Synthesis of 3,4-Dihydropyrimidinones using Nano γ-Al2O$_3$/BF$_3$/Fe$_3$O$_4$ as an Efficient Magnetic Nanocatalyst under Solvent-free Conditions

Abdolhamid Bamoniri[1,], Bi Bi Fatemeh Mirjalili[2] and Mahnaz Mahmoodi Fard Chegeni[1]*

[1]*Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran*

[2]*Department of Chemistry, Faculty of Science, Yazd University, Yazd, Iran*

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ABSTRACT

Nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ nanoparticles were synthesized and characterized by Fourier Transform Infrared (FT-IR), Powder X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Vibrating Sample Magnetometer (VSM), Brunauer–Emmett–Teller (BET) and Thermal Gravimetric Analysis (TGA). Dihydropyrimidinones (DHP) have some biological activities such as antiviral, antibacterial, antifungal, antiinflammatory, antioxidant, anticarcinogen, calcium channel blockers, antihypertensive, anti-cancer and anti-HIV. Nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ nanoparticles as an efficient catalyst were used for mild and green one-pot multicomponent synthesis of 3,4-dihydro pyrimidine-2(1H)-ones/thiones under solvent-free conditions. Biginelli reaction proceeds through an aldehyde, β-keto ester and urea or thiourea to form dihydropyrimidinone. Excellent yields of dihydropyrmidinones were achieved within a short reaction time. The proposed method offers several advantages such as short reaction time, high efficiency, smooth purification, cleaning reaction, ease of catalyst recovery. The structures of the above mentioned compounds were confirmed using FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. Meanwhile, the physical property of products were compared with reported ones.

INTRODUCTION

Magnetic nanoparticles (MNPs) have attracted great deal of attention because of unique features including good biocompatibility, low toxicity, easy preparation and functionalization, facile separation using an external magnet and a high degree of chemical stability [1-3]. Multi-component reactions (MCRs) are one of the most important processes in organic synthesis and medicinal chemistry because of their comprehensive range of applications and numerous advantages *versus* conventional linear type syntheses. Firstly, the Biginelli reaction was reported for the synthesis of dihy- dropyrimidine-2(1H)-ones *via* condensation reaction of acetyl acetone, benzaldehyde and urea in ethanol. Dihydropyrimidinones (DHP) have some biological activities such as antiviral, antibacterial, antifungal, antiinflammatory, antioxidant, anticarcinogen, calcium channel blockers, antihypertensive, anticancer and anti-HIV. A large number of solid acid catalysts such as lanthanum chloride [4], silica sulfuric acid [5], cellulose sulfuric acid [6], alumina sulfuric Acid [7], SbCl$_5$.SiO$_2$ [8], nano-TiCl$_4$.SiO$_2$ [9], Nano-ZrO$_2$ sulfuric acid [10], nano- silica-phosphoricacid [11], Cu–EDTA-modified APTMS-Fe$_3$O$_4$@SiO$_2$ [12], phosphomolybdic acid nanoparticles on imidazole functionalized Fe$_3$O$_4$@ SiO$_2$

* Corresponding Author Email: bamoniri@kashanu.ac.ir

[13], MgFe$_2$O$_4$/cellulose/SO$_3$H [14] and potassium phthalimide [15] have been utilized for the above mentioned reaction. Herein, we wish to report an efficient protocol for the synthesis of 3,4-dihydro-pyrimidin-2(1*H*)-ones in the presence of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ [16,17].

MATERIALS AND METHODS
Material
A commercial-grade of aliphatic diamines and 1,2-dicarbonyl compounds were purchased from Merck and Fluka chemical companies and applied without any additional purification. All other reagents were obtained from Merck and utilized as received unless otherwise noted. The course of 3,4-dihydropyrimidinones synthesis was observed by TLC on silicagel plates. FT-IR spectra of all compounds were done on a Nicolet Magna series FTIR 550 spectrometer using KBr pellets. A Bruker (DRX-400 Avance) NMR was used to record the NMR spectra. Powder X-ray diffraction (XRD) was obtained on a Philips diffractometer of X'pert company with monochromatized Cu Ka radiation (k = 1.5406 Å). FESEM was recorded on a Mira Tescan. The magnetization of the prepared catalyst was charactraized by using a Vibrating Sample Magnetometer (Meghnatis Daghigh Kavir Co. Kashan, I.R. IRAN). Sizes and morphologies of the catalyst were obtained by Philips CM120 transmission electron microscopy (TEM) and were used with a LaB6 cathode and accelerating voltage of 120 kV. Thermal gravimetric analysis (TGA) was conducted using "STA 504" instrument. Brunauer–Emmett–Teller (BET) surface area of catalyst was done with Micromeritics, Tristar II 3020 analyzer.

