SO$_3$H-Functionalized Epoxy-Immobilized Fe$_3$O$_4$ Core−Shell Magnetic Nanoparticles as an Efficient, Reusable, and Eco-Friendly Catalyst for the Sustainable and Green Synthesis of Pyran and Pyrrolidinone Derivatives

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ABSTRACT: A SO$_3$H-functionalized epoxy-immobilized Fe$_3$O$_4$ core−shell magnetic nanocatalyst was prepared through a simple three-step procedure, and it was identified by various analyses such as Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), differential thermal gravity (DTG), Brunauer−Emmett−Teller (BET) analysis, transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), vibration sample magnetometry (VSM), and powder X-ray diffraction (PXRD). BET analysis showed that the as-prepared nanocatalyst was synthesized with a mesoporous structure and high specific area (35.45 m^2 g^{-1}). The TEM image clearly showed that the particle size distribution was in the range of 47−65 nm. The designed magnetic nanocatalyst was used successfully in the synthesis of pyran derivatives via the reaction of dimedone, malononitrile, and various aromatic aldehydes and synthesis of pyrrolidinone derivatives via the reaction of various aromatic aldehydes, aniline, and diethyl acetylenedicarboxylate. The nanocatalyst was simply isolated from the reaction mixture utilizing an external magnet and reused several times according to the model reactions without significant loss in its efficiency.
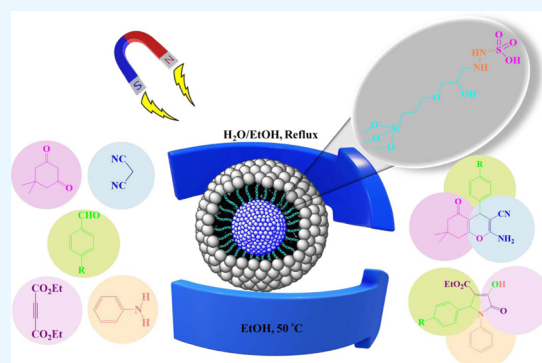
1. INTRODUCTION

The most widely used magnetic nanoparticles (MNPs) are core−shell magnetite (Fe$_3$O$_4$) nanocomposites, which have been used for a variety of applications, including microwave absorption, information storage, medical diagnosis, catalysis, and color imaging.[1,2] Recently, due to their high stability, low toxicity, and high surface area, magnetic nanoparticles, as a notable type of reusable material, have drawn considerable attention among researchers in materials science for the preparation of organic compounds.[3,4] The high sensitivity of magnetic nanoparticles to accumulation and oxidation is due to their high surface-to-volume ratio and high chemical reactivity, which can be overcome by covering the surface of these nanoparticles with all kind of supports.[5] In recent years, effective catalytic processes, as modified magnetic nanoparticles have been applied in several chemical advances.[6,7] Due to the great importance of magnetic catalysts used in the synthesis of valuable materials and organic conversions, simple recovery of catalysts and reusability in several runs with a slight reduction of their magnetic nature are two prominent features in catalytic systems.[8,9] Homogeneous Lewis and Brønsted acids are strongly favored by chemists due to their wide and varied catalytic applications in industrial and chemical processes.[10] Many

organic processes have been catalyzed through some homogeneous acid catalysts such as sulfonic acid comprising materials, metal complexes, biocatalysts, metal ions, hydrogen halides, and organic metal complexes.[11,12] However, most of these methodologies have some drawbacks such as recovery and separation problems, low thermal stability, harsh reaction conditions, and agglomeration during the reaction process. Accordingly, the major challenge of green chemistry processes is the replacement of expensive, hazardous, and polluting acidic catalysts with recyclable, environmentally friendly, and highly stable heterogeneous catalysts. Owing to the increase in the surface area of nanoparticles, they have become one of the most marvelous and significant support for acid catalysts.[13,14]

Sulfonic acid has been proven to be one of the strongest and most popular acids that have been grafted to Fe$_3$O$_4$ nanoparticles and widely applied in various organic conversions.[15,16]
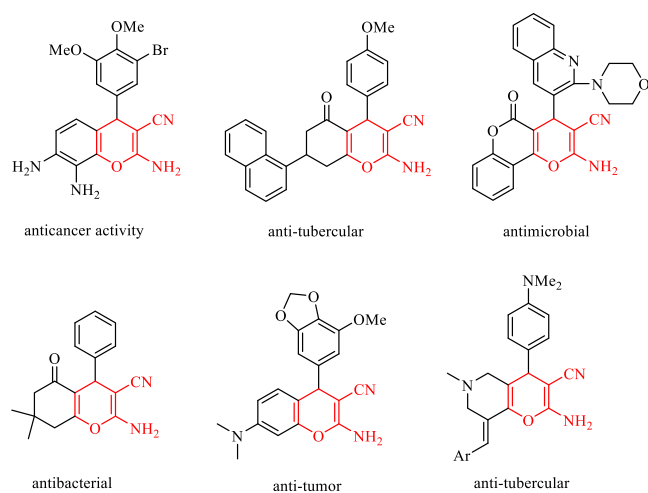
Figure 1. Selected examples of biologically active molecules based on 4H-pyran.
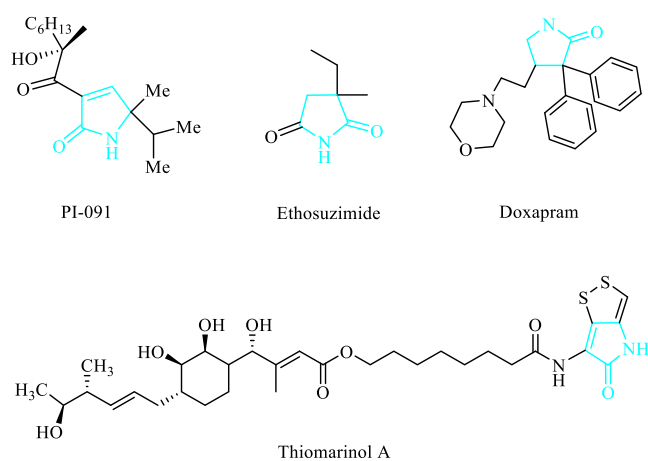

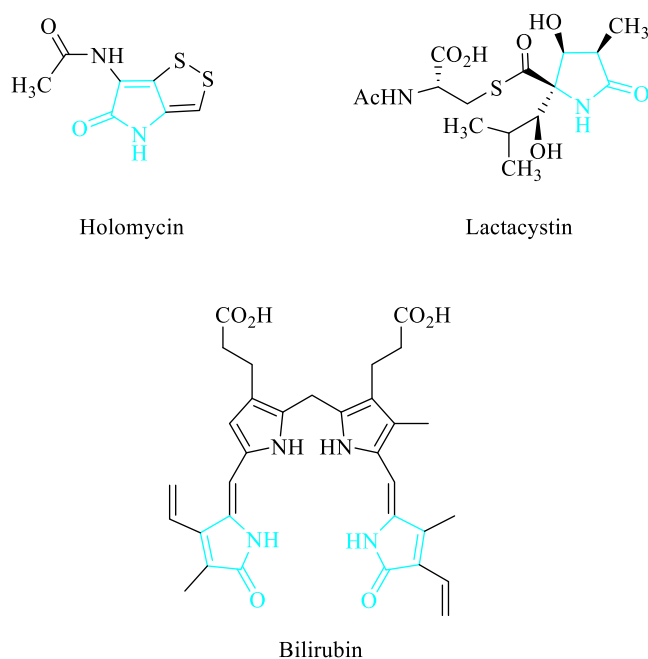**Figure 2.** Selected drugs containing the 2-pyrrolidinone moiety.

Figure 3. Selected examples of natural products containing the 2-pyrrolidinone moiety.

The sulfonic acid group chemical bond on MNPs is attained through diverse procedures such as the stabilization of perfluorosulfonic acid triethoxysilanes, oxidation of immobilized thiols, and hydrolysis of sulfonic acid chlorides.[15−17] Several catalysts have been recently expanded, including Fe_3O_4@Fe_2O_3-OSO_3H,[15] $SiMNP$-FSO_3H,[18] Fe_3O_4@MCM-48-OSO_3H,[19] Fe_3O_4@SiO_2@$PrSO_3H$,[20] and $SiMNP$-SO_3H.[21]

Although recent sulfonic acid supported catalytic systems bear important advantages compared with their homogeneous counterparts, such as reusability and recoverability nevertheless, most of them have been utilized at high temperatures and in high loading.[22−25] In addition, since these are not lipophilic in nature, the diffusion of organic substrates on their surface is low. Hence, one of the most important issues among chemists is the design and synthesis of heterogeneous magnetic hybrid organic−inorganic NP-functionalized powerful HSO_3 groups. Of course, over recent years multicomponent reactions have received remarkable attention and have turned into a highly active field of research that provides new chemical scaffolds in one step and is also ecologically and economically attractive.[26−28] Tetrahydrobenzo[*b*]pyrans as one of the most significant compounds in organic chemistry are synthesized by applying MCRs with special biological and medicinal activities, including anticoagulant, anti-cancer, anti-anaphylactic, and antispasmodic, which have found an acceptable place as synthetic agents.[29] Figure 1 illustrates some 4H-pyran derivatives with strong pharmacological activity.[30] Thus, they are used as cognitive enhancers to treat neurodegenerative diseases such as Parkinson's illness, AIDS-associated dementia, Huntington's sickness, Down's syndrome, amyotrophic lateral sclerosis, and Alzheimer's disease as well as for the therapy of schizophrenia and myoclonus.[31,32] In drug discovery, heterocyclic compounds comprising nitrogen have performed a very notable role. Due to the existence of heterocyclic compounds comprising a 2-pyrrolidinone core in natural products and their biological activity (Figure 2), they are one of the most important categories of heterocyclic compounds.[33] Many natural products such as thiomarinol A4,[34] holomycin and thiolutin,[35] and lactacystin[36] contain a 2-pyrrolidinone scaffold (Figure 3). Especially, there is a wide range of pharmacological effects such as anti-tumor,[37] antibacterial, and anticonvulsant[38] in 2-pyrrolodinones. Therefore, the synthesis of 2-pyrrolodinones is another vital issue among chemists.

