Silicon (2019) 11:2933–2943
https://doi.org/10.1007/s12633-019-0087-2

ORIGINAL PAPER

Sulfonic Acid-Functionalized Silica-Coated Magnetic Nanoparticles as a Reusable Catalyst for the Preparation of Pyrrolidinone Derivatives Under Eco-Friendly Conditions

Zahra Hosseinzadeh[1] · Ali Ramazani[1] · Hamideh Ahankar[2] · Katarzyna Ślepokura[3] · Tadeusz Lis[3]

Received: 21 November 2018 / Accepted: 17 January 2019 / Published online: 22 January 2019

Abstract

The surface of silica-coated $CoFe_2O_4$ magnetic nanoparticles ($CoFe_2O_4@SiO_2$), which is resistant to the oxidation due to silicone coating, was functionalized using chlorosulfonic acid and used as an efficient and recyclable catalyst for the preparation of 3-pyrrolin-2-ones from diethyl acetylenedicarboxylate, an aldehyde and aniline in ethanol solvent at 60 °C. In the presented study, some fascinating chracterities of such catalyst, such as magnetically separable, simple workup and obtaining a high purity of products by simple recrystallization, have been successfully obtained. The structural features of $CoFe_2O_4@SiO_2\text{-}SO_3H$ catalyst were elucidated by X-ray powder diffraction (XRPD), thermo-gravimetric studying (TGA), scanning electron microscopy (SEM) and FT-IR spectra.

Keywords Cobalt ferrite · Silica-coated · Sulfonic acid-functionalized · Reusable catalyst · Magnetic nanoparticles · 3-pyrrolin-2-ones

1 Introduction

In recent years, Fe_3O_4 magnetic nanoparticles (MNPs) have been extremely studied due to their significant characteristics such as unique size, high saturation magnetization, low-cost, non-toxicity, and biocompatibility. They are also green, enevironmentally-friendly and reusable. Although magnetic nanoparticles (MNPs) are easily separable by an external magnet, the naked MNPs are sensitive to air oxidation and tend to aggregate, so the surface coating of the iron oxide nanoparticles is essential. Silica is one of the most common coating layers because of its strange characteristics such as stability, non-toxicity, and inactivity. Also, the surface functionalization of silica is easy [1–5]. In this work, we prepared $CoFe_2O_4$, that is more stable than Fe_3O_4, by the simple procedure without N_2 atmosphere usage and used as an efficient catalyst in the preparation of several derivatives of pyrrolidinone.

Multi-component reactions (MCRs) have been introduced as an efficient synthetic method to prepare various and complicated molecular structures. High yields of products, easy methods without any isolation of intermediates and the complexity of the resultant products are some advantages of these reactions [6–11].

Among the heterocyclic compounds, nitrogen-containing heterocyclic compounds have played a very significant role in drugs discovery. The heterocyclic compounds containing 2-pyrrolidinone core (Fig. 1) are one of the important classes of heterocyclic compounds owing to their existence in natural products and their biological activity [12, 13]. Many of natural products are 2-pyrrolidinone scaffold included such as Holomycin and Thiolutin [14], Thiomarinol A4 [15], Oteromycin [16], Pyrrocidine A, B [17], Quinolactacin C [18], Ypaoamide [19], Lactacystin [20], Salinosporamide A [21] and (−)-Azaspirene [22] (Fig. 2). In particular, 2-Pyrrolodinones are found to possess a wide range of pharmacological effects like antibacterial, antifungal [23], antitumor [24] and anticonvulsant [25].

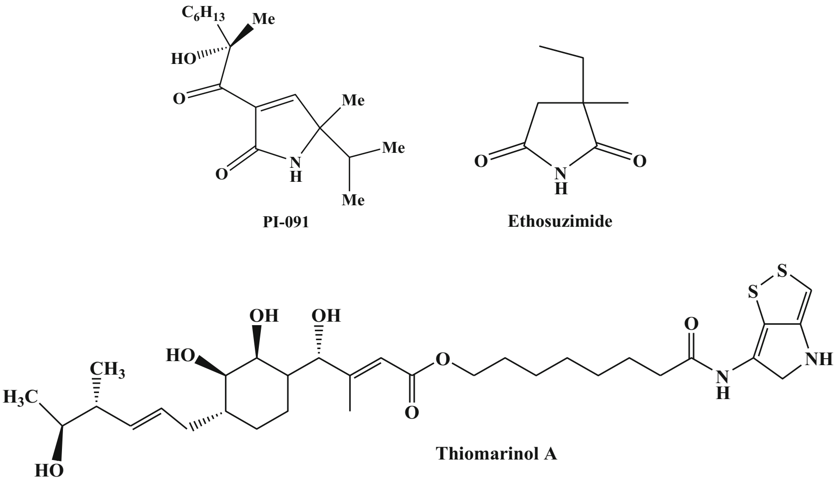
✉ Ali Ramazani
aliramazani@gmail.com

[1] Department of Chemistry, University of Zanjan, P O Box 45195-313, Zanjan, Iran

[2] Department of Chemistry, Abhar Branch, Islamic Azad University, Abhar, Iran

[3] Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie St, 50383 Wrocław, Poland