Preparation of Fe₃O₄ nanoparticles
A mixture of FeCl$_3$.6H$_2$O (5.838 g, 0.022 mol) and FeCl$_2$.4H$_2$O (2.147g, 0.011 mol) in 100 ml of distilled water was poured in a three-necked flask (250 ml) at 80°C under nitrogen atmosphere. Afterward, 10 ml of aqueous NH$_3$ solution (32%) was added to the mixture in 30 minutes with an active mechanical stirrer. Magnetic nanoparticles were isolated from solution by a strong magnet and washed (3 times) with 200 ml of distilled water over to neutral. Finally, the products was dried at 80 °C in vacuum to form Fe$_3$O$_4$ nanoparticles.

Preparation of nano-γ-Al₂O₃/BF₃
BF$_3$.OEt$_2$ (5 ml) was added drop-wise to a vessel which includes a mixture of nano-γ-Al$_2$O$_3$ (5 g) and CH$_2$Cl$_2$ (10 ml). The composed suspension was stirred at room temperature for 1 hour, filtered, washed with chloroform and dried at room temperature to form nano-γ-Al$_2$O$_3$/BF$_3$.

Preparation of nano-γ-Al₂O₃/BF₃/Fe₃O₄
Fe$_3$O$_4$ nanoparticles (1.5 g) were added to a mixture of nano-γ Al$_2$O$_3$/BF$_3$ (1.5 g) and CH$_2$Cl$_2$ (40 mL) and were dispersed by ultrasonic bath for 40 minutes. Afterward, the reaction mixture was filtered, and the precipitate was washed five times with CH$_2$Cl$_2$ and the product was dried to form nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$.

General procedure for the synthesis of 3,4-dihydropyridinone/thiones
A mixture of aldehyde (1 mmol), β-diketone or β-ketoester (1 mmol), and urea or thiourea (1.2 mmol) was stirred in oil-bath at 80 °C in the presence of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ (0.04 g) under solvent-free conditions. After completion of the reaction, nano magnetite catalyst was separated by strong external magnet. Ethanol (2 ml) was added to remain product and then poured on crushed ice. The obtained solid product was separated by simple filtration, washed with EtOH and dried at room temperature. The resulting solid product was recrystallized from ethanol to give pure product.

Spectral Data
5-Ethoxycarbonyl-6-methyl-4-(4-hydroxyphenyl)-3,4-dihydropyrimidine-2(1H)-one
FTIR [$\overline{\upsilon}$ (cm^{-1}((KBr)]: 1098 (C-O stretch.), 1232 (C-N stretch.), 1369 (CH$_3$ bend.), 1440, 1600 (C=C aromatic stretch.), 1666 (C=O stretch.), 2979 C-H aliphatic stretch.), 3122 (=C-H stretch.), 3295 (OH stretch.), 3512 (NH stretch.). ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 1.08 (t, 3H, *J* =7.2 Hz, CH$_3$), 2.22 (s, 3H, CH$_3$), 3.96 (q, 2H, *J* = 7.2 Hz, CH$_2$), 5.02 (s, 1H), 6.67 (s, 2H), 7.02 (d, 2H, *J* = 8.0 Hz), 7.60 (s, 1H, NH), 9.09 (s, 1H, NH), 9.32 (s, 1H, OH).