Given the interesting advantages of MCRs or recent developments in nanomaterial synthesis in catalysis science, herein, we reported for the first time the preparation of an efficient and recoverable novel magnetic Fe_3O_4 grafted sulfonic acid (SO_3H/NH_2NH_2/$GPTMS$/Fe_3O_4) and its application in the synthesis of pyran derivatives from dimedone, aldehydes derivatives, and malononitrile under reflux conditions in a 1:1 mixture of H_2O/EtOH, and the synthesis of substituted pyrrolidinones from aniline, aromatic aldehydes, and diethyl acetylenedicarboxylate in ethanol at a temperature of 50 °C in high yields (Scheme 1). We used a green catalyst and solvent, and mild reaction conditions for the one−pot synthesis of pyran and pyrrolidinone derivatives without generating harmful by-products. We found that no reference has been reported for the production of the various desired compounds in the presence of a green solvent, and magnetic Fe_3O_4 grafted sulfonic acid. Simple separation of products from the reaction mixture in high to excellent yields, low catalyst loading, good turnover frequency, and eco-friendliness are some astounding benefits of the present work.
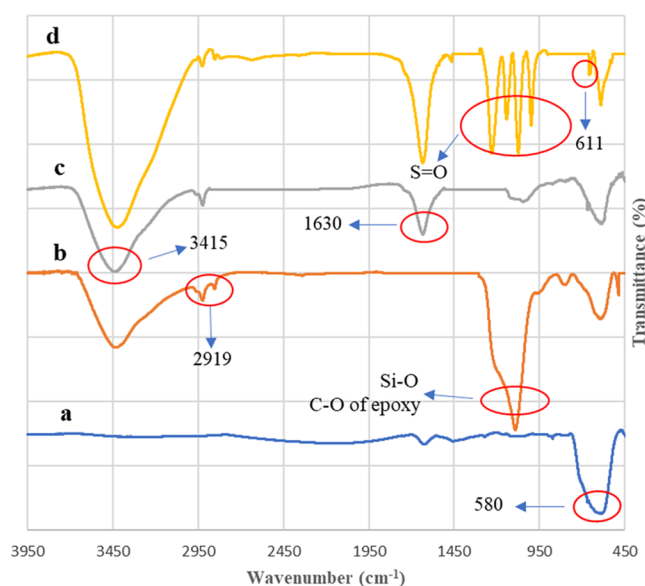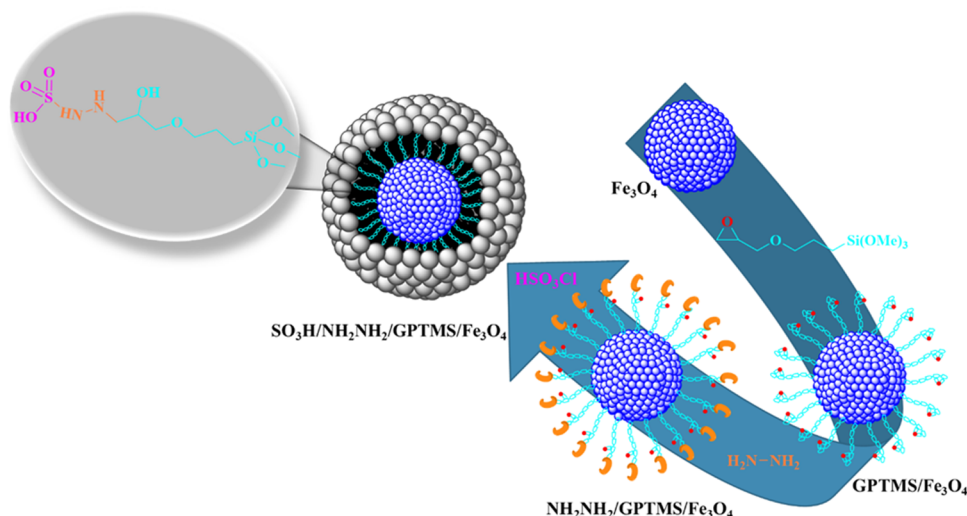
Scheme 1. Preparation of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ NPs

Figure 4. FT-IR spectra of (a) Fe$_3$O$_4$, (b) GPTMS/Fe$_3$O$_4$, (c) NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$, and (d) SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$.
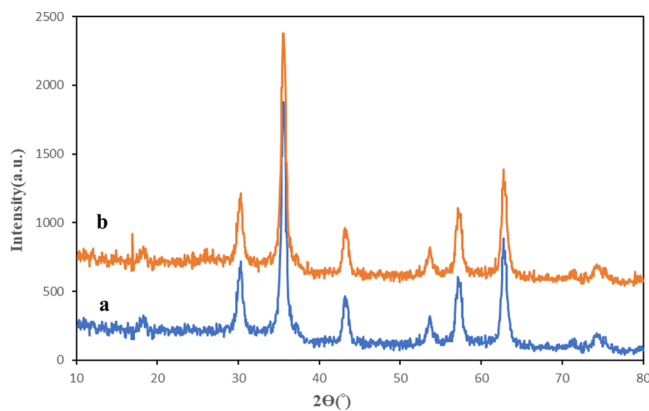
Figure 5. PXRD patterns of (a) Fe$_3$O$_4$ and (b) SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$.

Table 1. PXRD Data for SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$

| entry | 2Θ (deg) | peak width (FWHM) | Miller indices | | | particle size (nm) | inter-planar distance (nm) |
			h	k	l		
1	18.26	0.5904	1	1	1	13.6	0.485
2	30.37	0.4428	2	2	0	18.6	0.296
3	35.56	0.3444	3	1	1	24.2	0.253
4	43.19	0.6888	4	0	0	12.4	0.209
5	53.67	0.2952	4	2	2	30.2	0.171
6	57.29	0.7872	5	1	1	11.5	0.161
7	62.65	0.2952	4	4	0	31.5	0.148

2. EXPERIMENTAL SECTION

2.1. General. All materials containing iron (III) chloride, FeSO$_4$·7H$_2$O, aqueous ammonia (25%), ethanol, GPTMS, toluene (anhydrous), hydrazine hydrate, chlorosulfuric acid, benzaldehyde derivatives, dimedone, malononitrile, diethyl acetylenedicarboxylate, and aniline were provided from Fluka, Sigma-Aldrich, and Merck companies. FT-IR analyses were performed on a Perkin-Elmer 597 spectrophotometer. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DRX-250 AVANCE spectrometer at 250 and 62.90 MHz, respectively. The crystallinity of the SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ catalyst was surveyed using PXRD analysis (an X'Pert-Pro advanced diffractometer operated at 40 kV and 40 mA at 25 °C). EDAX was applied for elemental analysis of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ and achieved by applying an EDAX detector. SEM analysis was performed with a TE-SCAN (Brno, Czech Republic). Transmission electron microscopy (TEM) images were recorded on a Zeiss EM10C microscope, operated at 80 kV. VSM analysis was used to determine the magnetic properties of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ (VSM, Taban, Tehran, Iran).

2.2. Synthesis of Fe$_3$O$_4$ NPs. Fe$_3$O$_4$ magnetic nanoparticles were prepared by utilizing an improved chemical precipitation procedure.[39] First, FeSO$_4$·7H$_2$O and FeCl$_3$ (Fe^{2+}/Fe^{3+} molar ratio = 1:2) were mixed in 120 mL of distilled H$_2$O at 80 °C. Next, 120 mL of a 25% aqueous solution of NH$_3$ (1.5 M) was added dropwise to the reaction mixture under a N$_2$ gas atmosphere. The obtained mixture was stirred in an N$_2$ gas atmosphere for 30 min. The reaction mixture was cooled to 25
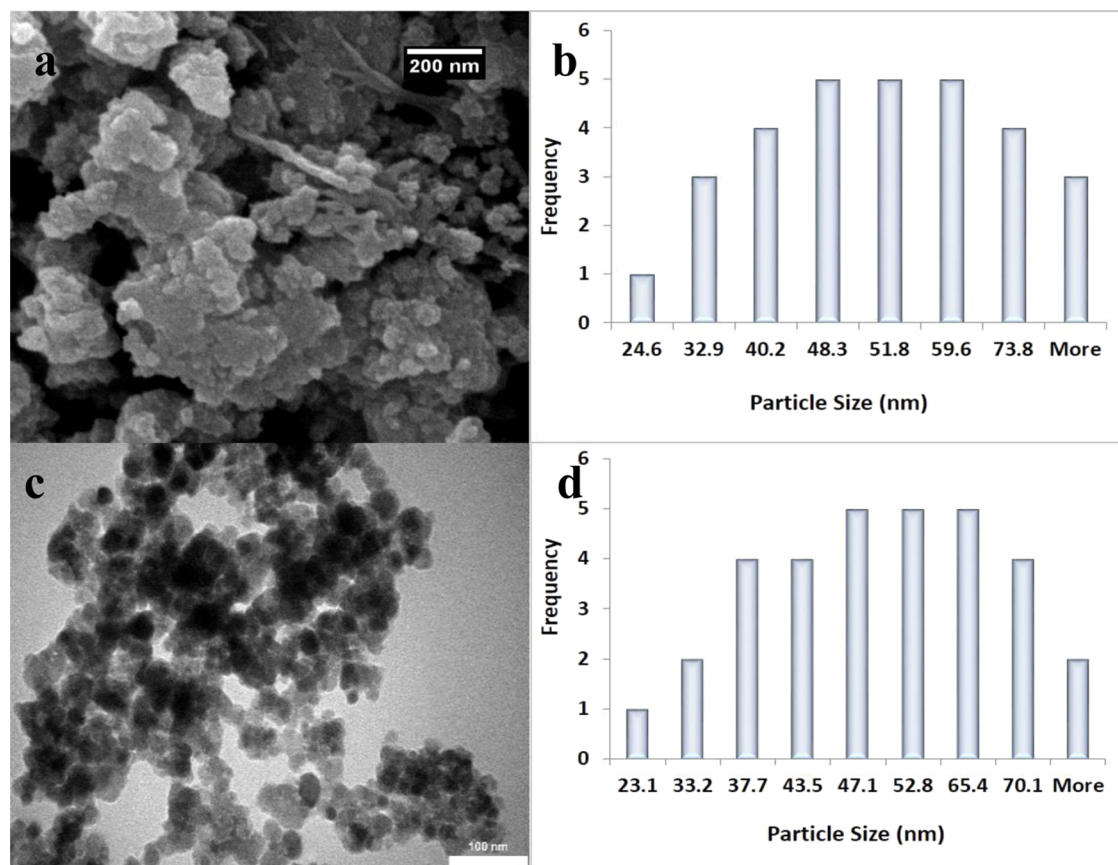
Figure 6. Microscopic analysis of $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$. (a) FE-SEM micrograph and (b) its size distribution diagram. (c) The TEM analysis and (d) its size distribution diagram.

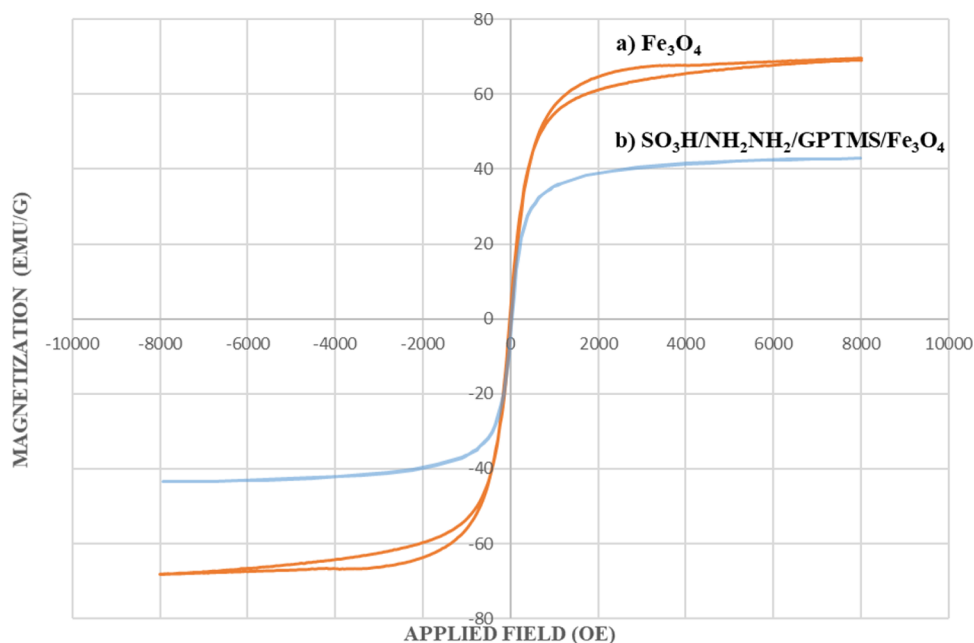**Figure 7.** VSM analysis of (a) Fe_3O_4 and (b) $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$.

