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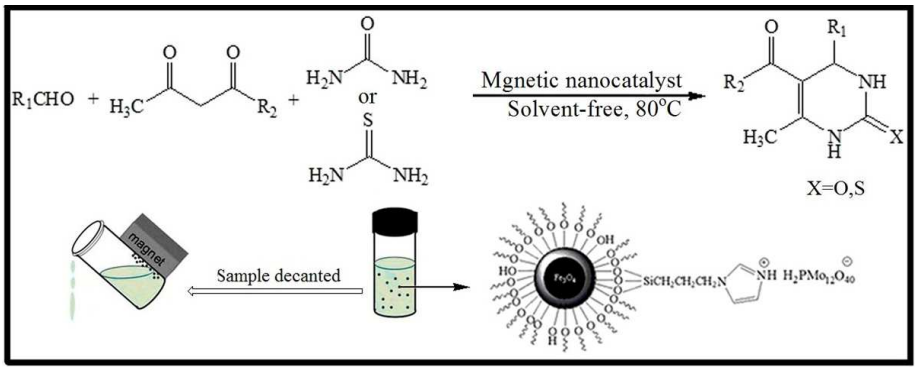
Graphical abstract



Fe_3O_4@SiO_2-imid-PMA^n: A novel and reusable nanocatalysts

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Immobilization of Phosphomolybdic Acid nanoparticles on Imidazole Functionalized Fe_3O_4@SiO_2: A novel and reusable nanocatalysts for one-pot synthesis of Biginelli-type 3,4-dihydro- pyrimidine-2-(1H)-ones/thiones under solvent-free conditions

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Abstract

This article introduces of Fe_3O_4@SiO_2-imid-$H_3PMo_{12}O_{40}$ nanoparticles as heterogenic catalyst for the synthesis of 3,4-dihydropyrimidinones under solvent-free condition. This reaction proceeds through acetoacetate esters and aldehyde derivatives followed by cyclisation with an urea to the dihydropyrimidinone. Excellent yields of dihydropyrmidinones are obtained within a short reaction time. The suggested method offers several advantages such as short reaction times,

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high yields, easy purification, a cleaner reaction and ease of recovery and reusability of the catalyst by a magnetic field. Also, the aforementioned nanocatalyst can be easily recovered by an external magnetic field and reused for subsequent reactions at least 5 times without noticeable deterioration in catalytic activity. Particle size distribution, surface area, magnetic properties and percent of leaching of $H_3PMo_{12}O_{40}$ (PMA) after any reaction were investigated by dynamic light scattering (DLS), nitrogen physisorption method (BET) and Inductively Coupled Plasma (ICP) analyzer.

Keywords

3,4-Dihydropyrimidine; Biginelli Reaction; Solvent-Free; Magnetic Nanocatalyst; Heteropolyacids

Introduction

3,4-Dihydropyrimidin-2(1H)-ones are interesting compounds due to their biological importance and exhibit a wide range of pharmaceutical and therapeutic properties.[1] These products are medicinally important as calcium channel blockers, anti-inflammatory agents, antihypertensive, anti-tumor, anti-inflammatory, adrenergic and neuropeptide antagonists.[2] They are prepared by Biginelli reaction. The Biginelli's reaction consists of three compound condensation of an aldehyde, α,β-ketoester and urea in the presence of an acid catalyst.[3]

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Recently, several procedures have been reported by Lewis acids and protic acids as catalyst for the synthesis of dihydropyrimidinones derivatives.[4] Although most of reported methods are worthwhile, many of them have one or more of the following drawbacks: tedious workup of the reaction mixture, difficulty in separation and recovery of the catalyst, expensive moisture sensitive reaction conditions, toxic metals, low yields and long reaction times.

Therefore, in spite of a large number of methods reported for this transformation, development of more efficient, simple and milder protocols by suitable catalysts are needed.

Brønsted acids such as Keggin-type heteropolyacids (HPAs) have been used as efficient catalysts for a variety of organic reactions because of their superacidic and redox properties, low toxicity, ease of handling, low cost, high thermal stability, high proton mobility, water tolerance, stronger acids than homogeneous acid catalysts, development of clean technologies, recoverability and reusability.[5] Although HPAs in their acidic form are versatile compounds, their main disadvantages are high solubility in polar solvents and low surface area (<10 m^2/g). Therefore, in a homogeneous reaction the isolation of the products and the reuse of the catalyst after reaction become difficult.[6] Therefore, in order to overcome this problem, these materials disperse on supports (such as silica, acidic ion-exchange resins, active carbon and etc.) which possess large surface area. The

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use of support allows the heteropolyacids to be dispersed over a large surface area and increases theirs catalytic activity.[7]

Nanoparticles have properties intermediate between those of bulk and single particles.[8] They are expected to be suitable candidates for the design of highly active and selective catalysts. Nanostructured materials, a new branch of materials research, are attracting a great deal of attention because of their potential applications in areas such as optics,[9] ceramics,[10] electronics,[11] catalysis,[12] magnetic data storage,[13] and nanocomposites. The unique properties and the improved performances of nanomaterials are determined by their sizes, surface structures and inter-particle interactions.