5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidine-2(1H)-one
FTIR [$\overline{\upsilon}$ (cm^{-1}((KBr)]: 1091 (C-O stretch.), 1291 (C-N stretch.), 1387 (CH$_3$ bend.), 1420, 1463 (C=C aromatic stretch.), 1701 (C=O stretch.), 2977 C-H aliphatic stretch.), 3116 (=C-H stretch.), 3244 (NH stretch.). ^{1}H NMR (DMSO-d_6 400 MHz) δ (ppm): 1.08 (t, 3H, *J* = 7.2 Hz), 2.23 (s, 3H, CH$_3$), 3.97 (q,

2H, *J* = 7.2 Hz), 5.13 (s, 1H), 7.22 (d, 2H, *J* = 7.6 Hz), 7.32 (t, 3H, *J* = 7.6 Hz), 7.72 (s, 1H, NH), 9.18 (s, 1H, NH).

5-Ethoxycarbonyl-6-methyl-4-(4-methoxyphenyl)-3,4 dihydropyrimidine-2(1H)-one

FTIR [$\overline{\upsilon}$ (cm^{-1}((KBr)]: 1090 (C-O stretch.), 1223 (C-N stretch.), 1385 (CH$_3$ bend.), 1451, 1649 (C=C aromatic stretch.), 1705 (C=O stretch.), 2955 C-H aliphatic stretch.), 3112 (=C-H stretch.), 3242 (NH stretch.). ^{1}H NMR (DMSO-d_6 400 MHz) δ (ppm): 1.08 (t, 3H, *J* = 7.2 Hz), 2.22 (s, 3H, CH$_3$), 3.70 (s, 3H, CH$_3$), 3.96 (q, 2H, *J* = 7.0 Hz), 5.07 (s, 1H), 6.86 (d, 2H, *J* = 8.4 Hz), 7.13 (d, 1H, *J* = 8.4 Hz), 7.66 (s, 1H, NH), 9.14 (s, 1H, NH).

5-Methoxycarbonyl-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidine-2(1H)-one

FTIR [$\overline{\upsilon}$ (cm^{-1}((KBr)]: 1093 (C-Cl), 1140 (C-O stretch.), 1235 (C-N stretch.), 1425 (CH$_3$ bend.), 1488, 1616 (C=C aromatic stretch.), 1701 (C=O stretch.), 2927)C-H aliphatic stretch.), 3120 (=C-H stretch.), 3288 (NH stretch.). ^{1}H NMR (DMSO-d_6 400 MHz) δ (ppm): 2.11 (s, 3H, CH$_3$), 2.27 (s, 3H, CH$_3$), 5.23 (s, 1H), 7.23 (d, 2H, *J* = 8.4 Hz), 7.37 (d, 2H, *J* = 8.4 Hz), 7.86 (s, 1H, NH), 9.23 (s, 1H, NH).

5-Ethoxycarbonyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidine-2(1H)-thione

FTIR [$\overline{\upsilon}$ (cm^{-1}((KBr)]: 1106 (C-O stretch.), 1177 (C-N stretch.), 1346 (CH$_3$ bend.), 1457, 1600 (C=C aromatic stretch.), 1521 (N=O stretch.), 1690 (C=S stretch.), 2981)C-H aliphatic stretch.), 3357 (NH stretch.).^{1}H NMR (DMSO-d_6 400 MHz) δ (ppm):

1.08 (t, 3H, *J* = 7.2 Hz), 2.30 (s, 3H, CH$_3$), 3.99 (q, 2H, *J* = 7.2 Hz), 5.29 (s, 1H), 7.47 (d, 2H, *J* = 8.4 Hz), 8.22 (d, 2H, *J* = 8.4 Hz), 9.75 (s, 1H, NH), 10.49 (s, 1H, NH).

5-Ethoxycarbonyl-6-methyl-4-(4-hydroxyphenyl)-3,4-dihydropyrimidine-2(1H)-thione

FTIR [$\overline{\upsilon}$ (cm^{-1}((KBr)]: 1104 (C-O stretch.), 1179 (C-N stretch.), 1371 (CH$_3$ bend.), 1461, 1573 (C=C aromatic stretch.), 1688 (C=S stretch.), 2975)C-H aliphatic stretch.), 3196 (OH stretch.), 3512 (NH stretch.).^{1}H NMR (DMSO-d_6 400 MHz) δ (ppm): 1.08 (t, *J* =7.1 Hz, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 3.98 (q, 2H, *J* = 7.0 Hz), 5.04 (s, 1H), 6.69 (d, 2H, *J* = 8.4 Hz), 6.99 (d, 2H, *J* = 8.4 Hz), 9.42 (s, 1H, NH), 9.54 (s, 1H, NH), 10.23 (s, 1H, OH).