°C, and the resulting black product was collected by using a simple magnet and eluted completely several times, first with distilled H_2O and then with EtOH. Fe_3O_4 magnetic nanoparticles were isolated and finally dried at 40 °C for 24 h (yield: 92%).

2.3. Synthesis of GPTMS/Fe₃O₄. GPTMS/Fe_3O_4 was synthesized from GPTMS modified with Fe_3O_4 using an easy strategy.[40] Briefly, 1 g of Fe_3O_4 was suspended in 100 mL of anhydrous toluene for 20 min. Then, (3-glycidyloxypropyl)-trimethoxysilane (10 mmol) was added dropwise to the Fe_3O_4
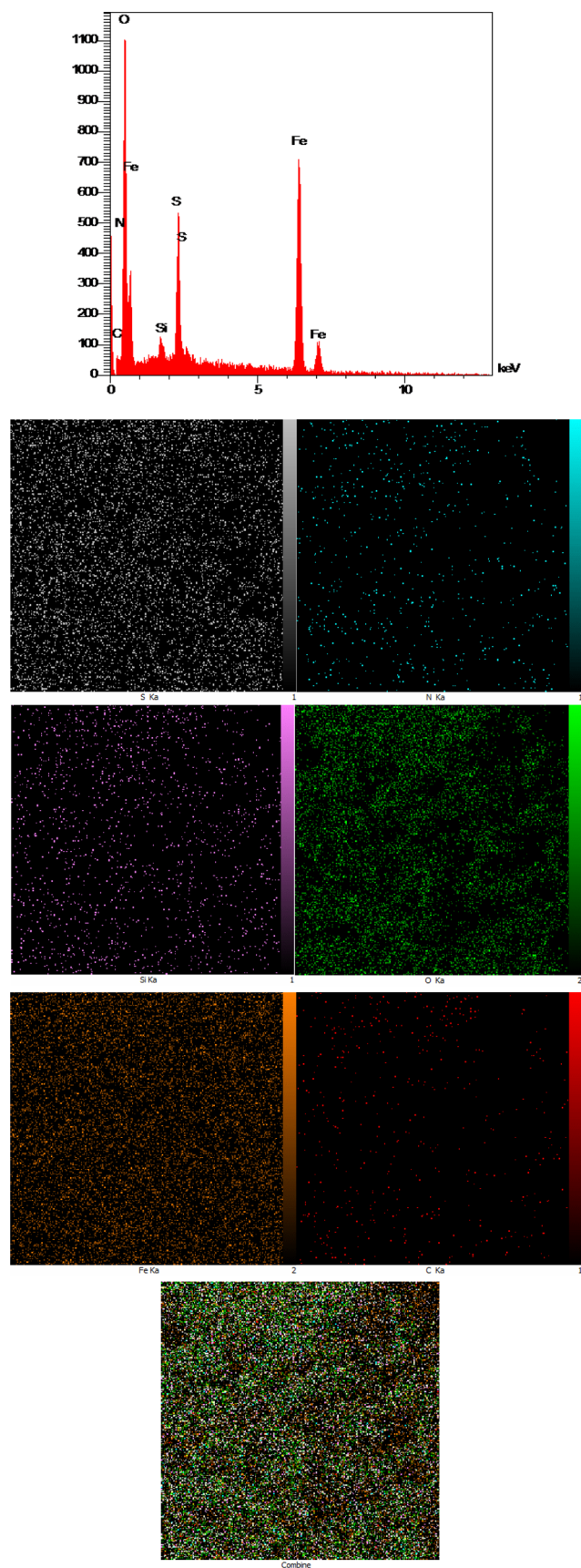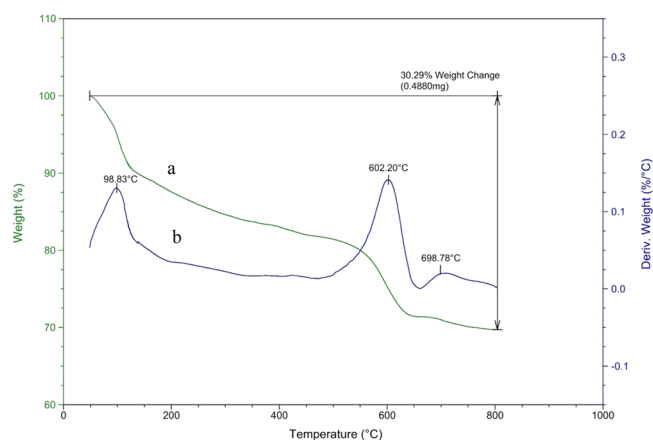
Figure 9. (a) Thermal gravimetric analysis (TGA) and (b) derivative thermal gravimetric (DTG) curves of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ NPs.

solution and was refluxed for 8 h under the protection of nitrogen. Finally, GPTMS/Fe$_3$O$_4$ was separated by applying a simple external magnet field and rinsed 2 times with benzene, and dried for 24 h at ambient temperature.

2.4. Synthesis of NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$. First, 1 g of GPTMS/Fe$_3$O$_4$ in 100 mL of dry toluene was suspended for 20 min. Next, hydrazine hydrate (12 mmol) was added to the GPTMS/Fe$_3$O$_4$ solution at reflux conditions under nitrogen gas for 24 h. Then, NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ was separated by utilizing an external magnet, rinsed with benzene, and dried for 24 h at ambient temperature.

2.5. Synthesis of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$. 1 g of NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ NPs in 75 mL of dry CH$_2$Cl$_2$ were dispersed under ultrasound irradiation for 10 min. Afterward, 1 mL of ClSO$_3$H (15 mmol) was dissolved in 20 mL of CH$_2$Cl$_2$ and added dropwise to the NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ stirring mixture over 30 min and the residual HCl was eventually eliminated by utilizing suction. Eventually, the obtained product was dried at 60 °C (Scheme 1).[41]

2.6. General Procedure for the Synthesis of Pyrans (4a–n) by Using SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$. A mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol), and dimedone (1 mmol) for the synthesis of products (4a–n) containing SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ (0.01 g) was stirred in 2 mL of EtOH:H$_2$O (1:1) and refluxed for appropriate times. The reaction progress was investigated by utilizing TLC. Following the termination of the reaction, the nanocatalyst was eliminated from the reaction mixture by a simple external magnetic field, and then the precipitated product was recrystallized from ethanol.

2.7. General Procedure for the Preparation of Pyrrolidinones (7a–l) by utilizing SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$. A mixture of aromatic aldehyde (1 mmol), aniline (1 mmol), diethyl acetylenedicarboxylate (1 mmol), and SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ (0.015 g) in EtOH (2 mL) was stirred at 60 °C. TLC was applied to follow the reaction, then the obtained products were heated in EtOH until dissolved. After removing the nanocatalyst from the reaction mixture by employing a simple magnet, the pure products were prepared through recrystallization from hot EtOH.

2.8. FT-IR and NMR Spectral Data of Some Products.
2.8.1. 2-Amino-7,7-dimethyl-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydrobenzo[b]pyran (4a). FT-IR (KBr): 3380, 3182, 2958, 2188, 1675, 1604, 1491, 1418, 1364, 1246, 1216,
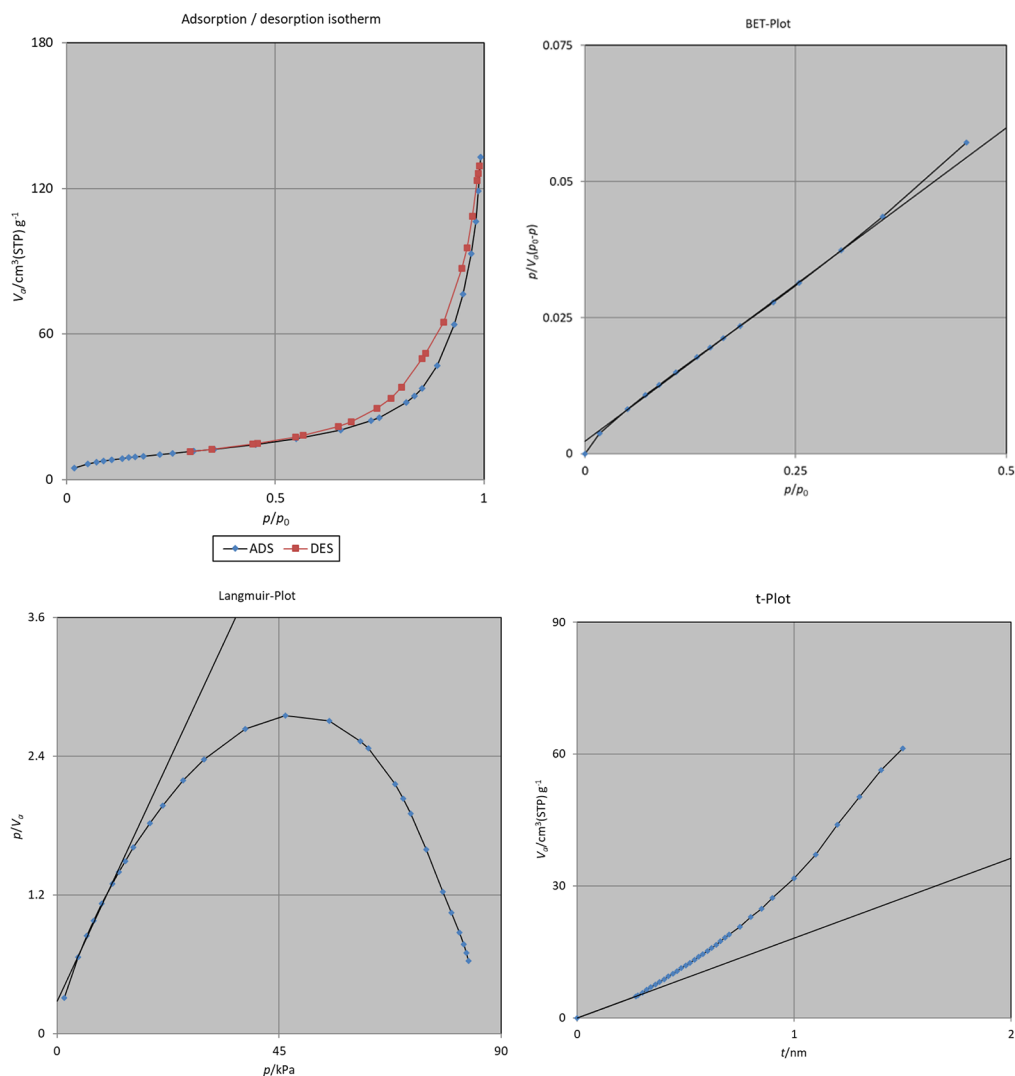
Figure 8. EDX and X-ray atomic mapping spectrum of SO$_3$H-functionalized epoxy-immobilized Fe$_3$O$_4$ core−shell MNPs.