In previous work,[14] we introduce a simple, repaid, inexpensive and one step method, solvothermal, for synthesis of $H_3PMo_{12}O_4$ nanoparticles (PMA^n) from $H_3PMo_{12}O_4$ bulk particles (PMA^b). Acidity of as-prepared nanoparticles was investigated by pyridine adsorption method. Results showed rising acidity by declining particle size of HPAs.

In recent years, nanomagnetic materials have emerged as viable alternatives to conventional heterogeneous supports.[15] The magnetic separation technology offers many advantages over conventional filtration and other purification methods.

In family of nanomagnetic materials, magnetite (Fe_3O_4) exhibits excellent properties, so that makes it great potential applications in magnetic bio-separations,[16] drug delivery,[17] magnetic resonance imaging (MRI) contrast agents,[18] hyperthermia treatment of cancer cells[19] and catalysts[20].

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In our previous study[21], PMA^n were supported on magnetic $Fe_3O_4@SiO_2$-imid nanoparticles. Compared to other substrates (silica, acidic ion-exchange resins, active carbon and nano titania[7b]), Fe3O4@SiO2–imid nanoparticles have various advantages such as high loading capacity, low leaching and simple and efficient recovery procedure. Fig. 1 presents the procedure for the preparation of Fe3O4@SiO2–imid–PMA^n stepwise. In this work, we tried to synthesize dihydropyrimidin derivatives with using $Fe_3O_4@SiO_2$-imid-PMA^n and $Fe_3O_4@SiO_2$-imid-PMA^b catalysis.

Results and discussion

In our previous work[21], the Fe_3O_4, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$–imid–PMAn nano catalysts were characterized by various methods such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), dynamic light scattering (DLS), Fourier transform infrared (FT-IR), vibrating sample magnetometer (VSM) and etc. As shown in Fig. 1 $Fe_3O4@SiO_2$–imid–PMA^n nanoparticles have spherical shapes with approximately 50 nm diameters. The size distribution of these is centered at a value of 55 nm. The magnetic properties of Fe_3O_4, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-imid-PMA^n nanoparticles were measured by VSM at room temperature. All the samples show a typical superparamagnetic behavior. Hysteresis phenomenon was not found and the magnetization and demagnetization curves were coincident. The saturation magnetization of samples (a–c) is 63.4, 39.7, 33.2 emu/g, respectively.

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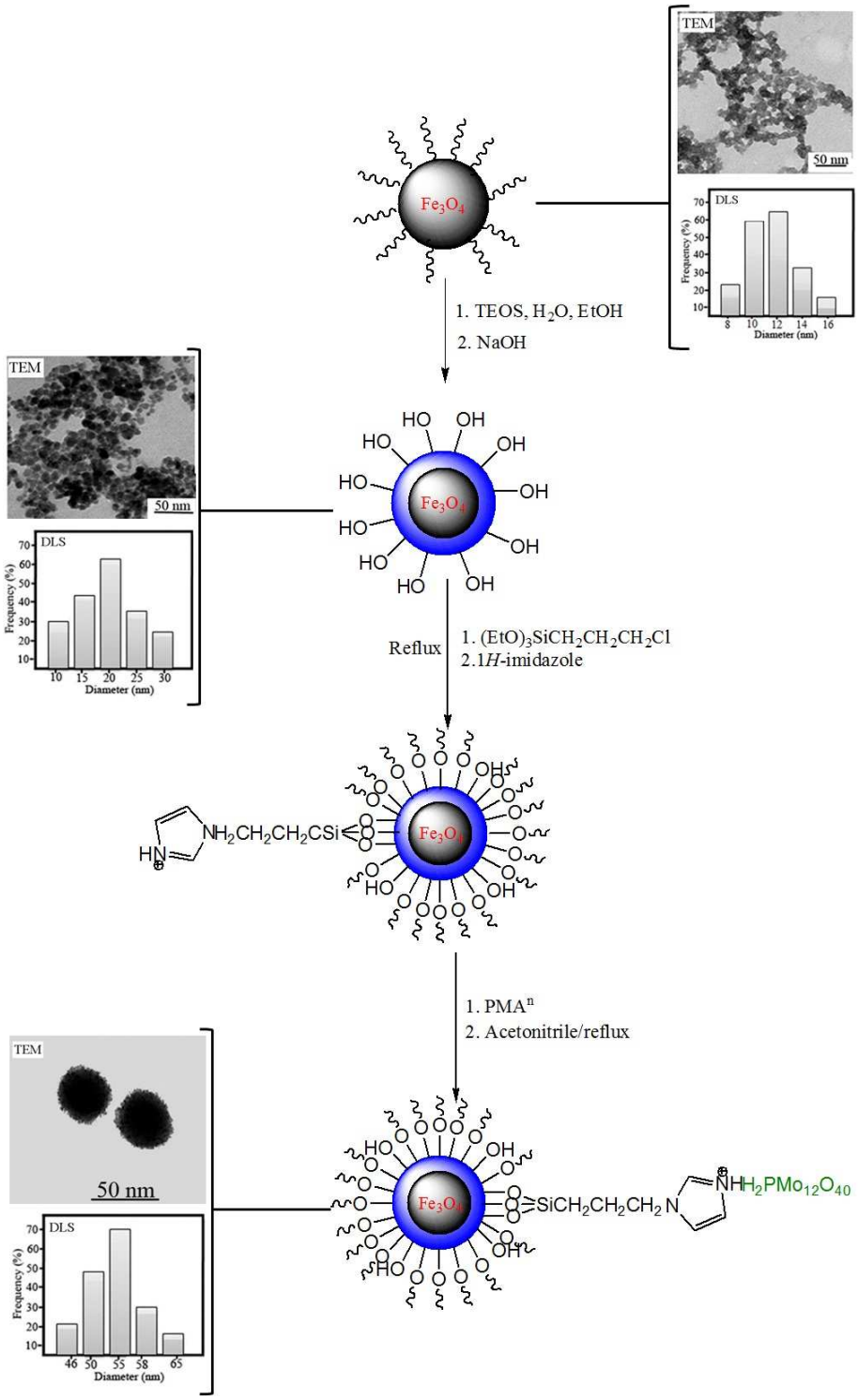