RESULTS AND DISCUSSION

The XRD pattern of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ is shown in Fig. 1. The signals at 2θ equal to 37, 45 and 67 are shown nano-γ-Al$_2$O$_3$ structure and the values of 2θ equal to 30.27, 35.64, 57.31 and 62.88 with FWHM equal to 0.5510, 0.3936, 0.62298 and 0.6298 respectively, show the existence of Fe$_3$O$_4$.

The FT-IR spectrum of Fe$_3$O$_4$ NPs, the wide band at 1627 and 3446 cm^{-1} are regarding to the H-O-H and O-H groups adsorption of Fe$_3$O$_4$ NPs, while the bands at 459 and 598 cm^{-1} are respectively corresponding to the octahedral bending and tetrahedral stretching vibration of the Fe-O functional group. Meanwhile the band at 630 cm^{-1} indicates the formation of Fe$_3$O$_4$ structure (Fig. 2a). The FT-IR spectrum of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ shows significant bands at 1095 and 796 cm^{-1} corresponding to symmetrical and asymmetrical
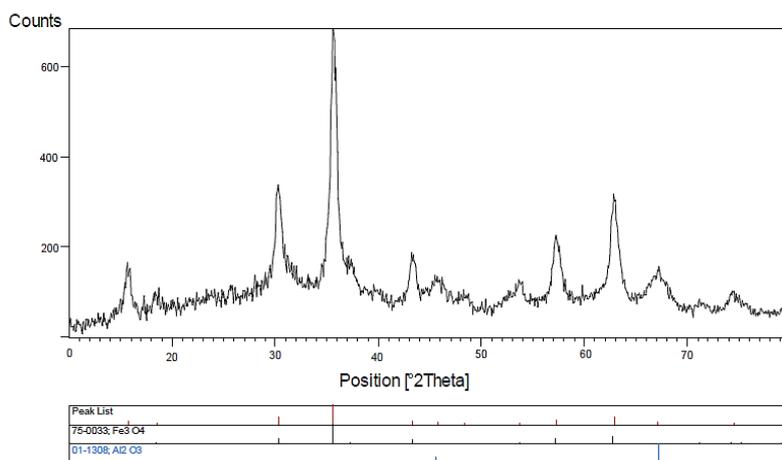

Fig. 1. XRD pattern of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$
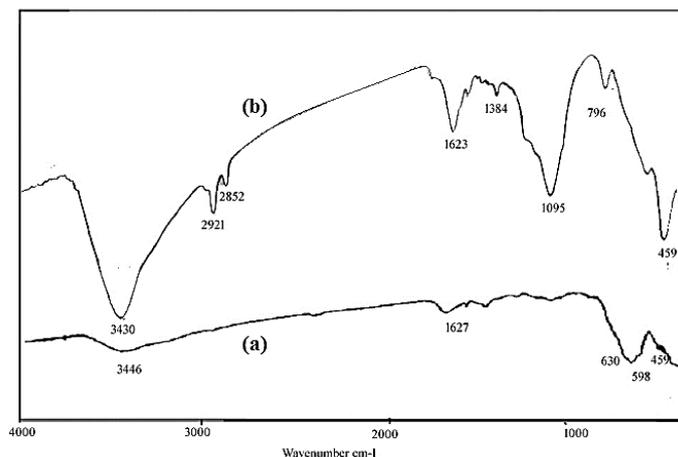
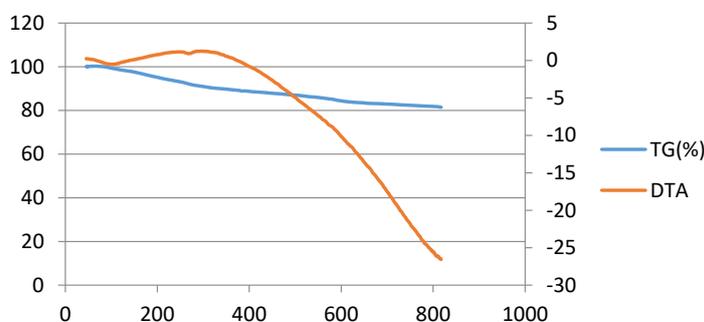Fig. 2. FT-IR (ATR) spectra of: (a) nano-Fe$_3$O$_4$, (b) nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$

Fig. 3. Thermal gravimetric analysis (TG-DTG) pattern of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$

vibrations of Al–O–Al, respectively (Fig. 2b).