Figure 10. BET plot of the N$_2$ adsorption−desorption and BET plot of N$_2$ adsorption isotherms of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$.

1140, 1094, 1032, 1014, 854, 770. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ_H = 0.92 (s, 3H, CH$_3$), 1.00 (s, 3H, CH$_3$), 2.07 (d, J = 15.7, 1H, CH$_2$), 2.22 (d, J = 15.7, 1H, CH$_2$), 2.48 (br, 2H, CH$_2$), 4.16 (s, 1H, CH), 7.03−7.33 (m, 6H, 4CH$_{Ar}$, NH$_2$). ^{13}C NMR (62.90 MHz, DMSO-d_6): δ = 22.8, 24.2, 27.7, 31.1, 36.1, 45.9, 53.7, 108.3, 115.5, 124.2, 125.1, 127.1, 139.7, 154.4, 158.6, 191.6.

2.8.2. 2-Amino-7,7-dimethyl-4-(4-bromophenyl)-5-oxo-5,6,7,8- tetrahydrobenzo[b]pyran (4b). FT-IR (KBr): 3399, 3323, 2964, 2191, 1686, 1605, 1486, 1406, 1362, 1254, 1217, 1160, 1038, 845, 562. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ_H = 0.95 (s, 3H, CH$_3$) 1.09 (s, 3H, CH$_3$), 2.08−2.17 (m, 2H, CH$_{2)}$, 2.46 (br, 2H, CH$_2$), 4.13 (s, 1H, CH), 7.04−7.43 (m, 6H, 4CH$_{Ar}$, NH$_2$). ^{13}C NMR (62.90 MHz, DMSO-d_6): δ = 23.9, 24.2, 27.7, 34.8, 36.1, 45.9, 56.7, 108.2, 115.5, 124.6, 125.4, 127.1, 140.1, 154.4, 158.5, 191.6.
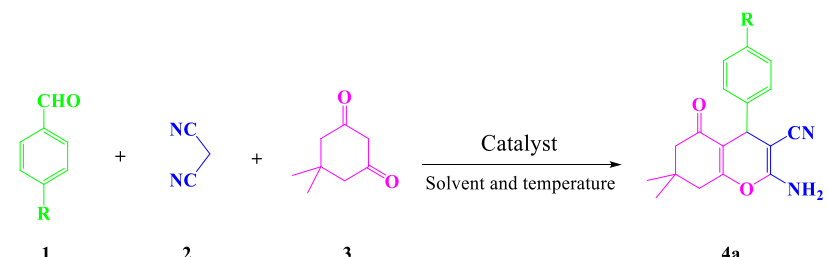
2.8.3. 2-Amino-7,7-dimethyl-4-(4-cyanophenyl)-5-oxo-5,6,7,8-tetrahydrobenzo[b]pyran (4c). FT-IR (KBr): 3353, 2962, 2228, 2193, 1690, 1604, 1503, 1362, 1253, 1215, 1039, 859. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ_H = 0.92 (s, 3H, CH$_3$), 1.00 (s, 3H, CH$_3$), 2.07 (d, J = 15.5, 1H, CH$_2$), 2.22 (d, J = 14.2, 1H, CH$_2$), 2.49 (br, 2H, CH$_2$), 4.26 (s, 1H, CH), 7.12 (s, 2H, NH$_2$), 7.33 (d, J = 7.5 Hz, 2H, CH$_{Ar}$), 7.73 (d, J = 7.2 Hz, 2H, CH$_{Ar}$). ^{13}C NMR (62.90 MHz, DMSO-d_6): δ = 22.8, 24.1,

27.7, 31.7, 35.0, 45.7, 53.0, 105.3, 107.6, 114.6, 115.2, 124.2, 128.3, 146.1, 154.5, 159.0, 191.6.

2.8.4. Ethyl 2-(4-Chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7a). FT-IR (KBr): 3287, 2960, 1721, 1683, 1652, 1369, 1258, 1216, 1190, 1035, 687. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ_H = 1.01 (t, 3H, CH$_3$), 3.97 (q, 2H, CH$_2$), 6.41 (s, 1H, CH), 7.14−7.72 (m, 9H, CH$_{Ar}$),11.64 (br s, 1H, OH).^{13}C NMR (62.90 MHz, DMSO-d_6): δ = 9.9, 55.7, 107.7, 118.5, 121.4, 124.2, 125.7, 128.5, 131.7, 132.0, 148.8, 159.7.

2.8.5. Ethyl 2-(2-Chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7b). FT-IR (KBr): 3300, 2986, 1728, 1499, 1076. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ_H = 1.01 (t, 3H, CH$_3$), 3.97 (q, 2H, CH$_2$), 6.41 (s, 1H, CH), 7.14−7.72 (m, 9H, CH$_{Ar}$),11.84 (1H, OH). ^{13}C NMR (62.90 MHz, DMSO-d_6): δ = 9.8, 52.6, 57.9, 107.8, 118.4, 122.2, 123.4, 124.8, 125.6, 126.9, 130.3, 131.5, 132.1, 149.6, 157.7, 160.1.

2.8.6. Ethyl 2-(4-Fluorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7c). FT-IR (KBr): 3295, 2984, 2926, 1717, 1498, 1026. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ_H = 1.06 (s, 3H, CH$_3$), 4.02 (s, 2H, CH$_2$), 6.06 (s, 1H, CH),7.02−7.53 (m, 9H, CH$_{Ar}$), 11.73 (1H, OH).^{13}C NMR (62. 90 MHz, DMSO-d_6): δ = 10.0, 55.7, 107.9, 110.9, 111.2,

Table 2. Optimizing the Catalyst Amount, Solvent, and Temperature According to the Model Reaction for the Preparation of 4a[a]

entry	catalyst (g)	solvent	temperature (°C)	time (min)	yield (%)[b]
1				120	trace
2		H$_2$O/EtOH (1:1)	reflux	120	10
3	0.005	EtOH	r.t.	150	50
4	0.005	H$_2$O	r.t.	260	45
5	0.005	CH$_3$CN	r.t.	260	28
6	0.005	DMF	r.t.	260	25
7	0.005	CH$_2$Cl$_2$	r.t.	300	35
8	0.005	ethyl acetate	r.t.	300	30
9	0.005	toluene	r.t.	300	15
10	0.005	H$_2$O/EtOH (1:1)	r.t.	150	78
11	0.01	H$_2$O/EtOH (1:1)	r.t.	90	83
12	0.02	H$_2$O/EtOH (1:1)	r.t.	50	70
13	0.005	H$_2$O/EtOH (1:1)	70	90	82
14	0.01	H$_2$O/EtOH (1:1)	70	35	88
15	0.02	H$_2$O/EtOH (1:1)	70	60	78
16	0.005	H$_2$O/EtOH (1:1)	reflux	35	87
17	0.01	H$_2$O/EtOH (1:1)	reflux	15	95
18	0.02	H$_2$O/EtOH (1:1)	reflux	15	90

[a]Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), and dimedone (1 mmol), solvent (2 mL), and catalyst. [b]Isolated yield.

Table 3. Comparison of the Activity of Different Catalysts in the Preparation of 4a[a]

entry	catalyst	condition	time (min)	yield (%)[b]
1		H$_2$O/EtOH, reflux	120	25
2	H$_2$SO$_4$	H$_2$O/EtOH, reflux	20	65
3	HSO$_4$Cl	H$_2$O/EtOH, reflux	120	
4	SO$_3$H/NH$_2$NH$_2$/GPTMS	H$_2$O/EtOH, reflux	45	65
5	Fe$_3$O$_4$	H$_2$O/EtOH, reflux	60	48
6	FeCl$_3$	H$_2$O/EtOH, reflux	60	52
7	FeSO$_4$·7H$_2$O	H$_2$O/EtOH, reflux	90	45
8	GPTMS/Fe$_3$O$_4$	H$_2$O/EtOH, reflux	60	23
9	NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$	H$_2$O/EtOH, reflux	50	79
10	SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$	H$_2$O/EtOH, reflux	15	95

[a]Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), and dimedone (1 mmol), solvent (2 mL), and catalyst (0.01 g), under reflux. [b]Isolated yield.

118.6, 121.4, 124.7, 125.9, 128.8, 132.1, 148.8, 155.6, 157.9, 159.9.

2.9. X-ray Crystallography. Crystallographic measurements of 7a and 7d were carried out on a κ-geometry Agilent Technologies Xcalibur R four-circle diffractometer (ω scans) with Mo Kα radiation (λ = 0.71073 Å) and a Ruby CCD detector at 100(2) K. The collected data were corrected for the Lorentz and polarization effects. Data collection, cell refinement, data reduction, and analysis, including empirical (multi-scan) absorption correction, were performed with *CrysAlisPRO*.[42] Structures were solved using SHELXT-2014[43] and refined by a full-matrix least-squares technique with the anisotropic displacement parameters for non-H atoms with the use of SHELXL-2014.[44] The structure of 7a was refined as a two-component twin. The H atoms in both structures were found in difference Fourier maps or were included from geometrical considerations, and were initially refined isotropically. In the final refinement cycles, the C-bonded H atoms in both 7a and 7d, and hydroxyl H atoms in 7a were repositioned in their computed positions and refined using a riding model, with C−H = 0.95−1.00 Å, O−H = 0.84, and U_{iso}(H) = 1.2U_{eq}(C) for CH and CH$_2$, and 1.5U_{eq}(C, O) for CH$_3$ and OH. A hydrogen atom of the hydroxyl group in 7d was refined freely. Labels of atoms in both structures have been adjusted to the structure deposited at the Cambridge Structural Database (CSD, Version 5.40)[45] with the CSD refcode LIFBEJ.[46] The XP and Diamond programs were used to create the figures.[47,48] Details of structures refinement and crystals data can be found in Table S1 as well as in the crystallographic information files (CIF) deposited at the Cambridge Crystallographic Data Centre (CCDC No. 2215544 and 2215545).