Fig. 1 Selected drugs containing 2-pyrrolidinone core



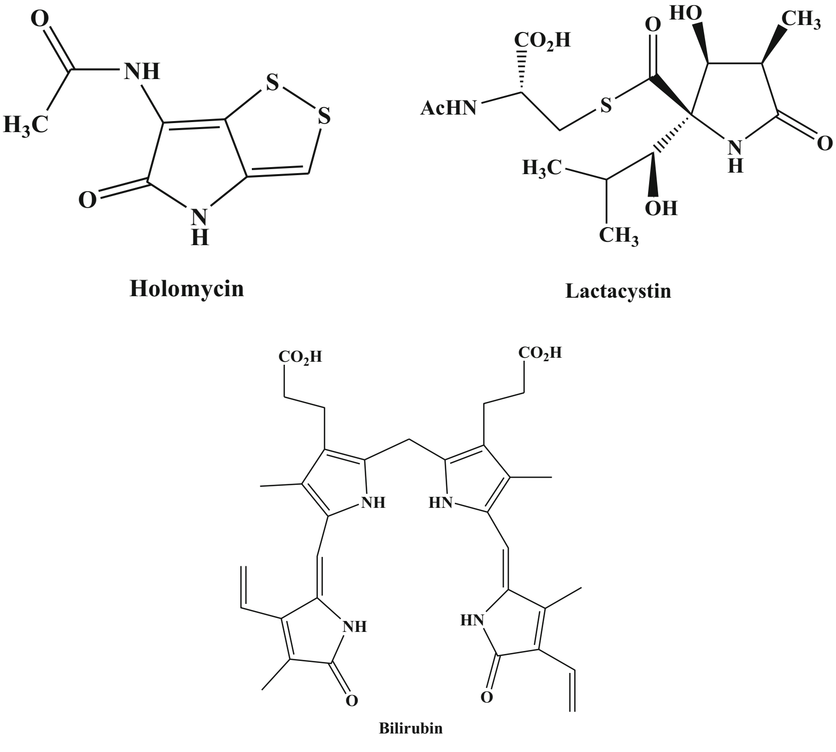
In this work, regarding green chemistry, we presented the synthesis of $CoFe_2O_4$@Silica sulfuric acid, as an effective and recyclable additive, for the preparation of pyrrolidinone analogs under eco-friendly conditions as demonstrated in Scheme 1. Two of the products which have not been reported previously were elucidated by FT-IR, ^{1}H-NMR, ^{13}C-NMR spectra and melting point. Melting points of the known products were compared with reported values in the literature as shown in Table 4. The crystal structure of **4c** was also verified by X-ray studying.

2 Experimental

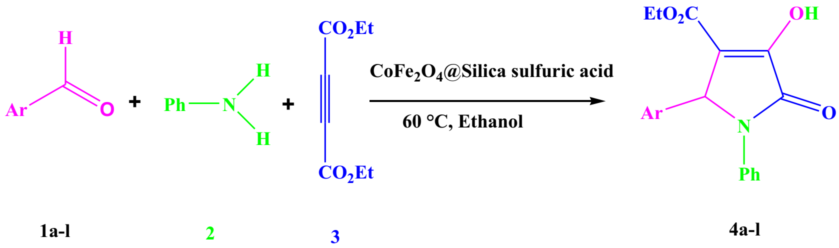
2.1 Materials and Methods

Chemical reagents were provided by Merck, Fluka, and Aldrich. TLC was utilized to follow the reactions. Fourier transform infrared spectra were measured with a Mattson (UnicamLtd.,Cambridge,UK). ^{1}HNMR ($CDCl_3$) and ^{13}CNMR ($CDCl_3$) spectra were recorded on a Bruker DRX-250 Avance spectrometer at 250.13 and 62.90 MHz, respectively. X-ray powder diffraction

Fig. 2 Selected natural products containing 2-pyrrolidinone core



Scheme 1 Preparation of functionalized pyrrolidinone under eco-friendly conditions



(XRPD) information were gathered with an XD-3A diffractometer using Cu Kα radiation. The particle size and morphology of the $CoFe_2O_4$@SiO_2 sulfuric acid were investigated by a scanning electron microscope (ZeissEVO18). The amount of sulfuric acid coated on the magnetic nanoparticles was studied by the thermogravimetric analyzer (TGA; STA 1500 tool).

2.2 Preparation of $CoFe_2O_4$ MNPs

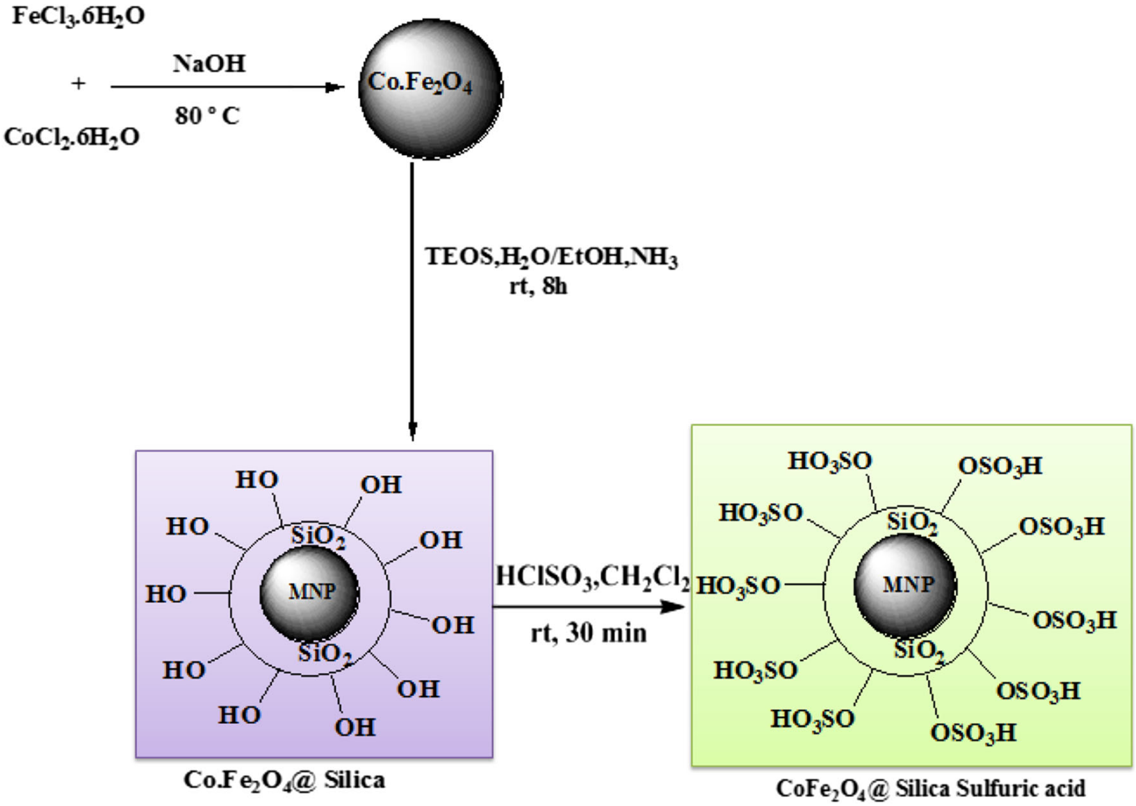
Initially, $FeCl_3·6H_2O$ (0.54 g) and $CoCl_2·6H_2O$ (0.238 g) were dissolved in a 10 ml deionized in a 1:2 M ratio. Next, to this solution dissolved NaOH (1.2 g) in 10 ml was added to this solution and stirred for 30 min at 80 °C. The nanomagnetic particles were gathered by an external magnetic and dried after washing with deionized water [2].

