of polyfunctionalized pyrans (tetrahydrobenzo[b]pyrans, 2-amino-3-cyano-4H-pyrans) and polyhydroquinolines

Entry	Products	Time (min)	Yield^a (%)	Mp (^{0}C)	
				Found	Reported
4a		20	84	232-233	229-231[14]
4b		20	90	234-236	-----
4c		30	82	222-224	-----
4d		40	80	256-257	257-259[17]

4e		40	82	219-221	-----
4f		20	92	232-233	232-233[14]
4g		30	82	199-201	196-198[20]
4h		40	80	196-198	-----
4i		20	83	209-211	210-212[17]
4j		15	85	228-230	225-227[14]

4k		10	92	209-211	210-212[16]
4l		30	83	234-236	236-238[19]
6a		90	86	188-190	189-191[14]
6b		60	90	179-181	182-184[14]
6c		90	84	180-182	183-184[21oz]
6d		60	90	173-175	174-176[14]

6e		70	84	194-196	195-196[14]
7a		40	86	241-243	240-241[32]
7b		40	90	204-206	207-209[32]
7c		40	88	252-254	251-253[38]

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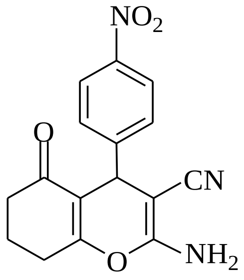
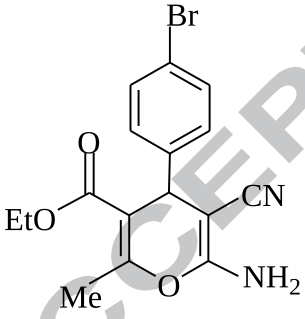
[a] Isolated yields.

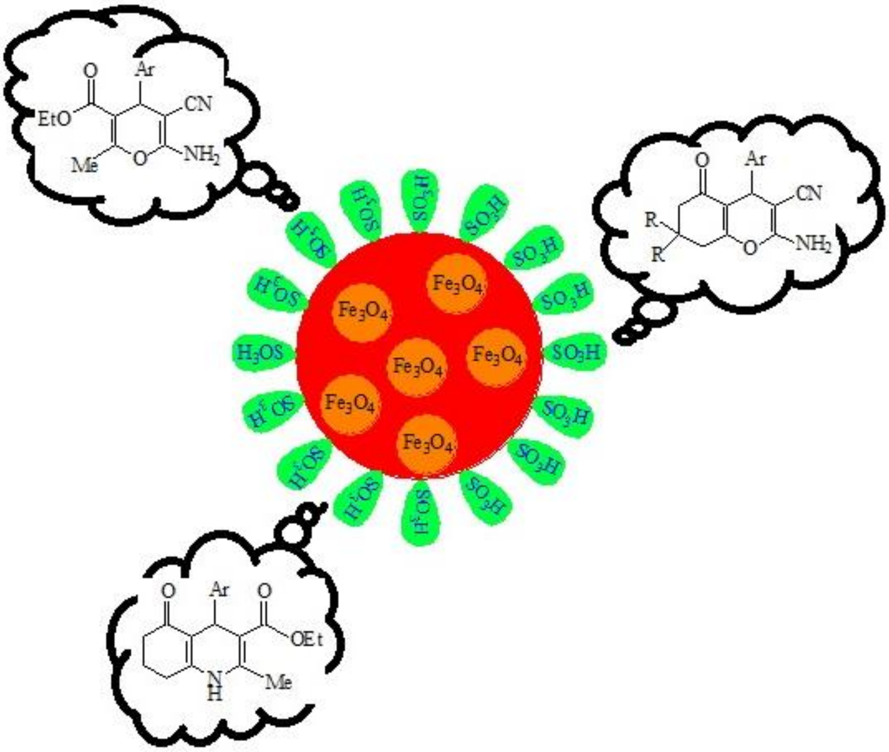
Table 3. Studies on the reuse of Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H for the synthesis of polyfunctionalized pyrans (tetrahydrobenzo[b]pyrans, 2-amino-3-cyano-4H-pyrans) and polyhydroquinolines

Entry	**Number of recycle**	**1**	**2**	**3**	**4**	**5**
4a	Yield (%)	84	80	80	78	74
	Time (min)	20	20	20	20	20
6b	Yield (%)	90	90	86	84	80
	Time (min)	60	60	60	60	60
7b	Yield (%)	90	86	82	82	82
	Time (min)	40	40	40	40	40

Table 4 Comparison of methods for the synthesis of polyfunctionalized pyrans

Compounds	**Conditions**	**Time (min)**	**Yield (%)**
 **4f**	**Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H/EtOH/reflux (present work)**	20	92
	$NiFe_2O_4$-$H_3PW_{12}O_{40}$/ EtOH/reflux[15]	20	90
	$NH_4H_2PO_4$/Al_2O_3/solvent-free/100 °C [16]	15	90
 **6b**	**Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H/EtOH/reflux (present work)**	60	90
	Fe_3O_4@D-NH_2-HPA/EtOH/reflux[18]	20	86
	$CuFe_2O_4$/chitosan/EtOH/rt[23]	60	93
	Nano MgO/H_2O/80 °C[26]	70	96

Graphical Abstract:



- The synthesis of magnetic acidic catalyst based on dendrimer for the first time.
- The catalyst can be simply recovered by magnetic separation.
- It catalyzed efficiently one-pot synthesis of polyfunctionalized pyrans and polyhydroquinolines.
- The new polyfunctionalized pyrans were synthesized.