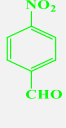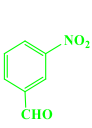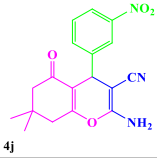**Table 4. Preparation of 4H-Pyran Derivatives[51−57] Catalyzed by SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$[a]**
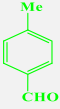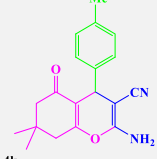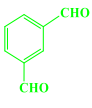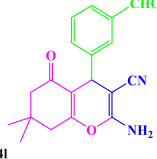
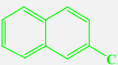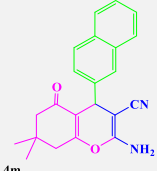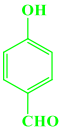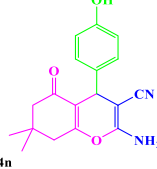| Entry	Aldehyde	Products (4a-n)	Time (min)	Yield (%)[b]	M.P. (°C)	M.P. (°C) (Ref.)
1		4a	15	95	215-217	215-217[51]
2		4b	20	95	220-222	221–223[52]
3		4c	10	96	226-228	225-228[53]
4		4d	20	93	197-201	198-202[54]
5		4e	15	93	233-235	233-235[54]
6		4f	15	95	188-189	187-188[52]
7		4g	20	76	155-156	154-156[52]
8		4h	17	82	175-177	174-177
9		4i	10	96	179-181	178-180[54]

Table 4. continued

Entry	Aldehyde	Products (4a-n)	Time (min)	Yield (%)[b]	M.P. (°C)	M.P. (°C) (Ref.)
10		4j	15	96	205-207	206-208[55]
11		4k	20	92	220-222	223-225[56]
12		4l	25	89	202-204	203-205[52]
13		4m	15	86	230-231	229-231[55]
14		4n	20	86	225-227	224-226[57]

[a]Reaction conditions: aromatic aldehyde (1 mmol), malononitrile (1 mmol), and dimedone (1 mmol), H_2O:EtOH (2 mL), and catalyst (0.01 g), under reflux. [b]Isolated yield.

3. RESULTS AND DISCUSSION

Magnetic Fe_3O_4 grafted sulfonic acid ($SO_3H/NH_2NH_2/$ GPTMS/Fe_3O_4) was successfully prepared in an operationally simple procedure in three steps (Scheme 1). First, epoxy-functionalized Fe_3O_4 core−shell MNP (GPTMS/Fe_3O_4) was obtained through grafting Fe_3O_4 NPs with GPTMS and subsequently, epoxy-attached Fe_3O_4 core−shell MNP were immobilized with hydrazine and finally, chlorosulfonic acid was immobilized on NH_2NH_2/GPTMS/Fe_3O_4 core−shell MNPs by employing a dropwise approach. The nanostructured magnetic catalyst was identified by utilizing Fourier transform infrared (FT-IR) spectroscopy, Brunauer−Emmet−Teller (BET) analysis, field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray analysis (EDX), vibrating sample magnetometry (VSM), thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD).

The FT-IR technique was utilized to detect diverse functional groups of Fe_3O_4@GP@NH_2NH_2@SO_3H step by step (Figure 4). The FT-IR spectra of (a) Fe_3O_4, (b) GPTMS/Fe_3O_4, (c) NH_2NH_2/GPTMS/Fe_3O_4, and (d) SO_3H/NH_2NH_2/GPTMS/ Fe_3O_4 are illustrated in Figure 4. Figure 4a−d shows the strong vibration band related to the Fe−O group at 580 cm^{-1}. The wide peaks at 1089−1186 cm^{-1} were assigned to Si−O and the epoxy groups of (3-glycidyloxypropyl)trimethoxysilane (GPTMS) as depicted in Figure 4b−d. Also, the alkyl CH_2 stretching vibration appeared at 2919 cm^{-1} (Figure 4b−d). A broad

absorption peak at 3415 cm^{-1} appeared belonging to the NH and OH groups. N−H bending vibration of hydrazine appears at 1630 cm^{-1} (Figure 4b−d). The appearance of a new peak at 1000−1350 cm^{-1} can be assigned to the stretching vibration peak of S=O bonds. Also, the C−S band at 611 cm^{-1} was observed in Figure 4d. These data emphasize the successful coating of chlorosulfonic acid moieties onto the NH_2NH_2/ GPTMS/Fe_3O_4 surface.

The PXRD patterns of the Fe_3O_4 and SO_3H/NH_2NH_2/ GPTMS/Fe_3O_4 are depicted in Figure 5. The strong and sharp diffraction peaks of the synthesized nanocatalyst at 2θ = 18.26, 30.37, 35.56, 43.19, 53.67, 57.29, and 62.65° associated with the various planes such as the (111), (220), (311), (400), (422), (511), and (440) were readily specified from the PXRD pattern of cubic Fe_3O_4 (JCPDS 88-0866).[49] PXRD analysis confirms the successful preparation of the designed nanocatalyst with the sameness of the pure phase pattern of SO_3H/NH_2NH_2/ GPTMS/Fe_3O_4 with the Fe_3O_4 pattern. Also, the Miller indices, peak width (FWHM), inter-planar distance, and size of SO_3H/ NH_2NH_2/GPTMS/Fe_3O_4 in the 18.26−62.65 range were calculated and the obtained results are represented in Table 1. The average crystallite size and inter-planar distance were respectively determined at 20.28 and 0.246 nm through the Scherrer equation $[D = K\lambda/(\beta \cos \Theta)]$ and Bragg equation $[d_{hkl} = \lambda/(2 \sin \Theta)]$.

Scheme 2. Suggested Mechanism for the Formation of 4H-Pyran Derivatives
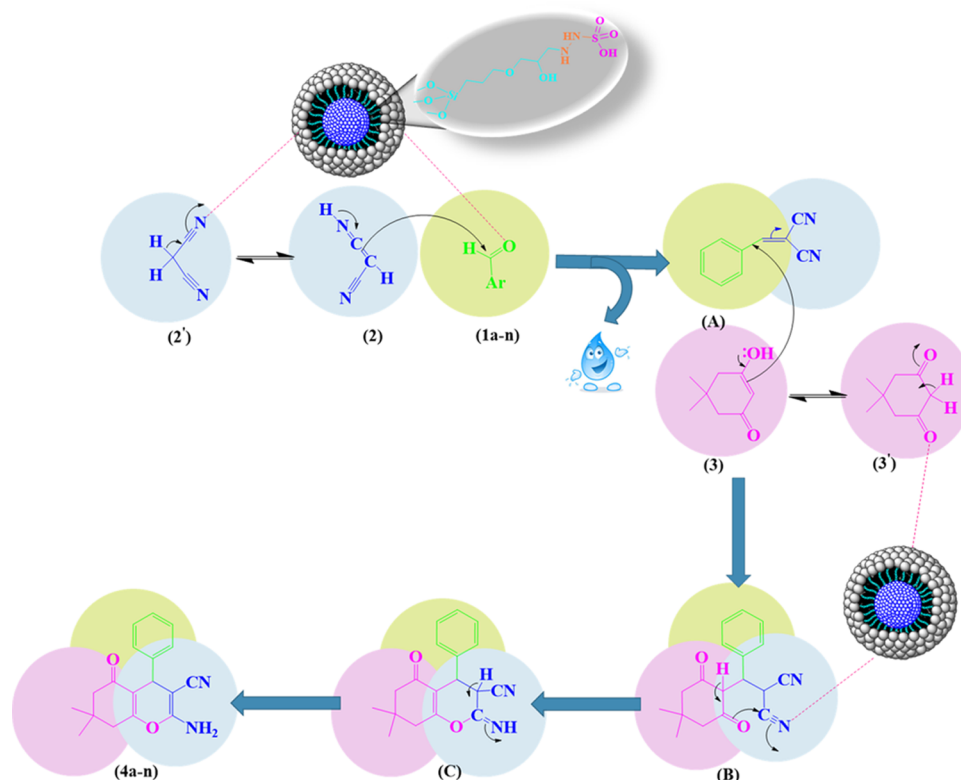
Table 5. Effect of the Catalyst Amount, Solvent, and Temperature on the Preparation of 4a[a]
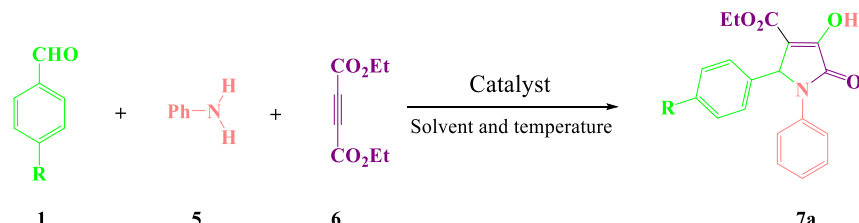
entry	catalyst (g)	solvent	temperature (°C)	time (min)	yield (%)[b]
1		EtOH	50	54	
2	0.005	EtOH	50	18	61
3	0.01	EtOH	50	15	80
4	**0.015**	**EtOH**	**50**	**15**	**93**
5	0.02	EtOH	50	15	86
6	0.015	EtOH	r.t.	36	trace
7	0.015	EtOH	reflux	18	78
8	0.015	H$_2$O/EtOH (1:1)	reflux	18	67
9	0.015	H$_2$O	reflux	18	35
10	0.015	CH$_3$CN	reflux	36	69
11	0.015		50	36	49
12	0.015	CH$_2$Cl$_2$	reflux	36	67
13	0.015	CH$_3$OH	reflux	36	75
14	0.015	ethyl acetate	reflux	36	65

[a]Reaction conditions: 4-chlorobenzaldehyde (1 mmol), aniline (1 mmol) and diethyl acetylenedicarboxylate (1 mmol), solvent (2 mL), and catalyst. [b]Isolated yield.

FE-SEM images (Figure 6a,b) specified the structural features, morphologies, and particle size of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$. Actually, FE-SEM analysis shows a uniform size distribution diagram with an average size of 48−59 nm (Figure 6b). TEM imaging of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ illustrates the core−shell structure (Figure 6c) with the uniform

size distribution diagram with an average size of 47−65 nm (Figure 6d).

The magnetic characteristics of (a) Fe$_3$O$_4$ and (b) SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ were identified through VSM at 25 °C (Figure 7). For the Fe$_3$O$_4$, the saturation magnetization value was obtained as 69.8 emu·g^{-1}. The magnetization value of

Table 6. Comparison of the Activity of Different Catalysts in the Preparation of 7a[a]

entry	catalyst	conditions	time (min)	yield (%)[b]
1	H_2SO_4	EtOH, 50 °C	145	
2	HSO_4Cl	EtOH, 50 °C	145	
3	$SO_3H/NH_2NH_2/GPTMS$	EtOH, 50 °C	20	58
4	Fe_3O_4	EtOH, 50 °C	145	
5	$FeCl_3$	EtOH, 50 °C	145	
6	$FeSO_4·7H_2O$	EtOH, 50 °C	145	
7	$GPTMS/Fe_3O_4$	EtOH, 50 °C	145	
8	$NH_2NH_2/GPTMS/Fe_3O_4$	EtOH, 50 °C	145	
9	$SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$	EtOH, 50 °C	15	93

[a]Reaction conditions: 4-chlorobenzaldehyde (1 mmol), aniline (1 mmol) and diethyl acetylenedicarboxylate (1 mmol), solvent (2 mL), and catalyst (0.015 g), 50 °C. [b]Isolated yield.

$SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ was 45 emu·g^{-1}, which was lower than that of the Fe_3O_4 NPs. These results represented that the magnetization of Fe_3O_4 NPs decreased after the modification process with silica layers and organic compounds.

The EDX image was applied for obtaining information about the elemental distribution in the $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ structure (Figure 8). In the case of $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$, coating functional groups onto the surface of MNPs was confirmed by the presence of C, Fe, O, S, Si, and N signals (Figure 8). It could be concluded that the designed nanocatalyst has been successfully prepared. Also, the presence of C, Fe, O, S, Si, and N elements was exhibited by the elemental map of the $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ nanocatalyst (Figure 8).

As shown in Figure 9, TGA analysis was performed in the 25–800 °C range (Figure 9). The first weight loss of about 4% for $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ at 98.83 °C corresponds to H_2O and physically adsorbed solvents. The second mass reduction of about 17% occurred for the catalyst at ∼602 °C, which can be related to the demolition of diverse organic compounds immobilized onto the surface of Fe_3O_4 NPs. Also, the third mass reduction observed at nearly 698 °C is a result of the elimination of the silanol groups, which explains the weight loss of about 30.29%.

BET analysis was performed to know the mean pore diameter, total pore volume, surface area, and type of isotherm of $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$. Figure 10 shows the BET plot of the N_2 adsorption–desorption and BET plot of N_2 adsorption isotherm images. As can be seen, the total pore volume, surface area, and the mean pore diameter of $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ were 0.1842 cm^3 g^{-1}, 35.451 m^2 g^{-1}, and 23.156 nm, respectively. Also, the synthesized nanocatalyst is categorized as type IV isotherm, which belongs to the mesoporous range.[50]

After the determination of the survey structure of SO_3H-functionalized epoxy-immobilized Fe_3O_4 core–shell MNP, its catalytic efficiency was evaluated in the preparation of tetrahydrobenzo[b]pyran and 3-pyrrolin-2-one derivatives (Scheme 1).

Table 7. Preparation of 3-Pyrrolin-2-One Derivatives by Employing $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$[a] [58,59]

Entry	Aldehyde	Products (7a–l)	Time (min)	Yield (%)[b]	M.P. (°C)	M.P. (°C) (Ref.)
1		7a	15	93	194-197	195-198[27]
2		7b	20	92	205-206	204-207[27]
3		7c	15	92	192-195	193-196[27]
4		7d	15	87	200-203	202-205[27]
5		7e	15	91	210-211	211-213[58]
6		7f	20	87	224-226	225-228[27]
7		7g	20	90	180-183	181-183[59]
8		7h	20	91	224-226	225–227[60]
9		7i	20	92	190-193	190-192[61]
10		7j	15	88	179-181	178–180[62]
11		7k	20	92	183-185	184–187[60]
12		7l	15	91	203-204	202-205[61]

[a]Reaction conditions: aromatic aldehyde (1 mmol), aniline (1 mmol) and diethyl acetylenedicarboxylate (1 mmol), EtOH (2 mL), and catalyst (0.015), 50 °C. [b]Isolated yield.

To optimize the synthesis of pyrans, the effect of different parameters, for instance, solvents, amounts of the catalyst, and temperature in the reaction of malononitrile with 4-chlorobenzaldehyde and dimedone as a model reaction were tested (Table 2). Reaction performance with different solvents, including EtOH, H_2O, CH_3CN, DMF, CH_2Cl_2, ethyl acetate, toluene, and H_2O/EtOH (1:1) was performed to explore the solvent effect (Table 2, entries 3–10). As shown in Table 2, good yield (78%) was obtained in a short reaction time (150

Scheme 3. Proposed Mechanistic Path for the Preparation of Substituted 3-Pyrrolin-2-Ones
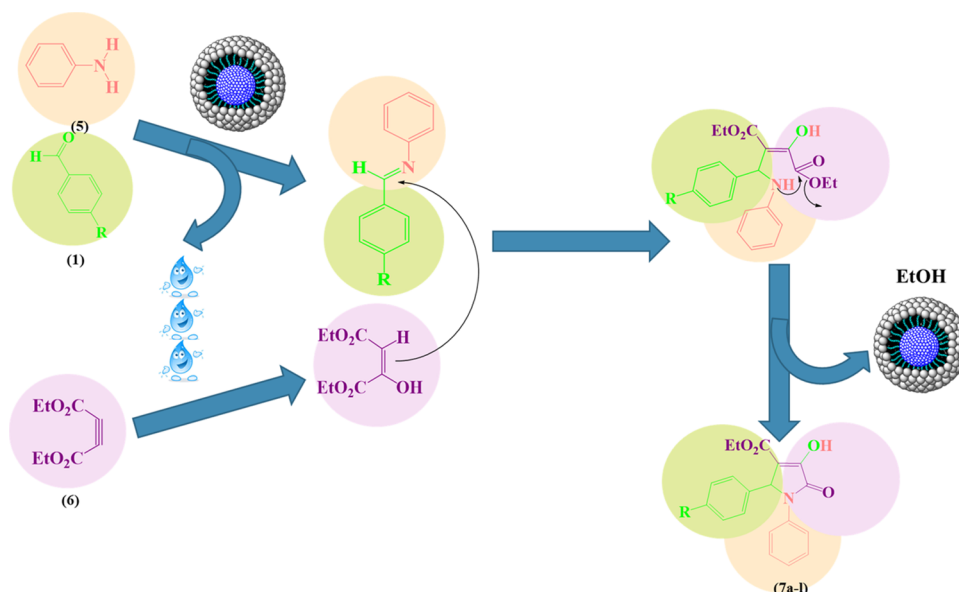
min) for 1:1 H₂O/EtOH compared with other solvents listed in the table in the presence of 0.005 g of the catalyst at room temperature (Table 2, entry 10). The results in Table 2 illustrate that the reaction is sensitive to temperature. Importantly, upon increasing the temperature, a decrease in the time and an increase in the reaction yield are observed (Table 2, entries 13–18). In our study, the effect of the catalyst amount was also perused based on the model reaction at 0.005, 0.01, and 0.02 g to discern their efficiency at 70 °C temperature and reflux conditions (Table 2, entries 13–18). Among the tested amounts, 0.01 g of the catalyst under reflux conditions was selected as the optimal amount and conditions in a 1:1 mixture of H₂O/EtOH (Table 2, entry 17). When the reaction was performed by employing 0.01 g of the catalyst under reflux conditions in a 1:1 mixture of H₂O/EtOH, the best product yield in a very shorter time of condensation of malononitrile with 4-chlorobenzaldehyde and dimedone was acquired (Table 2, entry 17).

Table 3 shows higher activity of the $SO_3H/NH_2NH_2/$ $GPTMS/Fe_3O_4$ catalyst, for instance, the loading catalyst, reaction time, and yield rather than other catalysts to synthesize product 4a. When H_2SO_4 (Table 3, entry 2), $SO_3H/NH_2NH_2/$ GPTMS (Table 3, entry 4), Fe_3O_4 (Table 3, entry 5), $FeCl_3$ (Table 3, entry 6), and $FeSO_4.7H_2O$ (Table 3, entry 7) were applied as the catalyst, a moderate yield was acquired for product 4a., although a decreased yield (23%) and a no yield was observed when $GPTMS/Fe_3O_4$ and HSO_4Cl was utilized, respectively (Table 3, entry 8). When $NH_2NH_2/GPTMS/$ Fe_3O_4 was utilized, the desired product **4a** was obtained with 79% yield (Table 3, entry 9).

Preparation of 4H-pyran derivatives was investigated by utilizing a series of aromatic aldehydes with malononitrile and dimedone under optimum conditions to evaluate the generality, limitation, and applicability of this method. As shown in Table 4, all aromatic aldehydes including aldehydes with electron-donating substitutions such as 4-HO-benzaldehyde, 4-MeO-benzaldehyde, 4-Me-benzaldehyde, and electron-withdrawing substitutions containing aldehydes such as 4-NO₂-benzalde-hyde, and 4-CN-benzaldehyde have led to the synthesis of the

corresponding tetrahydrobenzo[b]pyrans in high to excellent yields and no side products have been observed.

The suggested mechanism for the synthesis of 4H-pyran derivatives commences with the protonation of aldehyde and malononitrile and is shown in Scheme 2. First, intermediate A is formed from the reaction between malononitrile and aromatic aldehyde. Subsequently, E1cB elimination of water from intermediate A is facilitated by utilizing the $SO_3H/NH_2NH_2/$ $GPTMS/Fe_3O_4$ catalyst. Then, dimedone is converted to an enolized form in the presence of a catalyst and attacks intermediate A for forming intermediate B. In the next step, intermediate C is afforded after intramolecular cyclization. Finally, the pyran product is formed from intermediate C by employing a hydrogen shift (Scheme 2).