Fig. 1 Preparation and characterization of Fe3O4@SiO2–imid–PMA^n stepwise.

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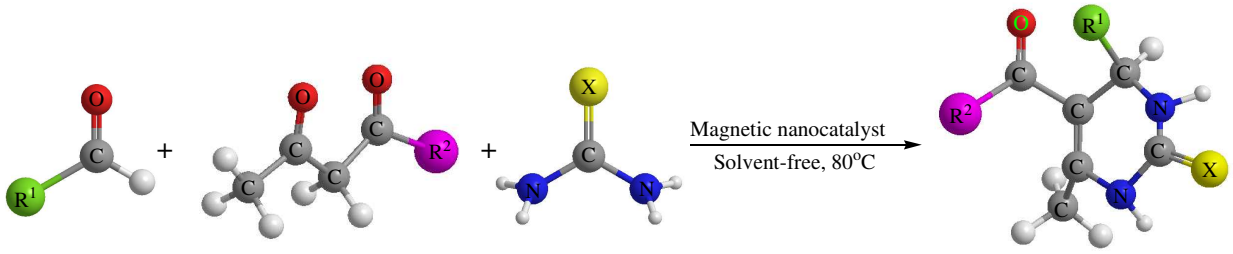
We wish to report that immobilization of phosphomolybdic acid on imidazole functionalized $Fe_3O_4@SiO_2$ ($Fe_3O_4@SiO_2$-imid-PMA^n and $Fe_3O_4@SiO_2$-imid-PMA^b) catalyzed the Biginelli reaction of aromatic aldehydes, acetoacetate esters and urea to yielding the dihydropyrimidinones. In pursuit of developing a solvent-free methodology for the preparation of these biologically important compounds, we decided to explore the use of these magnetic nanocatalysts for the synthesis of various substituted 3,4-dihydropyrimidin-2(1H)-ones by Biginelli protocol under solvent-free condition (Scheme 1).



Scheme.1 Synthesize dihydropyrimidin derivatives with using $Fe_3O_4@SiO_2$-imid-PMA^n nanocatalyst.

Initially the reaction between benzaldehyde (1mmol), acetoacetate esters (1mmol) and urea (1.5mmol), as the model reaction was examined in the presence of various amount of the nanocatalysts and the results are presented in Table 1, entries 1-5. The best result was attributed to the reaction of benzaldehyde (1mmol), ethyl acetoacetate (1mmol) and urea (1.5mmol) in presence of 0.03g or 0.04g of $Fe_3O_4@SiO_2$-imid-PMA^n or $Fe_3O_4@SiO_2$-imid-PMA^b nanocatalysts at 80°C (Table1, entry 4). The results show

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clearly that nanocatalysts are effective for this transformation and in the absence of it, the reaction did not take place even after higher reaction time (Table1, entry 1).