TG-DTA pattern of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ was identified by heating from 0 °C to 800 °C (Fig. 3). The catalyst TGA curve suggests a preliminary weight loss of 5% below 200 °C, related to physically adsorbed water on the support. According to the TGA diagram of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$, it was exposed that the catalyst is suitable for the promotion of organic reactions until 200 °C.

The magnetization curve of magnetite nanoparticles is shown in Fig. 4 at room temperature using VSM. Within the VSM magnetization curves of nano-Fe$_3$O$_4$ and γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ nanoparticles, there is a shortage of hysteresis, and the remanence and coercivity is negligible, which reveals the superparamagnetism of these nanomaterials (Fig. 4). The saturation magnetization value of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ (28.3 emu g^{-1}) is below that of Fe$_3$O$_4$ (62.3 emu g-1) because of the existence of a non-magnetic Al$_2$O$_3$/BF$_3$ in catalyst.
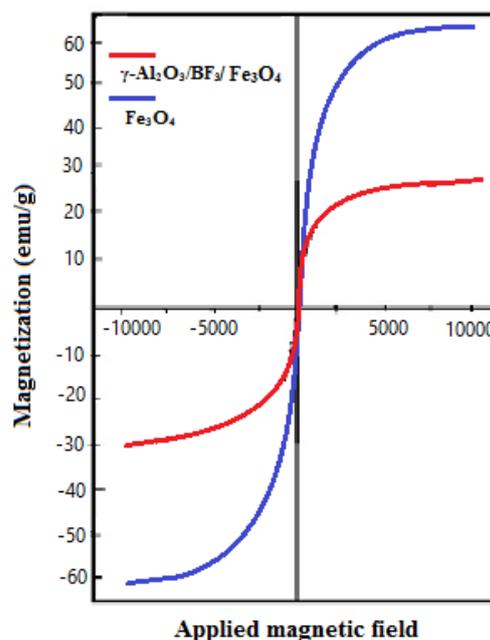
The specific surface area of catalyst was

Fig. 4. VSM images of a) Fe$_3$O$_4$ and b) nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$
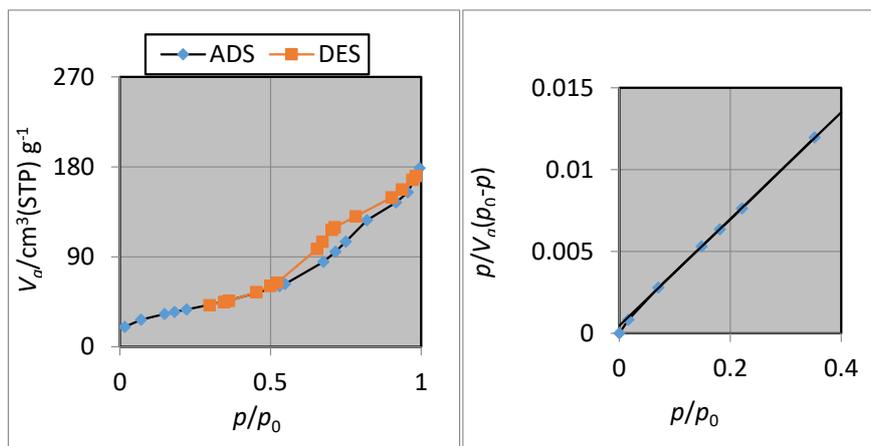
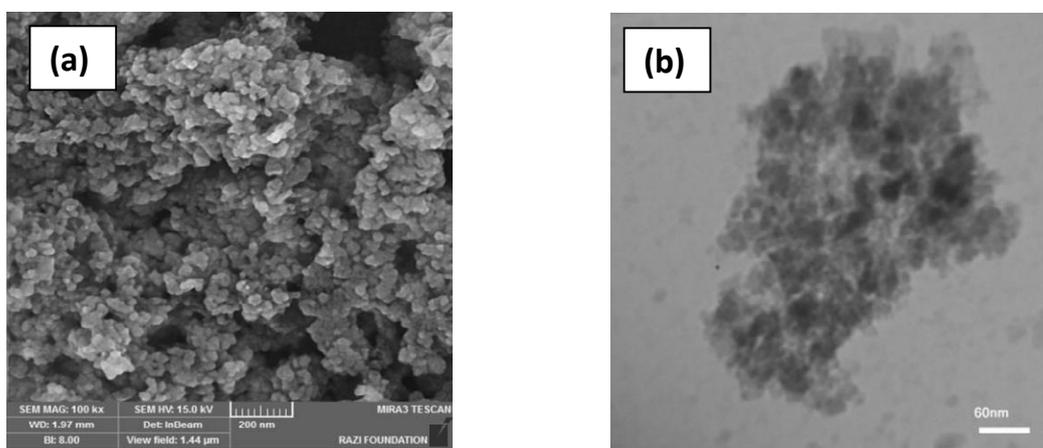Fig. 5. Nitrogen adsorption isotherm at 77.36 k of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$