In another study to investigate the catalytic activity of $SO_3H/$ $NH_2NH_2/GPTMS/Fe_3O_4$ in the formation of 3-pyrrolin-2-ones derivatives, the reaction of 4-chlorobenzaldehyde 1 (1 mmol), aniline 5 (1 mmol), and diethyl acetylenedicarboxylate 6 (1 mmol) was chosen as a model reaction. Optimization of the reaction conditions was done in terms of temperature, solvent, catalyst amount, time, and yield. Table 5 represents that the reaction without $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ and without the desired product was carried out for 54 min (Table 5, entry 1). The effect of the amount of nanocatalyst (0.005−0.02 g) on the model reaction was surveyed (Table 5, entries 2−5). Excellent yield (93%) and short reaction time (15 min) were acquired in 0.015 g of $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ in EtOH at 50 °C (Table 5, entry 4). Then, the amount of the nanocatalyst from 0.01 to 0.015 g, and 0.02 g was increased as the reaction yield and reaction time were not appropriate (Table 5, entries 3−5). As shown in Table 5, it is clear from entry 6 that the reaction with 0.015 g of the nanocatalyst at 50 °C is considered better than the reaction at 25 °C. Also, in order to choose the model reaction for the experiment, various solvents were tested (Table 5, entries 7−14). It is clear from entry 4 that the utilization of EtOH enhances the yield of the product (15 min, 93%). Finally, the best yield in a shorter time is found in the model reaction by applying just 0.015 g of $SO_3H/NH_2NH_2/$ $GPTMS/Fe_3O_4$ in 2 mL of EtOH at 50 °C.
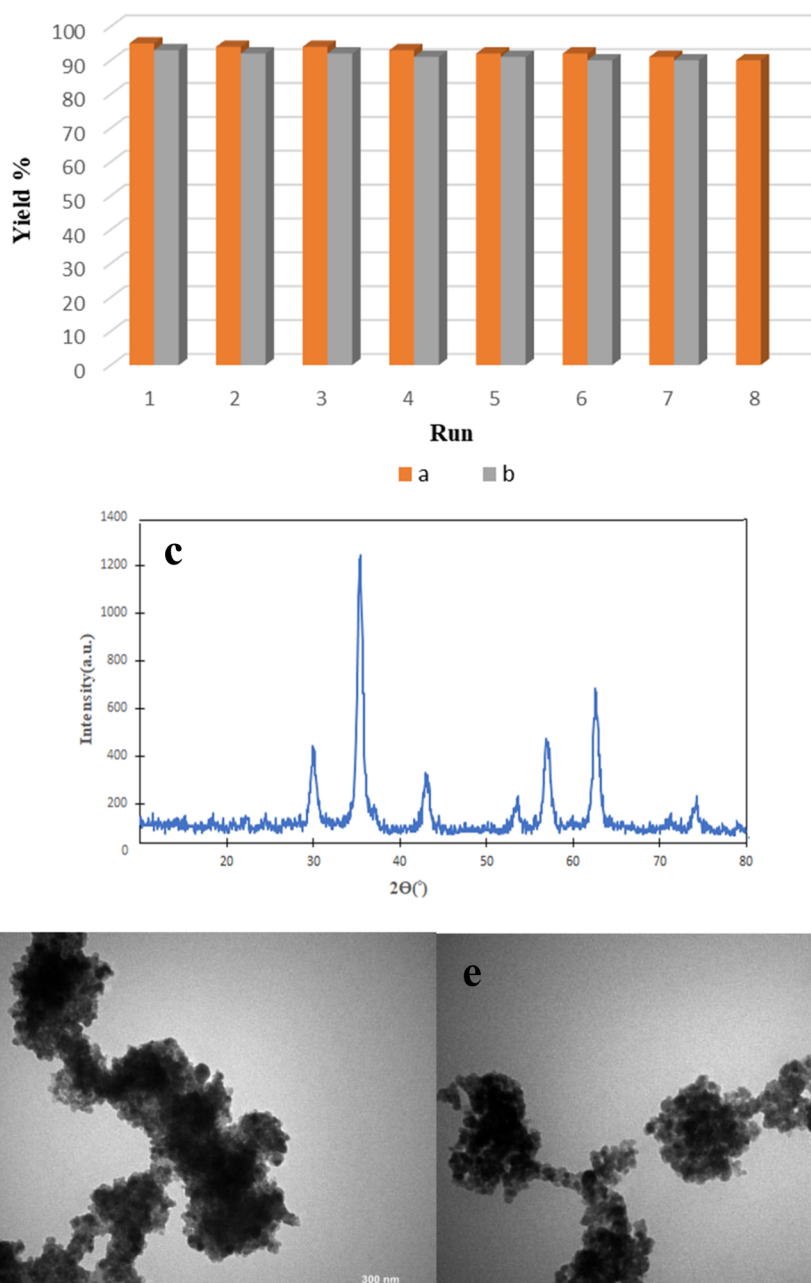
Figure 11. Reusability of the $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ nanocatalyst in the preparation of (a) **4a** and (b) preparation of **7a**, (c) XRD, (d) TEM, and (e) TEM analyses of $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ after 8 and 7 recycling experiments.

The higher activity of the $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ catalyst compared with some other catalysts for the synthesis of product 7a is indicated in Table 6. When H_2SO_4 (Table 6, entry 1), HSO_4Cl (Table 6, entry 2), Fe_3O_4 (Table 6, entry 4), $FeCl_3$ (Table 6, entry 5), $FeSO_4 \cdot 7H_2O$ (Table 6, entry 6), $GPTMS/Fe_3O_4$ (Table 6, entry 7), and $NH_2NH_2/GPTMS/Fe_3O_4$ (Table 6, entry 8) were employed as the catalyst, no yield was obtained for product **7a**, although the moderate yield (58%) was observed when $SO_3H/NH_2NH_2/GPTMS$ was used (Table 6, entry 3)

After optimization, a variety of electron-releasing and electron-withdrawing benzaldehydes were scrutinized for the preparation of derivatives of 3-pyrrolin-2-ones catalyzed by $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ in order to identify the generality and the high proficiency of the catalytic system (Table 7).

Scheme 3 represents a logical mechanism to afford substituted 3-pyrrolin-2-ones in the presence of $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ as an efficient, and reusable nanocatalyst. First, an imine is prepared during the reaction between aromatic aldehyde (**1**) and aniline (**5**). Next, diethyl acetylenedicarboxylate (**6**) during a nucleophilic addition with water forms a 1,3-dipolar intermediate and is added to the imine. Eventually, the desired product with nitrogen-containing five-membered ring (**7a–l**) is achieved through cyclization.

In the next stage, the reusability of the $SO_3H/NH_2NH_2/GPTMS/Fe_3O_4$ nanocatalyst was surveyed through the synthesis of substituted pyrans from dimedone, aldehydes derivatives, and malononitrile in the presence of 0.01 g of the catalyst under reflux conditions in a 1:1 mixture of $H_2O/EtOH$ and the preparation of substituted pyrrolidinone from aniline, aldehyde derivatives, and diethyl acetylenedicarboxylate in the
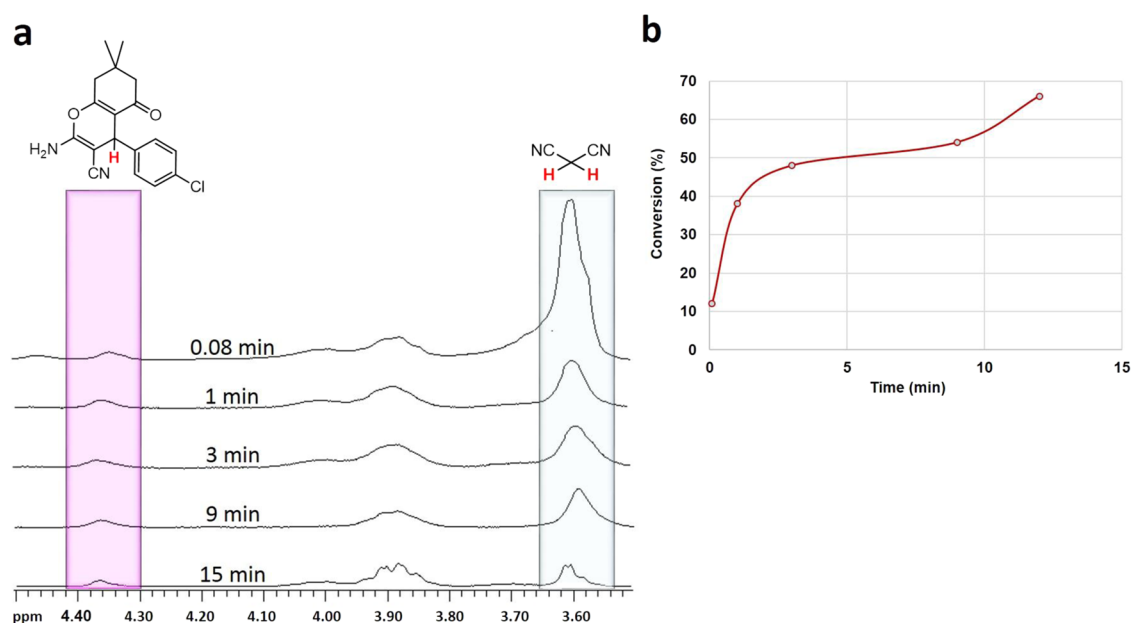
Figure 12. (a) Time-dependent ^{1}H NMR spectra recorded in CDCl$_3$ during the formation of 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile from a reaction mixture of malononitrile (1.0 mmol), dimedone (1.0 mmol), and 4-chlorobenzaldehyde (1.0 mmol), using the SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ nanocatalyst (0.01 g) in H$_2$O/EtOH (1:1) (2 mL) under reflux. (b) Catalytic activity of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ according to the turnover frequency, employing a time below the 50% conversion level for a more accurate comparison (3 min). TOF = (mmol of 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile)/(mmol of sulfur in the catalyst × time).
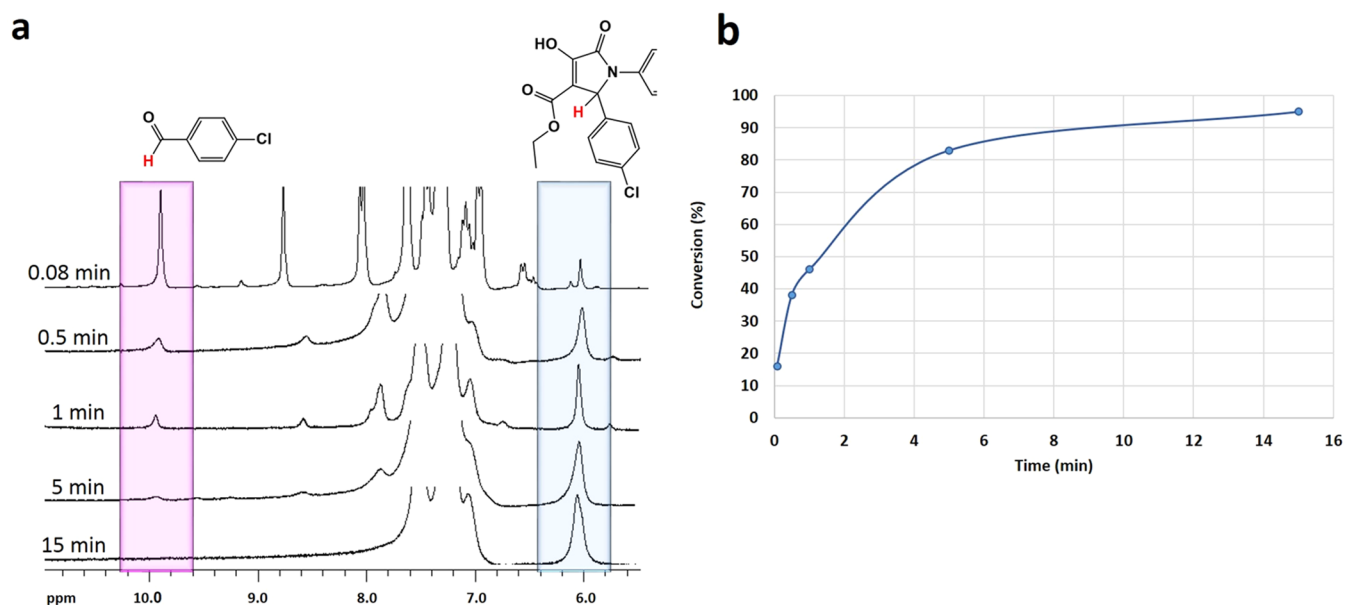
Figure 13. (a) Time-dependent ^{1}H NMR spectra recorded in DMSO during the formation of ethyl 2-(4-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate from a reaction mixture of 4-chlorobenzaldehyde (1.0 mmol), aniline (1.0 mmol), and diethyl acetylenedicarboxylate (1.0 mmol) using a SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ nanocatalyst (0.015 g) in EtOH (2 mL) at 50 °C. (b) Catalytic activity of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ according to the turnover frequency, employing a time below the 50% conversion level for a more accurate comparison (1 min). TOF = (mmol of ethyl 2-(4-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate)/(mmol of sulfur in the catalyst × time).