2.3 Preparation of $CoFe_2O_4$@Silica

$CoFe_2O_4$@SiO_2 were provided by the sol-gel method. In the other words, $CoFe_2O_4$@SiO_2 was provided by the ammonia-catalyzed reaction of tetraethyl orthosilicate (TEOS) in a water-ethanol solution. In this step, 20 ml of deionized water and 70 ml of ethanol were added to the mixtures of $CoFe_2O_4$ (1 g) and 4 ml of ammonia (25 wt%). 0.5 ml of TEOS was added after dispersing by ultrasonication for 10 min. After stirring eight hours, silica was then constituted on the surface of the $CoFe_2O_4$, following which the MNPs was gathered by magnet and washed with water and ethanol to give $CoFe_2O_4$@SiO_2 [26].

2.4 Preparation of $CoFe_2O_4$@Silica-SO_3H

$CoFe_2O_4$@Silica (2.5 g) MNPs were dispersed in dry CH_2Cl_2 (75 ml) by ultrasonics for 10 min. Afterwards, dissolved



Scheme 2 Synthesis of $CoFe_2O_4$@Silica sulfuric acid

Table 1 Structure refinement and crystal data of **4c**

Chemical formula	$C_{23}H_{19}NO_4$
M_r	373.39
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	90(2)
a, b, c (Å)	13.319(4), 6.138(2), 22.702(7)
β (°)	92.42(3)
V (Å^3)	1854.3(10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.37 × 0.34 × 0.18
Absorption correction	Multi-scan
$T_{\min}$, $T_{\max}$	0.964, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10,043, 5193, 4155
R_{int}	0.030
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.718
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.121, 1.02
No. of reflections	5193
No. of parameters	258
No. of restraints	0
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.40, −0.21

$ClSO_3H$ (15 mmol, 1 ml, 1.75 g, ca.) in CH_2Cl_2 (20 ml) was increased in 30 min by dropping funnel and the remaining HCl was finally removed by suction. Eventually, $CoFe_2O_4$@Silica-SO_3H was dried at 60 °C [27] (Scheme 2).

2.5 General Experimental Approach for the Preparation of 3-Pyrrolin-2-Ones Derivatives

A mixture of aldehyde **1a-l** (1 mmol), aniline **2** (1 mmol), diethyl acetylenedicarboxylate **3** (1 mmol) and $CoFe_2O_4$@Silica sulfuric acid (0.01 g) was stirred in ethanol solvent at 60 °C. To follow the reaction, TLC was used (*n*-Hexane: EtOAc, 10:7), afterwhich the desired products were heated in ethanol solvent until dissolved. The nanocatalyst was magnetically separated from the reaction mixture and washed three times by ethanol solvent for recovery. The pure products were provided by recrystallization from hot ethanol.

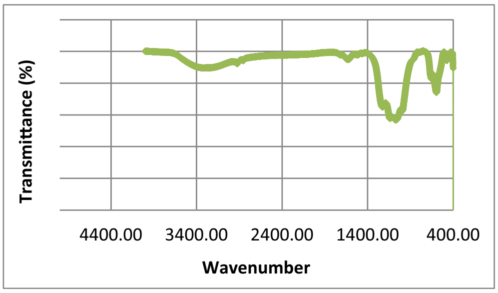


Fig. 3 IR spectra of Cobalt ferrite sulfonic acid-functionalized MNPs

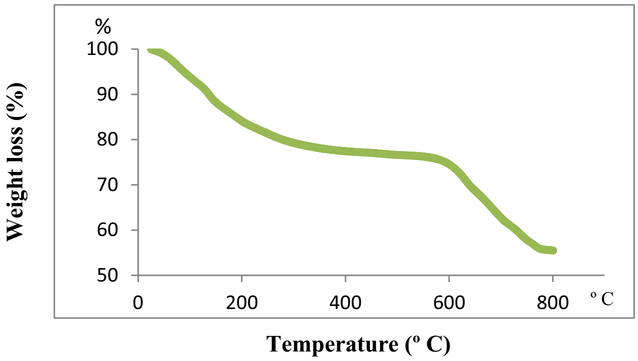


Fig. 4 TGA curves of $CoFe_2O_4$@Silica sulfuric acid MNPs

2.6 Spectral Data of Selected Products

4 h m.p. 185–188 °C, IR: $\nu_{\max}$/ cm^{-1} 3296, 2926, 1718, 1690, 1443, 1138 cm^{-1}, ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ_H 1.18 (t, 3H, $J = 7.01$ Hz), 4.17 (q, 2H, $J = 7.01$ Hz), 5.70 (1H, s), 6.68–7.45 (m, 9H), 9.08 (s, 1H); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ_C 13.93, 60.84, 61.30, 112.92, 115.47(d, $^2J_{CF} =$ 22.01 Hz), 122.37, 125.99, 129.04, 129.14 (d, $^3J_{CF} =$ 08.80 Hz), 130.83, 136.00, 156.45, 160.57 (d, $^1J_{CF} =$ 247.82 Hz), 162.70, 164.93.

4i m.p. 203–206 °C. IR: $\nu_{\max}$/ cm^{-1} 3298, 1726, 1494, 1024 cm^{-1}; ^{1}H NMR (250.13 MHz, $CDCl_3$) δ_H 1.17 (t, 3H, $J = 7.01$ Hz), 4.15 (q, 2H, $J = 7.01$ Hz), 6.10 (1H, s), 6.16–7.81 (m, 9H), 9.10 (s, 1H) ^{13}C NMR (62.90 MHz, $CDCl_3$) δ_C 13.71, 54.00, 61.25, 112.30, 115.49 (d, $^2J_{CF} = 22.01$ Hz), 121.69, 124.53, 125.86, 127.59, 129.05, 130.16 (d, $^3J_{CF} = 8.17$ Hz), 136.05, 157.01, 159.29 (d, $^1J_{CF} = 248.45$ Hz), 164.96.