Table1 Optimization of synthesis of 3,4-dihydro- pyrimidin-2-(1H)-ones /thiones

Entry	Solvent	Condition	Fe_3O_4@SiO_2-imid-PMA[n]			Fe_3O_4@SiO_2-imid-PMA[b]		
			Amount of catalysts (g)	Time (min)	Yield[b] (%)	Amount of catalysts (g)	Time (min)	Yield[b] (%)
1	Solvent-free	80°C	-	60	Trace	-	90	Trace
2	Solvent-free	80°C	0.01	60	71	0.02	90	62
3	Solvent-free	80°C	0.02	30	92	0.03	90	81
4	Solvent-free	80°C	0.03	30	93	0.04	45	89
5	Solvent-free	80°C	0.04	30	92	0.05	45	89
6	Solvent-free	60°C	0.03	45	82	0.04	60	78
7	Solvent-free	r.t	0.03	60	21	0.04	90	17
8	Toluene	reflux	0.03	60	83	0.04	90	73
9	THF	reflux	0.03	60	80	0.04	90	75
10	Ethanol	reflux	0.03	60	86	0.04	90	80
11	H_2O	reflux	0.03	60	38	0.04	90	26
12	CH_3CN	reflux	0.03	60	87	0.04	90	80
13	$CHCl_3$	reflux	0.03	60	45	0.04	90	33
14	CH_2Cl_2	reflux	0.03	60	51	0.04	90	32

[a] Reaction condition: benzaldehyde (1 mmol), ethylacetoacetate (1mmol), urea (1.5 mmol).
[b] Isolated yield.

The effect of temperature was studied by carrying out the model reaction at different temperatures under solvent-free condition (room temperature, 60◦C and 80°C) and the best results were obtained at 80°C (Table 1, entries 4, 6 and 7). Then, the reactions were conducted in refluxing toluene, THF, EtOH, H_2O, CH_3CN, CH_2Cl_2 and $CHCl_3$ as solvents and under solvent-less condition (Table1, entries 4 and 8-14). When the reaction was performed in solvent-free, the progress of the reaction was higher in comparison with

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solvent conditions. Therefore, the solvent-free condition was used for the synthesis of dihydropyrimidinones derivatives.

In order to study the generality of the procedure, a series of aromatic aldehydes with the electron-donating and electron-withdrawing substituent were reacted with ethyl acetoacetate and urea under the optimized conditions. The results are presented in Table 2. Aromatic aldehydes containing both electron donating and electron withdrawing groups afforded high yields of the desired products.

Also heterocyclic aromatic compounds, such as furyl-2-carbaldehyde and thiophen-2-carbaldehyde produced the corresponding dihydropyrimidinones in excellent yields (Table 2, entries11and12). Also, more importantly acid sensitive aldehydes such as 2-furfural, underwent condensation without formation of any side products (Table2, entry11).

The reaction of other 1,3-dicarbonyl compounds such as acetylacetone also run with benzaldehyde and urea in the presence of Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b nanoparticles under solvent free conditions and the corresponding dihydropyrimidinones were obtained in high yields (Table2, entry 15). Also, the reaction of benzaldehyde and its 4-chloro, 4-methyl and 4-methoxy derivatives were treated with ethyl acetoacetate and thiourea in the presence of nanocatalysts under solvent-free at 80^{o}C and the related Biginelli products were obtained in high yields (Table 2, entry16-19).

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Table2 Fe_3O_4@SiO_2-imid-PMA[n] and Fe_3O_4@SiO_2-imid-PMA[b] -catalyzed one-pot synthesis of 3,4-dihydro- pyrimidin-2(1H)-ones/thiones.[a]

Entry	R^1	R^2	X	Fe_3O_4@SiO_2-imid-PMA[n]		Fe_3O_4@SiO_2-imid-PMA[b]		m.p. (°C)	
				Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	Found	Reported[Ref]
1	C_6H_5	OEt	O	30	93	45	89	205-206	206-208[22]
2	4-Br-C_6H_4	OEt	O	35	86	55	81	213-214	213-215[23]
3	2-Cl-C_6H_4	OEt	O	35	88	50	83	215-216	216-218[24]
4	4-Cl-C_6H_4	OEt	O	35	90	50	87	215-216	214-215[25]
5	2-NO_2-C_6H_4	OEt	O	25	92	30	89	222-223	221[26]
6	3-NO_2-C_6H_4	OEt	O	25	90	30	92	227-228	229-231[27]
7	4-NO_2-C_6H_4	OEt	O	20	94	30	91	210	209-211[25]
8	4-Me-C_6H_4	OEt	O	35	91	50	88	203-204	205-206[22]
9	2-MeO-C_6H_4	OEt	O	40	91	60	85	262-263	262[28]
10	4-MeO-C_6H_4	OEt	O	40	90	60	82	200-201	201-203[25]
11	2-Furyl	OEt	O	25	95	30	91	205-206	203-205[29]
12	2-Thiophene	OEt	O	30	92	60	85	210-211	209-210[30]
13	PhCH=CH	OEt	O	40	85	60	80	223-224	225-227[27]
14	C_6H_5	OMe	O	30	92	50	89	208-209	207-210[25]
15	C_6H_5	CH_3	O	30	88	50	88	235-236	233-236[31]
16	C_6H_5	OEt	S	30	91	45	84	211	208-210[27]
17	4-Cl-C_6H_4	OEt	S	25	90	45	88	179-180	180-182[27]
18	4-Me-C_6H_4	OEt	S	30	89	45	86	191-193	192-194[27]
19	4-MeO-C_6H_4	OEt	S	35	87	45	83	153	152-153[32]

[a] Reaction condition aldehyde (1 mmol), β-diketoester (1mmol), urea or thiourea (1.5 mmol), Fe_3O_4@SiO_2-imid-PMA[n] (0.03g) or and Fe_3O_4@SiO_2-imid-PMA[b] (0.04g), solvent-free, 80°C.
[b] Isolated yield.