Fig. 6. a) FESEM and b) TEM images of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$
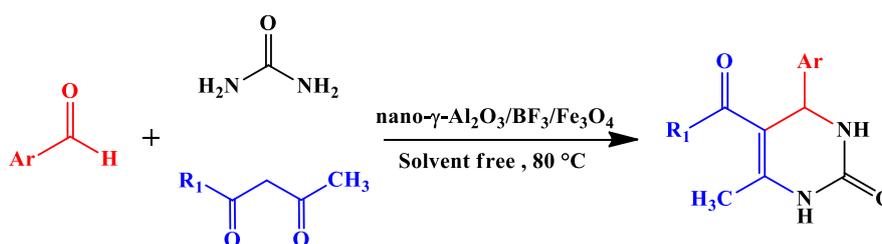
Fig. 7. Number of aromatic aldehydes, include electron-donating and electron-withdrawing substituents were reacted with ethyl acetoacetate and urea under the improved conditions

examined by Brunauer–Emmett–Teller (BET) theory. The single point surface area is 1.3173 m^2 g^{-1} while the mean pore diameter is 8.2525 nm and the total pore volume (P/P_0=0.990) is 0.2718 cm^{3}g^{-1}. The N$_2$ adsorption isotherm of catalyst is described in Fig. 5.

The FESEM and TEM images of the γ-Al$_2$O$_3$/BF$_3$/ Fe$_3$O$_4$ nanoparticles are exhibited in Figs. 6a and 6b. Using FESEM, the magnitude and morphology of the nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ was determined. They show an irregular spherical shape for nanoparticles below 5 μm.

In order to determination of dihydropyrimidinones synthesis in the presence of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$, initially, the reaction between benzaldehyde (1 mmol), ethylacetoacetate (1 mmol) and urea (1.2 mmol), was done under various conditions (Table 1). The best result was recognized in the presence of 0.8 mg nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ at 80 °C (Table1, entry 4). The results show clearly that nanocatalyst is effective for this reaction and in the absence of the catalyst, the reaction did not take place even after long reaction time (Table 1, entry 1).

The effect of temperature was determined using doing the model reaction at various temperatures (25 °C, 60 °C and 80 °C) under solvent-free condition. The best results were obtained at 80 °C (Table 1, Entry 4). Then, the reaction was refluxed in EtOH (Table1, entry 7). It was found that, the reaction under solvent free is better than under reflux condition. Therefore, the solvent-free condition was applied for the synthesis of dihydropyrimidinones derivatives.