2.7 X-Ray Crystallography

White solid of **4c** was heated in ethanol solvent until it dissolved and crystals of **4c** were prepared by slow evaporation procedure in excellent yields.

The crystallographic measurement of **4c** was carried out on a κ-geometry Agilent Technologies Xcalibur R (ω scans) automated four-circle diffractometer supplied

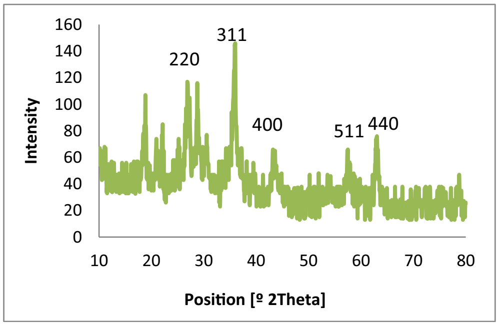


Fig. 5 XRPD pattern of $CoFe_2O_4$@Silica sulfuric acid MNPs

by graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) and a CCD camera Ruby. The information were gathered at 90(2) K through utilizing the Oxford-Cryosystems cooler. Information accumulation, cell purification and information decrement were performed with Xcalibur software, *CrysAlisPRO* [28]. Empirical (multi-scan) absorption amendment was also used. Structure was solved with direct procedures utilizing SHELXT-2014 and then purified by a full-matrix least-squares method by the use of anisotropic thermal parameters for non-H atoms with an utilizing of SHELXL-2014 [29]. All of the H atoms were refined isotropically and found in difference Fourier maps. At the end purification cycles, the C-bonded H atoms were replaced in their computed locations with C–H = 0.95–1.00 Å, and with U_{iso}(H) = 1.2U_{eq}(C) for CH and CH_2, and 1.5U_{eq}(C) for CH_3. The hydroxyl H atom was freely purified. Diamond program was applied for the making Figures [30]. Structure refinement data are brought in Table 1.

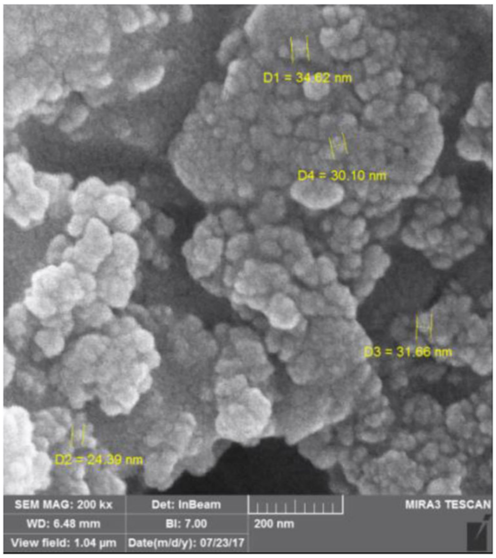


Fig. 6 SEM image of $CoFe_2O_4$@Silica sulfuric acid MNPs

Table 2 The impact of different quantity of catalyst in the formation of **4d**[a]

Entry	Catalyst (g)	Time (h)	Yield (%) [b]
1	None	14	–
2	0.005	14	59
3	0.009	12	78
4	0.010	12	90
6	0.020	12	84

[a] Reaction conditions: 4-chlorobenzaldehyde **1d** (1 mmol), aniline **2** (1 mmol) $C_8H_{10}O_4$ **3** (1 mmol) and $CoFe_2O_4$@Silica-SO_3H as a catalyst in ethanol at 60 °C

Table 3 Impact of solvents in the preparation of functionalized pyrrolidinones[a]

Entry	Solvent	T (°C)	Catalyst (g)	Time (h)	Yield (%)
1	H_2O	Reflux	0.01	14	35
2	C_2H_5OH	Reflux	0.01	14	76
3	Acetonitrile	Reflux	0.01	14	68
4	Ethanol	60	0.01	12	90
5	Solvent-free	60	0.01	12	48

[a] Reaction conditions: 4-chlorobenzaldehyde **1d** (1 mmol) aniline **2** (1 mmol) diethyl acetylenedicarboxylate

3 (1 Mmol) and $CoFe_2O_4$@SiO_2/SO_3H (0.01 g) as a Catalyst in Various Solvents

3 Results and Discussion

3.1 Catalyst Characterization

Magnetic cobalt ferrite nanoparticles, with sized between of 24 and 34 nm, were prepared by the co-precipitation and sol–gel procedure [2]. The hydrolysis and condensation of TEOS on surface iron hydroxyls are based on the sol–gel process. Therefore, the SiO_2 coating provides reaction sites for more modification and stability. Finally, $CoFe_2O_4$@SiO_2–SO_3H is formed via the mixing of the $CoFe_2O_4$@SiO_2 and chlorosulfuric acid in CH_2Cl_2 [27, 31].

The structural characteristics of the $CoFe_2O_4$@SiO_2-SO_3H catalyst were studied via scanning electron microscopy (SEM), TGA, IR spectra and X-ray powder diffraction (XRPD). The FT-IR spectra of $CoFe_2O_4$@Silica-SO_3H MNPs are illusrtated in Fig. 3. The FT-IR analysis of the $CoFe_2O_4$@Silica sulfuric acid indicates two basic distinctive peaks at ~ 3300 cm^{-1} (O–H stretching) and 591 cm^{-1} (M–O vibration) [32]. The peaks at 1061 cm^{-1}, 1073 cm^{-1}, and 474 cm^{-1} belong to the Si–O–Si group. The bands at 1217 cm^{-1} and 1124 cm^{-1} also confirm the presence of sulfonyl group in $CoFe_2O_4$@Silica-SO_3H [33].