A comparison among Fe_3O_4@SiO_2-imid-PMA[n] and Fe_3O_4@SiO_2-imid-PMA[b] and the other catalysts, which were reported in the literature, in synthesis of 3,4-dihydropyrimid-inones revealed advantages of these magnetic nanocatalysts over the most of them in term of higher yield and shorter reaction time (Table3). According to these findings,

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Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b led to the best result and produced the maximum conversion in the shortest time (Table3, entry1,2).

Table3 Comparison of the catalytic efficiency of Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b with that of reported catalysts in the preparation of ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5- carboxylate.

Entry	Catalyst	Time	Yield[a] (%)	literature reference
1	Fe_3O_4@SiO_2-imid-PMA^n	30 min	93	This work
2	Fe_3O_4@SiO_2-imid-PMA^b	45min	89	This work
3	12-Molybdophosphoric acid	5h	80	[24]
4	12-Tungstophosphoric acid (PWA)	6-7h	75	[33]
5	Trichloroisocyanuric acid (TCCA)	12h	94	[34]
6	Silica sulfuric acid	6h	91	[35]
7	Sulfuric acid	18h	71	[3]
8	Montmorilonite KSF	48h	82	[28]
9	$TiCl_4$-$MgCl_2$·$4CH_3OH$	3h	90	[36]
10	L-Pyrrolidine-2-carboxylicacid-4-hydrogen sulfate supported on silica gel	6h	92	[37]
11	Amberlyst-70	3h	81	[38]
12	$Sm(ClO_4)_3$	9	72	[39]
13	Chiral ligand/HCl	6 day	81	[40]
14	$NH_4H_2PO_4$	2h	85	[41]
15	poly(4-vinylpyridine-co-divinylbenzene)–Cu(II) complex	24h	70	[42]

[a]Isolated yield.

Considering the general mechanistic pathway, the suggested mechanism for the formation of **(3)** using Fe_3O_4@SiO_2-imid-PMA^n or Fe_3O_4@SiO_2-imid-PMA^b is shown in Scheme 2. Protonation of the carbonyl group by Brønsted acid generates an electrophilic center on the carbonyl carbon atom, which is easily attacked by the urea to form minimum intermediate **(1)**, which is the key rate-limiting step. Interception of this

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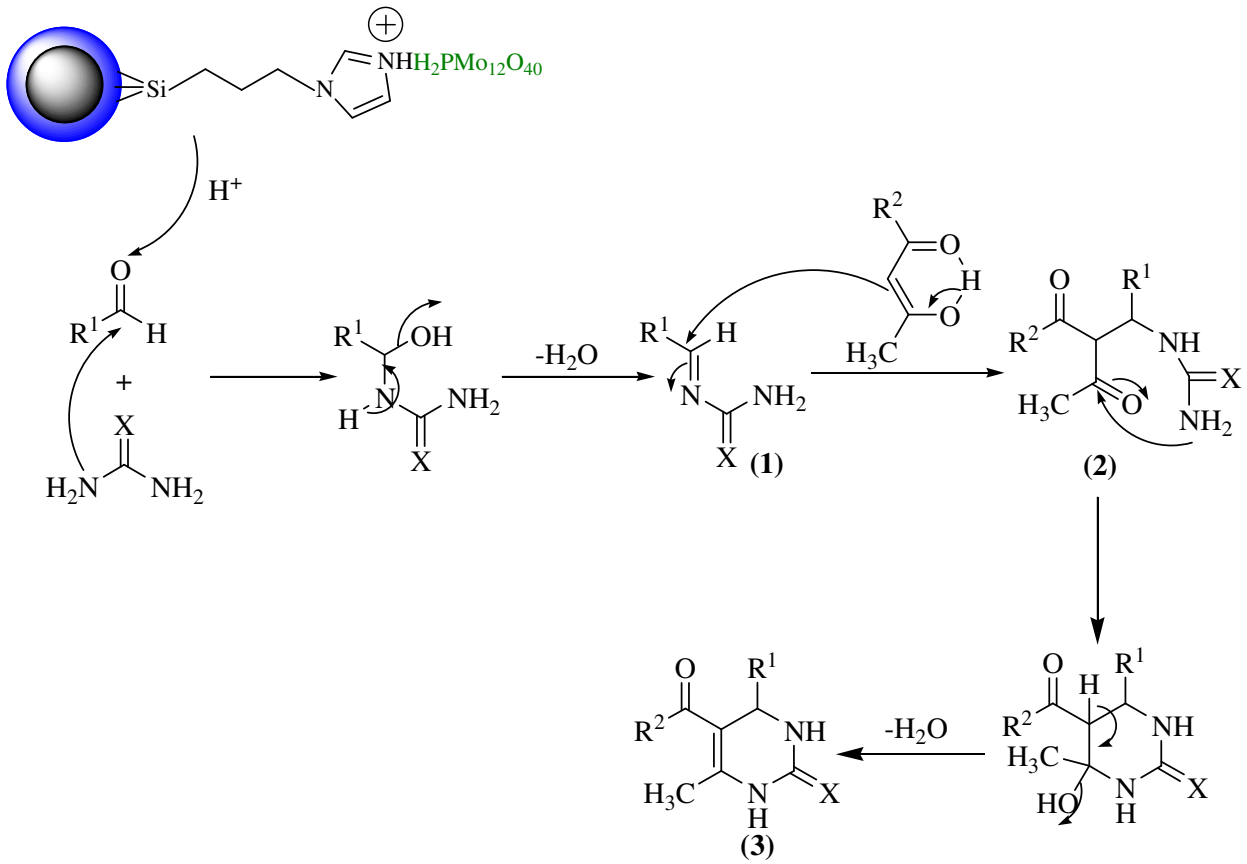
minimum intermediate **(1)** by *β*-dicarbonyl produces an open chain ureide **(2)**, which subsequently cyclizes through dehydration process yielding compounds (**3**).