presence of 0.015 g of the catalyst in ethanol at 50 °C. The nanocatalyst was reused for 8 cycles with the aim of preparing 4a and for 7 cycles aimed at preparing 7a according to the model reactions with an insignificant loss in its efficiency from 95 to 90% and from 93 to 90%, respectively (Figure 11). After recycling for 8 runs in the preparation of **4a** and for 7 runs in the preparation of **7a**, the XRD, TEM, and BET analyses for SO$_3$H/

NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ were performed. The XRD analysis of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ after 8 runs is represented in Figure 11c. The average crystallite size of the reused catalyst is ~30.38 nm, obtained by the Debye−Scherrer equation. One can find TEM analyses of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ after 8 runs in the preparation of **4a** and 7 runs of recycling in the preparation of **7a** Figure 11d,e. The TEM image of the fresh

Table 8. Comparison of the Performance of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ with Those of Some Other Catalysts for the Formation of 4a[a]

entry	catalyst	condition	time (min)	yield (%)[b]	reference
1		H$_2$O/EtOH, reflux	120	25	
2	MNPs-PhSO$_3$H (0.01 g)	H$_2$O/EtOH (1:1), 100 °C	15	90	62
3	Fe$_3$O$_4$@SiO$_2$@5-SA (0.02 g)	H$_2$O, 60 °C	100	92	63
4	Fe$_3$O$_4$@g-C$_3$N$_4$ (0.02 g)	EtOH, 60 °C	60	95	64
5	MNPs@Cu (10 mg)	solvent-free, 90 °C	15	93	65
6	DAHP (10 mol %)	H$_2$O/EtOH, 25 °C	240	85	66
7	Fe$_3$O$_4$/SiO$_2$-Met NPs (0.03 g)	H$_2$O/EtOH, reflux	60	86	67
8	t-ZrO$_2$ NPs (10 mol %)	H$_2$O, 80 °C	38	89	68
9	urea (10 mol %)	H$_2$O/EtOH, 25 °C	420	93	69
10	Fe$_3$O$_4$@SiO$_2$@propyl-ANDSA	H$_2$O, reflux	30	83	70
11	KF/Al$_2$O$_3$ (250 mg)	DMF, r.t.	60−180	81	71
12	Fe$_3$O$_4$@Ph-SO$_3$H (0.2 mol %)	H$_2$O, 50 °C	25	88	72
13	NiFe$_2$O$_4$@SiO$_2$@H$_{14}$[NaP$_5$W$_{30}$O$_{110}$] (0.02 g)	EtOH, reflux	20	67	73
14	SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$	H$_2$O/EtOH, reflux	15	95	this work

[a]Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol) and dimedone (1 mmol), solvent (2 mL), and catalyst. [b]Isolated yield.

Table 9. Comparison of the Performance of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ with Those of Some Other Catalysts for the Preparation of 7a[a]

entry	catalyst	condition	time (min)	yield (%)[b]	reference
1		EtOH, 50 °C	54		
2	CoFe$_2$O$_4$@silica-SO$_3$H (0.01 g)	EtOH, 60 °C	720	90	61
3	CoFe$_2$O$_4$@CA (75 mg)	EtOH, r.t.	720	89	60
4	citric acid monohydrate (2 mmol)	EtOH, r.t.	600	86	27
5		lactic acid	120	76	74
6		acetic acid	120	33	74
7	SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$	EtOH, 50 °C	15	93	this work

[a]Reaction conditions: 4-chlorobenzaldehyde (1 mmol), aniline (1 mmol) and diethyl acetylenedicarboxylate (1 mmol), solvent (2 mL), catalyst. [b]Isolated yield.
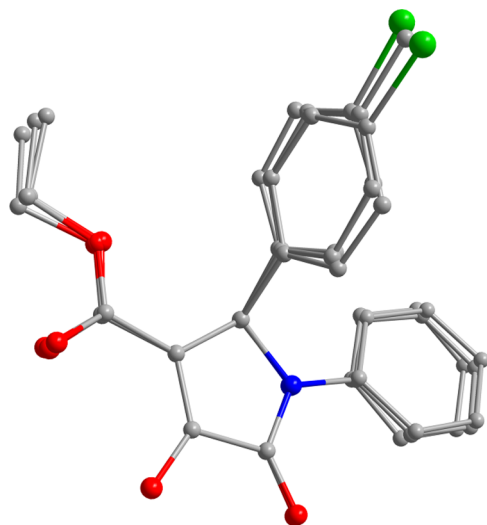
Figure 14. Comparison of the conformations of **7a** (two different molecules) and **7d**. The common reference points are pyrroline atoms. Hydrogen atoms are omitted for clarity. Color scheme: gray: C, blue: N, red: O, and green: Cl.

catalyst indicated the core−shell structure (Figure 6c) with a uniform size distribution diagram and an average size of 47−65 nm (Figure 6d). As can be seen, almost all SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ particles with the same size and morphology as the fresh catalyst confirm the spherical shape and the size of

these particles is in the range of 50−69 nm. Furthermore, BET analyses for SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ after 8 runs of recycling in the preparation of **4a** and 7 runs of recycling in the preparation of 7a were performed. The total pore volume, surface area, and the mean pore diameter of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ after 8 runs of recycling in the preparation of **4a** and 7 runs of recycling in the preparation of 7a were determined to be 0.1962 cm^3 g^{-1} and 33.031 m^2 g^{-1}, and 30.256 nm, and 0.2160 cm^3 g^{-1}, 34.301 m^2 g^{-1}, and 32.500 nm, respectively.

As a case study, the ^{1}H NMR spectrum of the reaction mixture of malononitrile (1.0 mmol), dimedone (1.0 mmol), and 4-chlorobenzaldehyde (1.0 mmol) in H$_2$O/EtOH (1:1) (2 mL) under reflux was employed to investigate the catalytic activity of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$, giving a turnover frequency of 504 h^{-1} (Figure 12).

As a case study, the ^{1}H NMR spectrum of the reaction mixture of 4-chlorobenzaldehyde (1.0 mmol), aniline (1.0 mmol), and diethyl acetylenedicarboxylate (1.0 mmol) in EtOH (2 mL) at 50 °C was employed to investigate the catalytic activity of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$, giving a turnover frequency of 1474 h^{-1} (Figure 13).

As shown in Tables 8 and 9, the yields and reaction times were tabulated in order to compare the performance of SO$_3$H/NH$_2$NH$_2$/GPTMS/Fe$_3$O$_4$ with the results reported by some other catalysts for the formation of **4a** and 7a. According to the results mentioned in Tables 8 and 9, it is clear that the short reaction time and high efficiency related to our method make this route useful as a protocol. Also, the new nanocatalyst has

Figure 15. Non-centrosymmetric molecular dimer observed in **7a** (a) compared with the centrosymmetric molecular dimer in **7d** (b). Top (left panel) and side (right panel) views are shown. Hydrogen bonds are shown in black, dotted lines. Some of the atoms in the figures on the right panel are omitted for clarity. Color scheme: gray: C, white: H, blue: N, red: O, and green: Cl.

unique features such as easy separation, non-toxicity, and good stability.

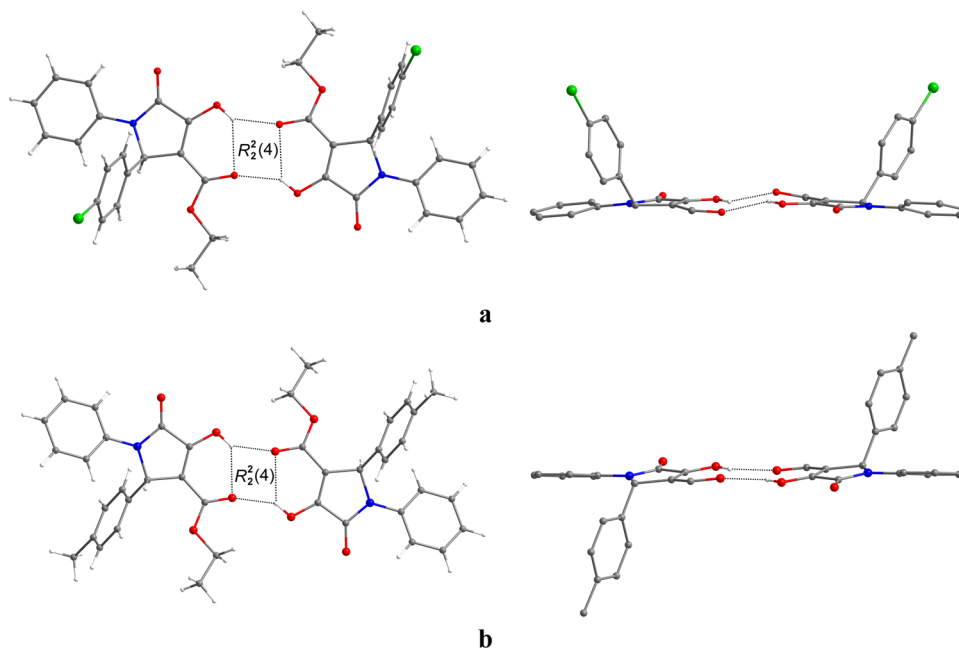The crystal structures of two compounds (**7a** and **7d**) were confirmed by single-crystal X-ray analysis. Both crystals are centrosymmetric and contain racemic compounds. There is one molecule in the asymmetric unit of crystal **7d** and two crystallographically different molecules in the crystal of **7a** (asymmetric units with atom-numbering schemes of both structures are presented in Figure S1). Conformations of the three of them are almost the same (Figure 14). As previously observed in analogous compounds [66,106,118,120,121,135,-136], in the case of both crystals presented here, molecules form dimers via O−H···O hydrogen bonds giving intradimeric $R_2^2(4)$ ring motifs (centrosymmetric in **7d** and non-centrosymmetric in **7a**) (Figure 15). Chlorine atom in **7a** is involved in the formation of hydrogen bonds with the CH group of the phenyl ring (Figure S2). Also, some details of the geometry of selected hydrogen bonds and selected geometric parameters are given in Tables S2 and S3.

4. CONCLUSIONS

SO$_3$H-functionalized epoxy-immobilized Fe$_3$O$_4$ core−shell MNPs as an effectual, reusable, and eco-friendly nanocatalyst was applied for the sustainable and green synthesis of pyran and pyrrolidinone derivatives. This synthesized nanocatalyst was prepared by employing a three-step procedure and investigated by utilizing FT-IR, BET, EDX, PXRD, SEM, VSM, TGA, TEM, and DTG. The isolation of the nanocatalyst from the reaction mixtures was carried out simply by applying a simple external magnetic field and reused for 8 cycles in the preparation of tetrahydrobenzo[*b*]pyran and 7 runs in the preparation of 3-pyrrolin-2-ones according to the model reactions with an insignificant loss in its efficiency. Some amazing advantages of the present methodology are the use of a recyclable and easily reusable catalyst, mild reaction conditions, use of a green solvent, eco-friendliness, low catalyst loading, and separation of products from the reaction mixtures without the requirement of a chromatographic column in high to excellent yields.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c01068.

Copies of FT-IR, ^{1}H NMR, and ^{13}C NMR spectra, and crystallographic data for some synthesized products (PDF)

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