Figure 4 delineates the TGA curves of $CoFe_2O_4$@Silica sulfuric acid powder. The weight loss at temperatures below 150 °C is due to the elimination of surface hydroxyl groups and physically adsorbed solvent. A weight loss that is observed between 600 and 800 °C pertain to the loss of SO_3H groups [34].

XRPD was utilized to describe the crystallinity of NPs. In addition, it presents an average diameter of all the NPs. The XRPD pattern of the $CoFe_2O_4$@Silica-SO_3H magnetic nanoparticles sample is demonstrated in Fig. 5. Data demonstrate that the discernible peaks in Fig. 5 were indexed to (220), (311), (400), (511) and (440) planes of a cubic unit cell (card no. 00–001-1121). The diameter of the $CoFe_2O_4$ was

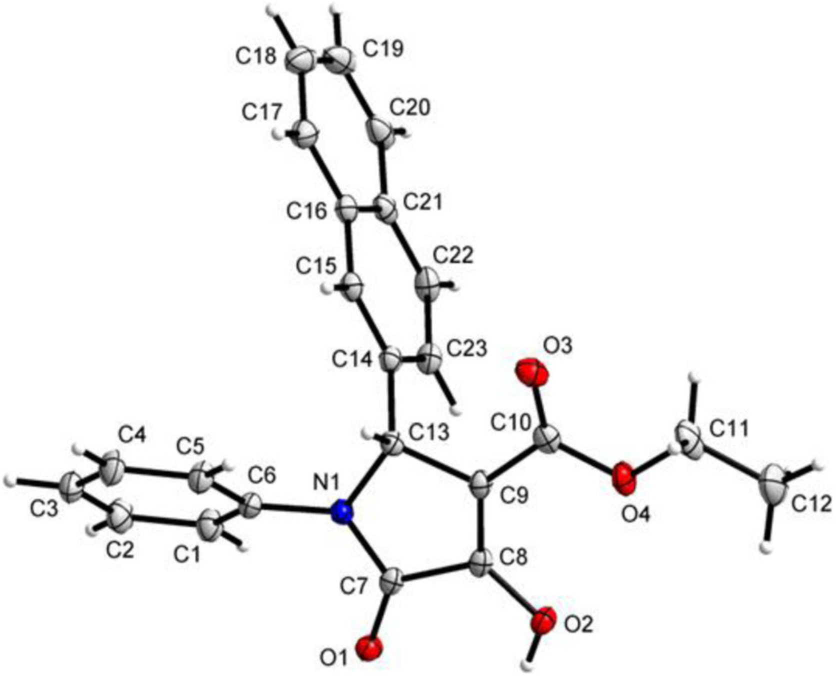


Fig. 7 The atom-numbering scheme was demonstrated by X-ray structure of **4c**

measured by the Debye-Scherrer equation with XRPD information (D = 0.94 λ/B Cos θ) 33 nm.

The Scanning electron microscopy (SEM) analysis suggests that the $CoFe_2O_4$@Silica sulfuric acid have nanocrystalline phase and their shape is spherically ranging from 24 to 34 nm (Fig. 6).

After the synthesis and characterization of $CoFe_2O_4$@Silica sulfuric acid, catalytic role of this MNPs was investigated in the preparation of functionalized 3-pyrrolin-2-ones from the reaction of aniline, diethyl acetylenedicarboxylate, and 4-chlorobenzaldehyde in ethanol solvent at 60 °C as a template reaction.

Scheme 3 Plausible reaction mechanism

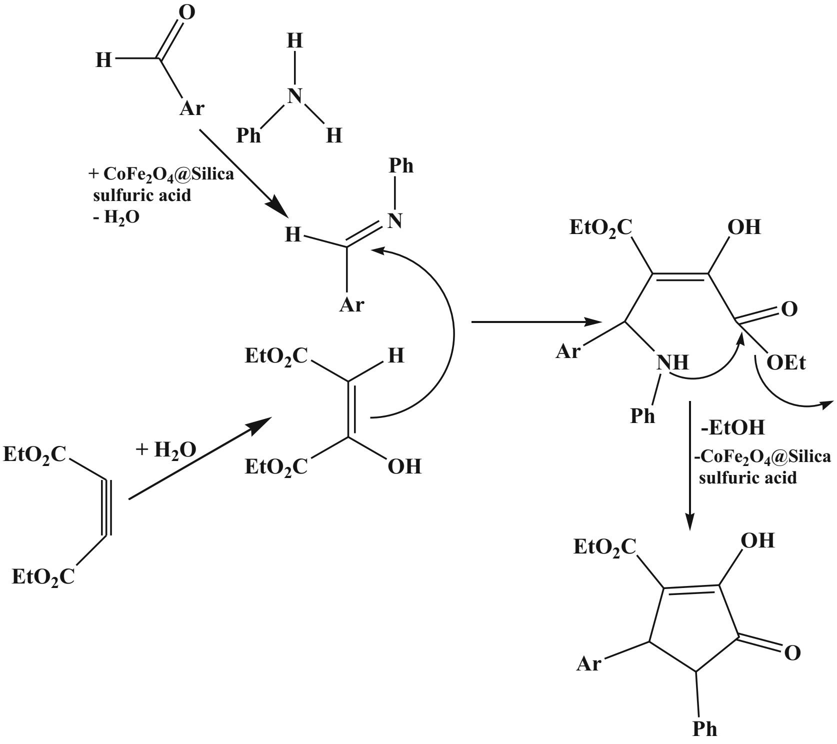


Table 4 Three-component condensation of aldehyde **1a-l,** aniline and diethyl acetylenedicarboxylate for the formation of 3-pyrrolin-2-ones