A comparison among nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ and other catalysts, which were reported for the

Table 1. Synthesis of 5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidine-2(1*H*)-one in the presence of nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$.
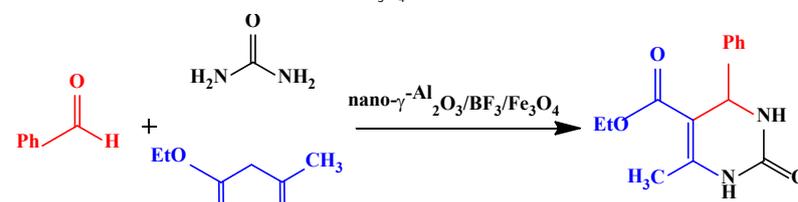
Entry	Solvent	Condition	Catalyst (mg)	Time (min)	Yield (%)
1	Solvent free	80°C	-	60	Trace
2	Solvent free	80°C	0.4	40	72
3	Solvent free	80°C	0.5	30	80
4	**Solvent free**	**80°C**	**0.8**	**30**	**95**
5	Solvent free	60°C	0.8	90	75
6	Solvent free	r.t	0.8	90	60
7	Ethanol	reflux	0.8	120	92

Reaction condition: benzaldehyde (1 mmol), ethylacetoacetate (1 mmol), urea (1.2 mmol).

Table 2. Comparison of the catalytic efficiency of nano- γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ with other reported catalysts in the preparation of 5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidine-2(1*H*)-one.
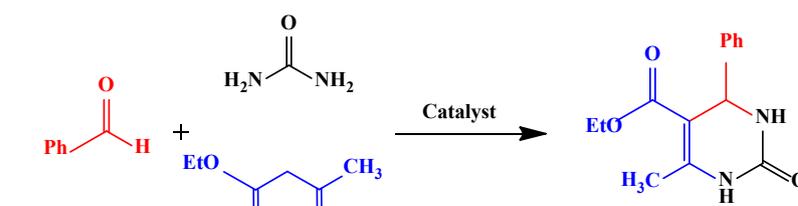
Entry	Catalyst	Time	Yield (%)	Reference
1	Nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$	30 min	95	This work
2	12-Molybdophosphoric acid	5h	80	[18]
3	12-Tungstophosphoric acid (PWA)	6-7h	75	[19]
4	Trichloroisocyanuric acid (TCCA)	12h	94	[20]
5	Silica sulfuric acid	6h	91	[5]
6	AlKIT-5[a]	18h	71	[21]
7	Montmorilonite KSF	48h	82	[22]
8	Ziegler–Natta catalyst[b]	3h	90	[23]
9	L-Pyrrolidine-2-carboxylic acid-4 hydrogen sulfate supported on silica gel	6h	92	[24]
10	Amberlyst-70	3h	81	[25]

[a]Mesoporous Aluminosilicate
[b]TiCl$_4$-MgCl$_2$ /MgCl$_2$·4 CH$_3$OH

Table 3. Nano-γ-Al$_2$O$_3$/BF$_3$ catalyzed one-pot synthesis of 3,4-dihydro- pyrimidin-2(1H) ones/thiones

| Entry	R^1	R^2	X	Time (min)	Yield (%)	m.p. (°C) [Ref.]
1	4-OH-C$_6$H$_4$	OEt	O	30	93	196-197 [23]
2	4-NO$_2$-C$_6$H$_4$	OEt	O	25	98	206-208 [24]
3	3-NO$_2$-C$_6$H$_4$	OEt	O	35	90	206-208 [24]
4	C$_6$H$_5$	OEt	O	30	92	202-204 [11]
5	2-OCH$_3$-C$_6$H$_4$	OEt	O	35	90	254-256 [18]
6	4-Cl-C$_6$H$_4$	OEt	O	25	98	210-212 [11]
7	3-OH-C$_6$H$_4$	OEt	O	30	92	196-197 [23]
8	4-OCH$_3$-C$_6$H$_4$	OEt	O	35	90	254-255 [13]
9	2-Cl-C$_6$H$_4$	OEt	O	35	90	205-211 [25]
10	2-NO$_2$-C$_6$H$_4$	OEt	O	40	84	224-225 [24]
11	2,3-Cl$_2$-C$_6$H$_3$	OEt	O	40	85	220-222 [23]
12	3,4-(OCH$_3$)$_2$-C$_6$H$_3$	OEt	O	38	85	175-178 [11]
13	4-Cl-C$_6$H$_4$	OMe	O	35	89	210-212 [25]
14	C$_6$H$_5$	OMe	O	30	92	180-185 [18]
15	4-NO$_2$-C$_6$H$_4$	OEt	S	40	94	206-208 [24]
16	4-Cl-C$_6$H$_4$	OEt	S	45	95	199-205 [23]
17	4-OH-C$_6$H$_4$	OEt	S	42	95	196-197 [23]
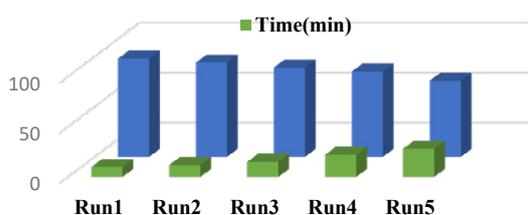
Fig. 8. Reusability of catalyst