Scheme.2 Proposed mechanism for synthesis of dihydropyrimidinones via Biginelli condensation protocol.

However, magnetically supported catalysts can be recovered with an external magnet due to the paramagnetic character of the support, resulting in remarkable catalyst recovery without the need for a filtration step (Scheme3).

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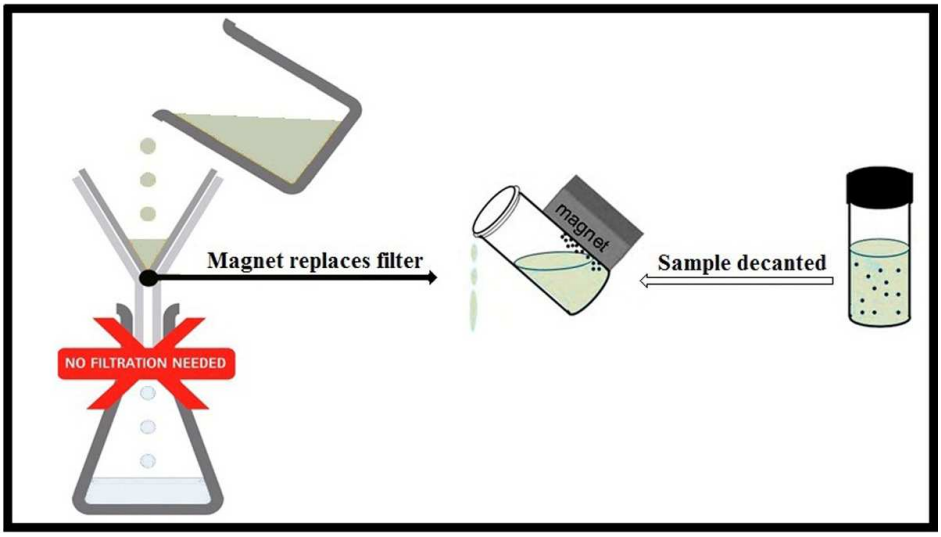

Scheme.3 Catalyst ability to effective recovery at the end of reactions by external magnetic field.

The activity of the recycle catalysts were also examined under the optimized conditions and the desired products were obtained in high yields after 4 runs without distinct deterioration in catalytic activity (Fig. 2).