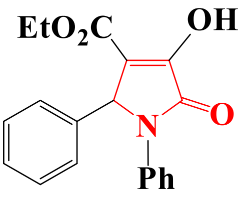
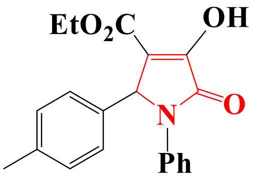
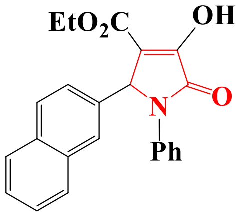
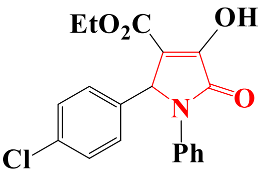
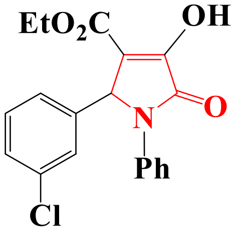
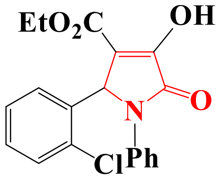
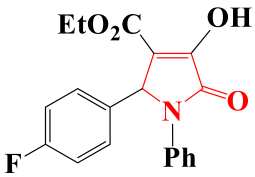
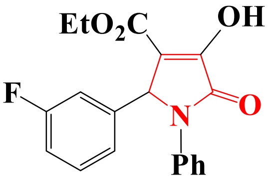
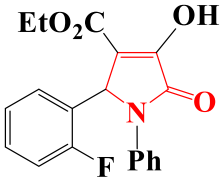
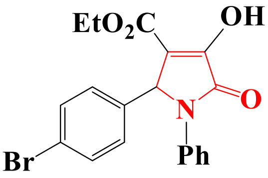
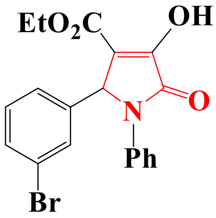
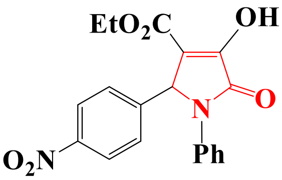
Entry	Ar	Time (h)	Product	Yield (%)	M.P (º C)	References
1	Ph	12	 **4a**	88	175-178	174-177 [35]
2	4-Me-C_6H_4	12	 **4b**	88	201-204	202-205 [35]
3	2-Naphthal	12	 **4c**	86	226-229	225-228 [35]
4	4-Cl-C_6H_4	12	 **4d**	90	194-197	195-198 [35]
5	3-Cl-C_6H_4	12	 **4e**	92	184-186	184-187 [35]
6	2-Cl-C_6H_4	12	 **4f**	90	203-206	204-207 [35]

Table 4 continued

7	4-F-C_6H_4	12	 **4g**	88	192-195	193-196 [35]
8	3-F-C_6H_4	12	 **4h**	92	184-187	-
9	2-F-C_6H_4	12	 **4i**	87	202-205	-
10	4-Br-C_6H_4	12	 **4j**	92	190-192	190-193 [35]
11	3-Br-C_6H_4	12	 **4k**	86	191-194	192-194 [35]
12	4-NO_2-C_6H_4	12	 **4l**	86	181-182	181-183 [35]

Reaction conditions: aldehyde **1a-l** (1 mmol), aniline **2** (1 mmol), diethyl acetylenedicarboxylate **3** (1 mmol) and $CoFe_2O_4$@Silica-SO_3H (0.01 g) as a catalyst in ethanol at 60 °C

To optimize the reaction situations, we investigated the effect of solvents, catalyst quantity and reaction time. At the beginning, the amount of the catalyst was studied in a template reaction of 4-chlorobenzaldehyde **1d** (1 mmol), diethyl acetylenedicarboxylate **3** (1 mmol) and aniline **2** (1 mmol) in the formation of product **4d.** The greatest yield of products was acquired when 0.01 g of $CoFe_2O_4$@Silica sulfuric acid was used as a catalyst for the reaction (Table 2).

Table 5 Elected torsion angles (°) and bond lengths (Å) of **4c**

O1—C7	1.2320(16)	N1—C6	1.4288(16)
O2—C8	1.3263(15)	N1—C13	1.4797(16)
N1—C7	1.3585(16)		
C7—N1—C6—C1	−50.97(19)	C7—N1—C13—C14	118.66(11)
C11—O4—C10—C9	−174.62(11)	N1—C13—C14—C15	115.38(13)
C8—C9—C10—O4	8.7(2)	C9—C13—C14—C15	−130.38(12)
C10—O4—C11—C12	−172.12(13)		

Then, various solvents, like H_2O, C_2H_5OH and CH_3CN, were evaluated in the preparation of **4d** (Table 3) just for improving the products yoelds. Since the solvent-free reaction that provided low yields of desired products (48%), so the presence of solvent is fundamental for this reaction. According to Table 2, ethanol as a green solvent was found to be most efficient among all the tested solvents because it has a suitable dissolving ability of the starting material. It is also noteworthy saying that water was less likely to give the satisfactory result as the starting materials were not dissolved as well in water, so ethanol was selected as an efficient solvent (Table 3).

After finding suitable conditions, the three-component reaction of diethyl acetylenedicarboxylate, some aldehydes **1a-l** and aniline were performed in ethanol solvent at 60 °C. In this method, different aldehydes, with electron-donating substituents and electron-withdrawing on the aromatic ring, were tested. The structures of all the synthesized products **4a-l** were elucidated by their FT-IR, ^1H NMR and ^{13}C NMR spectroscopic data. [35]. The crystal structure of **4c** was also verified by X-ray studying (Fig. 7).

In Scheme 3, a reasonable mechanism is brought for the preparation of functionalized pyrrolidinone (**4a-l**). One molecule of aniline was firstly condensed with an aromatic aldehyde,that activated by $CoFe_2O_4$@Silica sulfuric acid, to provide imine. Then, the nucleophilic addition of diethyl acetylenedicarboxylate to imine followed by cyclization which provides target product [35] Table 4.