synthesis of 3,4-dihydropyrimidinones. It was shown that our catalyst is better than the others in high yield and short reaction time (Table 2). According to these results, nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ led to the best outcome and created the maximum conversion in the shortest reaction time (Table 2, Entry1).

A number of aromatic aldehydes, include electron-donating and electron-withdrawing substituents were reacted with ethyl acetoacetate and urea under the improved conditions (Fig. 7).

The results are shown in Table 3. Aromatic aldehydes containing both electron-donating and electron-withdrawing groups produced high yields of the desired products. The reaction of other 1,3-dicarbonyl compounds such as acetylacetone was also operated with benzaldehyde and urea in the presence of γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ nanoparticles in solvent-free conditions, and the corresponding dihydropyrimidinones were collected in high yields (Table 3, Entry 13). Additionally, the reaction of 4-nitro, 4-chloro and 4-hydroxy benzaldehyde derivatives were employed with ethyl acetoacetate
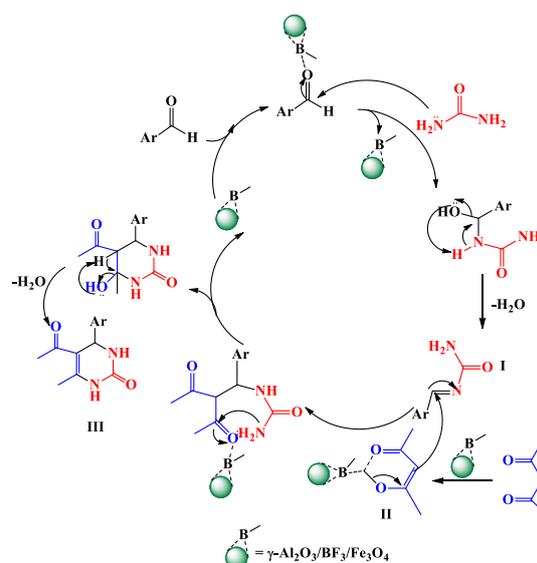
Fig. 9. A proposed mechanism of preparation of 3,4-dihydropyrimidinones using nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O

and thiourea in the presence of above mentioned nanocatalyst at 80 °C under solvent-free condition. The related Biginelli products were achieved in high yields (Table 3, Entries 15-17).

To determine the recycling of catalyst, the reaction of 3-chlorobenzaldehyde (Table 2, Entry 3) under the improved reaction conditions was studied. After separation of the catalyst from the reaction mixture, the catalyst was washed with CH$_2$Cl$_2$, dried at 50 °C under vacuum for 1 h and reused for the same reaction. This method was

done over five runs and all reactions led to the preferred product with high efficiency (Fig.8).

A reasonable pathway for the preparation of 3,4-dihydropyrimidinones using nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ is shown in Fig. 9. Protonation of the carbonyl group by Brønsted acid generates an electrophilic center on the carbonyl group, which is easily attacked by the urea to form intermediate (I), which is the rate-limiting step. Tracking of this intermediate (I) by β-dicarbonyl compound produces (II), which subsequently cyclizes through dehydration procedure yielding compound (III).

CONCLUSION

In conclusion, we have demonstrated a new pathway for synthesis of 3,4-dihydropyrimidinone/thiones using nano-γ-Al$_2$O$_3$/BF$_3$/Fe$_3$O$_4$ as an efficient solid acidic magnetic catalyst in solvent-free condition. The advantages of this process are easy work-up procedure and good to excellent yields of the final products. The catalyst was successfully recovered for five runs at least without significant loss in its activity.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript

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