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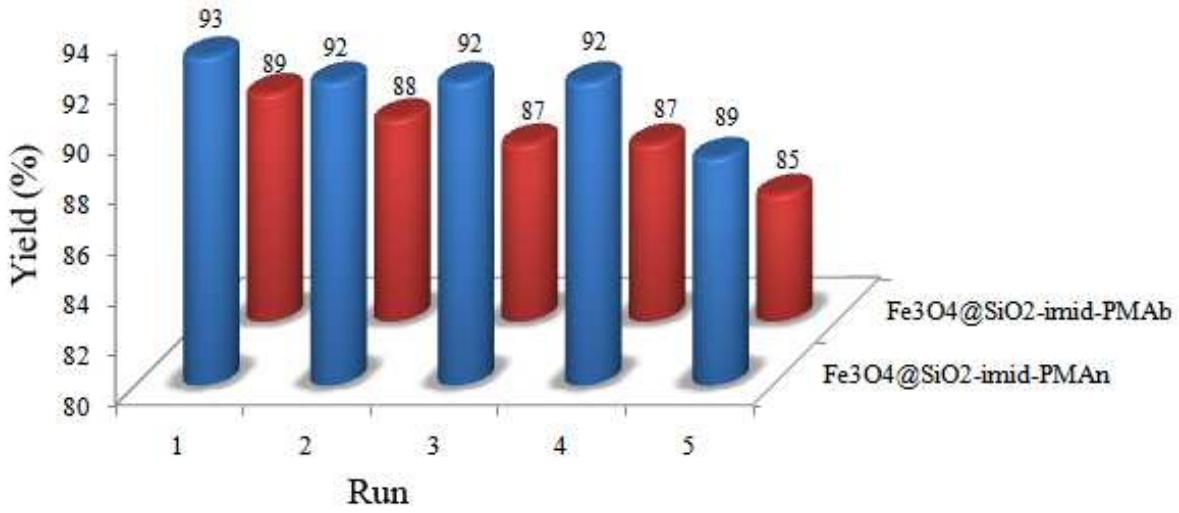

[a] Reaction condition: (A) benzaldehyde (1 mmol), ethyl acetoacetate (1mmol), urea or thiourea (1.5 mmol), Fe_3O_4@SiO_2-imid-PMA^n (0.03g), solvent-free, 80°C.
[b] Reaction condition: (A) benzaldehyde (1 mmol), ethyl acetoacetate (1mmol), urea or thiourea (1.5 mmol), Fe_3O_4@SiO_2-imid-PMA^b (0.04g), solvent-free, 80°C.

Fig.2 Recyclability of Fe_3O_4@SiO_2-imid-PMA^n (A) and Fe_3O_4@SiO_2-imid-PMA^b (B) in the synthesis of 3,4-dihydro- pyrimidin-2-(1H)-ones under solvent-free conditions.

The amounts of the nano heteropolyacid leaching for the reactions under the optimized conditions were detected. The molybdenum (Mo) amount in reaction medium after each reaction cycle was measured through ICP and details are provided in Table 4. The analysis of the reaction mixture by the ICP technique showed that the leaching of $H_3PMo_{12}O_{40}$ was negligible. Additionally, the size and surface area of catalysts after each reaction cycle was investigated by DLS and nitrogen physisorption method (BET) respectively and results are provided in Table 4. As shown, the size of catalysts will be

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increased after each cycle. Generally, leaching of $H_3PMo_{12}O_{40}$, increase of catalyst size and decrease of surface area led to a decrease in the yield of reaction.

Table 4 Mean article size, surface area and ratio of PMA^n leaching in each reaction cycle

Run	Mean article size (nm)[a]	surface area (m^2/g)[b]	Ratio of leaching (%)[c]
1	55	422	0.09
2	59	410	0.11
3	62	392	0.15
4	68	386	0.20
5	73	377	0.33

[a] By DLS
[b] By BET
[c] By ICP

Conclusion

In conclusion, we report here a high yielding one-pot synthesis of 3,4-dihydropyrimidin-2- (1H)-ones and thione analogs from readily available aldehydes, acetoacetate esters and urea or thiourea in presence of efficient magnetic nanocatalysts by Biginelli reactions under solvent-free conditions. The protocol offers several advantages such as easy preparation, heterogeneous nature and easy separation of the catalyst, short reaction times, easy isolation, very good yields and simple work up procedures. Also, in solvent-free reactions the purification process is simplified and the reaction is environmentally friendly. The nanocatalysts could be successfully recovered and recycled at least for five runs without noticeably decreasing in catalytic activity.

Experimental

General methods

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All starting materials were purchased from fluka. The reactions were monitored by thin layer chromatography (TLC). ^{1}H NMR, ^{13}C NMR spectra were obtained at 250MHz using a Bruker spectrometer in $CDCl_3$ as the solvent and tetramethyl silane (TMS) as internal reference. Fourier transform infrared (FT-IR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Melting points were determined on a Mel-Temp apparatus. Magnetic characterization was carried out on a vibrating sample magnetometer (Meghnatis Daghigh Kavir Co., Iran) at room temperature, and dynamic light scattering (DLS) was recorded on a HORIBA-LB550 instrument. A transmission electron microscope (Philips EM208) with an accelerating voltage of 100 kV was used to examine morphology, and size of the nanoparticles. All compounds were identified by comparison of their spectral data and physical properties with those of the authentic sample and all yields refer to isolated products.