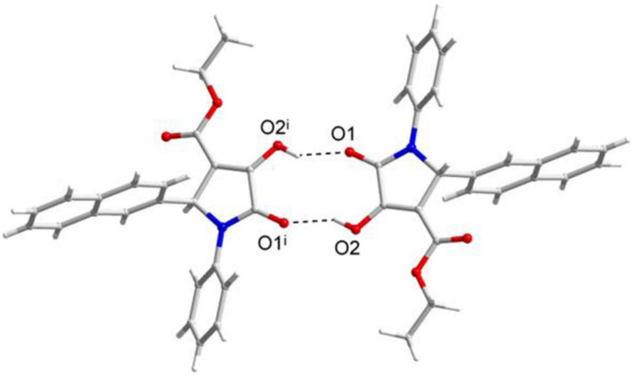


Fig. 8 Two molecules of **4c** joined by two O–H…O hydrogen links formed Centrosymmetric molecular dimers, giving raise to $\left[R_2^2(10)\right]$ ring motifs

Component crystallizes in the centrosymmetric space group, so it is racemic. The elected geometrical parameters are brought in Table 5. Interestingly, the Ph ring is significantly twisted relative to the pyrroline ring (see the C7—N1—C6—C1 torsion angle). Like it was previously observed in the analogous compounds [35, 36], in **4c** the C(O)OEt group is almost coplanar with the plane of the 3-pyrroline-2-one and also it is flat. The molecule adopts C=O$_{ester}$, C–OH antiperiplanar conformation, which is the same arrangement as in the N-(4-Cl-Ph)–4-C(O)OMe–5-Ph derivative [36], but different to conformation observed in N-Ph–4-C(O)OEt–5-(4-F-Ph) compound [35]. In the flint glass lattice as a result of different mutual orientation of C=O$_{ester}$ and C–OH groups, different molecular dimers are observed (Fig. 8). Two molecules of various chirality in the crystal of **4c** are bounded to one another via two O–H⋯O hydrogen links giving raise to centrosymmetric dimers with $\left[R_2^2(10)\right]$ ring motifs (Table 6). These are further connected by the $\pi\cdots\pi$ stacking and C–H$\cdots\pi$ interactions.

Finally, the recyclability of the catalyst was investigated. After magnetically separated via an external magnetic field, MNPs were washed by ethanol and used in the further reactions several times. As shown in Table 7, $CoFe_2O_4$@Silica sulfuric acid MNPs could be reused at least five times.

4 Conclusions

In summary, the given approach uses $CoFe_2O_4$@Silica sulfuric acid MNPs which not only is an efficient and facile but also is a single-step procedure for the preparation of 3-pyrrolin-2-ones analogues. Some significant superiorities of this method are no use of hazardous solvents, easy work-up, high yields,

Table 6 Hydrogen-link geometry (Å, °) for **4c**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^i	0.89(2)	1.92(2)	2.698(2)	146(2)
C13—H13···O1^{ii}	1.00	2.52	3.498(2)	167

Symmetry codes: (i) − x + 1, −y + 2, −z + 1; (ii) x, y−;iz

Table 7 Recovery of the catalyst

Run[a]	Yield (%) [b]
Fresh	90
First	90
Second	89
Third	89
Fourth	88

[a] Reaction conditions: aldehyde **1d** (1 mmol), aniline **2** (1 mmol), diethyl acetylenedicarboxylate **3** (1 mmol) and $CoFe_2O_4$@Silica-SO_3H (0.01 g) as a catalyst in ethanol at 60 °C. [b] Isolated yield

and high purity. Furthermore, the use of the recyclable, inexpensive, and efficient catalyst makes it a useful procedure in modern synthetic methodologies.

References

1. Koesnarpadi S, Santosa SJ, Siswanta D, Rusdiarso B (2015) Synthesis and characterizatation of magnetite nanoparticle coated humic acid (Fe_3O_4/HA). Procedia Environ Sci 30:103–108
2. Sadri F, Ramazani A, Massoudi A, Khoobi M, Azizkhani V, Tarasi R, Dolatyari L, Min B-K (2014) Magnetic $CoFe_2O_4$ nanoparticles as an efficient catalyst for the oxidation of alcohols to carbonyl compounds in the presence of oxone as an oxidant. Bull Kor Chem Soc 35:2029–2032
3. Tabatabaei Rezaei SJ, Shamseddin A, Ramazani A, Mashhadi Malekzadeh A, Azimzadeh Asiabi P (2017) Palladium nanoparticles immobilized on amphiphilic and hyperbranched polymer-functionalized magnetic nanoparticles: an efficient semi-heterogeneous catalyst for heck reaction. Appl Organomet Chem 31:3707
4. Tarasi R, Ramazani A, Ghorbanloo M, Khoobi M, Aghahosseini H, Joo SW, Shafiee A (2018) Synthesis of magnetic Fe_3O_4@polyethyleneimine. Mn (II) from Fe_3O_4,[3-(2, 3-epoxypropoxy) propyl] trimethoxysilane, polyethyleneimine and Mn (II) acetate as a novel silicon-containing polymeric organic-inorganic hybrid nanomaterial and its catalytic investigation towards the oxidation of cyclohexene, ethyl benzene and toluene in the presence of H_2O_2 as an oxidant. Silicon 10:257
5. Dayyani N, Ramazani A, Khoee S, Shafiee A (2018) Synthesis and characterization of the first generation of polyamino-ester dendrimer-grafted magnetite nanoparticles from 3-aminopropyltriethoxysilane (APTES) via the convergent approach. Silicon 10:595–601
6. Ramazani A, Reza Kazemizadeh A (2011) Preparation of stabilized phosphorus ylides via multicomponent reactions and their synthetic applications. Curr Org Chem 15:3986–4020
7. Reza Kazemizadeh A, Ramazani A (2012) Synthetic applications of passerini reaction. Curr Org Chem 16:418–450
8. Ramazani A, Rouhani M, Joo SW (2016) Catalyst-free sonosynthesis of highly substituted propanamide derivatives in water. Ultrason Sonochem 28:393–399
9. Ahankar H, Ramazani A, Joo SW (2016) Magnetic nickel ferrite nanoparticles as an efficient catalyst for the preparation of polyhydroquinoline derivatives under microwave irradiation in solvent-free conditions. Res Chem Intermed 42:2487–2500
10. Ramazani A, Farshadi A, Mahyari A, Sadri F, Joo SW, Asiabi PA, Fardood ST, Dayyani N, Ahankar H (2016) Synthesis of electron-poor N-Vinylimidazole derivatives catalyzed by silica nanoparticles under solvent-free conditions. Int J Nano Dimens 7:41
11. Taghavi Fardood S, Ramazani A, Golfar Z, Joo SW (2017) Green synthesis of Ni-cu-Zn ferrite nanoparticles using tragacanth gum and their use as an efficient catalyst for the synthesis of polyhydroquinoline derivatives. Appl Organomet Chem 31:3823
12. Anaraki-Ardakani H, Noei M, Tabarzad A (2012) Facile synthesis of N-(arylsulfonyl)-4-ethoxy-5-oxo-2, 5-dihydro-1H-pyrolle-2, 3-dicarboxylates by one-pot three-component reaction. Chin Chem Lett 23:45–48
13. Kangani M, Maghsoodlou M-T, Hazeri N (2016) Vitamin B12: an efficient type catalyst for the one-pot synthesis of 3,4,5-trisubstituted furan-2 (5H)-ones and N-aryl-3-aminodihydropyrrol-2-one-4-carboxylates. Chin Chem Lett 27:66–70
14. Ettlinger L, Gäumann E, Hütter R, Keller-Schierlein W, Kradolfer F, Neipp L, Prelog V, Zähner H (1959) Stoffwechselprodukte von actinomyceten 17. MitteilungHolomycin. Helv Chim Acta 42:563–569
15. Shiozawa H, Takahashi S (1994) Configurational studies on thiomarinol. J Antibiot 47:851–853
16. Singh SB, Goetz MA, Jones ET, Bills GF, Giacobbe RA, Herranz L, Stevens-Miles S, Williams Jr DL (1995) Oteromycin: a novel antagonist of endothelin receptor. J Org Chem 60:7040–7042
17. He H, Yang HY, Bigelis R, Solum EH, Greenstein M, Carter GT (2002) Pyrrocidines a and B, new antibiotics produced by a filamentous fungus. Tetrahedron Lett 43:1633–1636
18. Clark AJ, Dell CP, McDonagh JM, Geden J, Mawdsley P (2003) Oxidative 5-endo cyclization of enamides mediated by ceric ammonium nitrate. Org Lett 5:2063–2066
19. Chen J, Huang P-Q, Queneau Y (2009) Enantioselective synthesis of the R-enantiomer of the feeding deterrent (S)-Ypaoamide. J Org Chem 74(19):7457–7463
20. Omura S, Fujimoto T, Otoguro K, Matsuzaki K, Moriguchi R, Tanaka H, Sasaki Y (1991) Lactacystin, a novel microbial metabolite, induces neuritogenesis of neuroblastoma cells. J Antibiot 44: 113–116
21. Feling RH, Buchanan GO, Mincer TJ, Kauffman CA, Jensen PR, Fenical W (2003) Salinosporamide a: a highly cytotoxic proteasome inhibitor from a novel microbial source, a marine bacterium of the new genus Salinospora. Angew Chem Int Ed 42:355–357
22. Asami Y, Kakeya H, Onose R, Yoshida A, Matsuzaki H, Osada H (2002) Azaspirene: a novel angiogenesis inhibitor containing a 1-oxa-7-azaspiro [4.4] non-2-ene-4, 6-dione skeleton produced by the fungus Neosartorya sp. Org Lett 4:2845–2848
23. Li B, Lyle MP, Chen G, Li J, Hu K, Tang L, Alaoui-Jamali MA, Webster J (2007) Substituted 6-amino-4H-[1, 2] dithiolo [4, 3-b] pyrrol-5-ones: synthesis, structure–activity relationships, and cytotoxic activity on selected human cancer cell lines. Bioorg Med Chem 15:4601–4608
24. Zhu Q, Gao L, Chen Z, Zheng S, Shu H, Li J, Jiang H, Liu S (2012) A novel class of small-molecule caspase-3 inhibitors prepared by multicomponent reactions. Eur J Med Chem 54:232–238
25. Brine GA, Boldt KG (1983) Synthesis and anticonvulsant screening of 3, 3-diphenyl-2-pyrrolidone derivatives. J Pharm Sci 72:700–702
26. Stöber W, Fink A, Bohn E (1968) Controlled growth of monodisperse silica spheres in the micron size range. J Colloid Interface Sci 26:62–69
27. Naeimi H, Nazifi ZS (2013) A highly efficient nano-Fe_3O_4 encapsulated-silica particles bearing sulfonic acid groups as a solid

acid catalyst for synthesis of 1, 8-dioxo-octahydroxanthene derivatives. J Nanopart Res 15:2026

28. CrysAlisPRO in Xcalibur software (2012). Agilent Technologies, Yarnton, UK
29. Sheldrick GM (2015) SHELXT–integrated space-group and crystal-structure determination. Acta Crystallogr A 71:3–8
30. Brandenburg K, Diamond V (2014) 3.1 eM; Crystal Impact GbR, Bonn, Germany, 2005. Received: January 11
31. Zamani F, Izadi E (2014) Polyvinyl amine coated $Fe_3O_4@SiO_2$ magnetic microspheres for Knoevenagel condensation. Chin J Catal 35:21–27
32. Lin Y, Chen H, Lin K, Chen B, Chiou C (2011) Application of magnetic particles modified with amino groups to adsorb copper ions in aqueous solution. J Environ Sci 23:44–50
33. Kassaee M, Masrouri H, Movahedi F (2011) Sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles as an efficient and reusable catalyst for one-pot synthesis of α-amino nitriles in water. Appl Catal A Gen 395:28–33
34. Nemati F, Afkham MG, Elhampour A (2014) Nano-Fe_3O_4-encapsulated silica particles bearing sulfonic acid groups as a magnetically separable catalyst for green synthesis of 1, 1-diacetates. Green Chem Lett Rev 7:79–84
35. Ahankar H, Ramazani A, Slepokura K, Lis T, Joo SW (2016) Synthesis of pyrrolidinone derivatives from aniline, an aldehyde and diethyl acetylenedicarboxylate in an ethanolic citric acid solution under ultrasound irradiation. Green Chem 18:3582–3593
36. Sun J, Wu Q, Xia EY, Yan CG (2011) Molecular diversity of three-component reactions of aromatic aldehydes, arylamines, and acetylenedicarboxylates. Eur J Org Chem 2011:2981–2986