General procedure

Preparation of Fe_3O_4@SiO_2 Core-Shell

The core–shell Fe_3O_4@SiO_2 nanospheres were prepared by a modified Stober method in our previous work.[12] In a typical procedure, the mixture of $FeCl_3.6H_2O$ (1.3g, 4.8mmol) in water (15ml) was added to the solution of polyvinyl alcohol (PVA 15000), as a surfactant, and $FeCl_2.4H_2O$ (0.9g, 4.5mmol) in water (15 ml), which was prepared by completely dissolving PVA in water followed by addition of $FeCl_2.4H_2O$. The resultant solution was left to be stirred for 30 min in 80^{o}C. Then, hexamethylentetraamine

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(HMTA) (1.0mol/l) was added drop by drop with vigorous stirring to produce a black solid product when the reaction media reaches pH 10. The resultant mixture was heated on water bath for 2h at 60°C and the black magnetite solid product was filtered and washed with ethanol three times and was then dried at 80°C for 10h.Then Fe_3O_4 nanoparticle (0.50g, 2.1mmol) was dispersed in the mixture of ethanol (50mL), deionized water (5mL) and tetraethoxysilane (TEOS) (0.20mL), followed by the addition of 5.0mL of NaOH (10wt%). This solution was stirred mechanically for 30 min at room temperature. Then the product, Fe_3O_4@SiO_2, was separated by an external magnet, and was washed with deionized water and ethanol three times and dried at 80°C for 10 h.

4.2.2. Preparation of $H_3PW_{12}O_{40}$ nanoparticles (PMA^n)

PMA^n nanoparticles were prepared in our previous work.[14] In a typical procedure, 5 mmol of bulk $H_3PMo_{12}O_{40}$ (PMA^b) was dispersed in 50 mL n-Octane and the resulting dispersion was stirred vigorously for 30 min at room temperature to form a homogeneous dispersion. This dispersion was transferred into a Teflon-lined stainless autoclave filling 80% of the total volume. The autoclave was sealed and maintained at 150°C for 12 h. The autoclave was then cooled to room temperature. Finally, the resulted powder was filtered and washed for several times by Octane, and dried in a vacuum at 80°C for 12 h.

Preparation of Fe_3O_4@SiO_2-imid-PMA^n

Fe_3O_4@SiO_2 (1g) was added to the solution of 3-chlorotriethoxypropylsilane (1 mmol, 0.241 g) and imidazole (1 mmol, 0.0680 g) in *p*-xylene (20 mL) and the resultant mixture

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was under reflux for 24h under nitrogen atmosphere. After refluxing for about 24 h, the mixture was cooled to room temperature, filtered by an external magnet and the product was washed with xylene to remove no reacted species and dried at 70 ^{o}C for 6 h. Fe_3O_4@SiO_2-imid (1.0g) was added to an acetonitrile solution of PMA^n (1.0mmol) in 20mL was taken in a round-bottom flask. The mixture was refluxed for 24h under nitrogen atmosphere. After 24h, the mixture was filtered by an external magnet, washed with acetonitrile and dichloromethane, and dried at 70^{o}C for 6h. Also, the same method was used for the synthesis of Fe_3O_4@SiO_2-imid-PMA^b (PMA^n = nano $H_3PMo_{12}O_{40}$, PMA^b= $H_3PMo_{12}O_{40}$).[21]

2.2.4. General procedure for the synthesis of 4-aryl-3,4-dihydropyrimidin-2(1H)-one

In a typical experiment, a mixture of aldehyde (10 mmol), β-diketoester (10 mmol) and urea or thiourea (15 mmol) in solvent-free conditions was stirred for few minutes at 80^{o}C, in the presence of Fe_3O_4@SiO_2-imid-PMA^n (0.03g) or Fe_3O_4@SiO_2-imid-PMA^b (0.04g). After completion of the reaction, ethyl acetate was added to the solidified mixture and the insoluble catalyst was separated by magnetic field. The filtrate was dried and organic medium was removed with a rotary evaporator under reduced pressure. Then, the resulting solid product was recrystallized from ethanol to give pure product.

Spectral Data

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Ethyl-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table2, entry 1)

White solid, m.p. 205-206 ◦C. 1H-NMR (250 MHz, CDCl3): δ= 1.15 (t, J= 7.1 Hz, 3H, CH3CH2O-), 2.34 (s, 3H, CH3), 4.05 (m, 2H, CH2), 5.39 (s, 1H, CH), 5.70 (s, 1H, NH), 7.21-7.32 (m, 5H, Ar-H), 8.12 (s, 1H, NH). 13C-NMR (62.9 MHz, CDCl3): δ= 14.11, 18.65, 55.73, 59.99, 101.34, 126.58, 127.93, 128.69, 143.68, 146.26, 153.26, 167.23. IR (KBr): 3244, 3116, 2931, 1728, 1701, 1651 cm-1.

Ethyl 4-(2-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 3)

White solid, m.p. 215-216 ◦C. 1H-NMR (250 MHz, CDCl3): δ= 1.05 (t, J= 7.10 Hz, 3H, CH3CH2-), 2.42 (s, 3H, CH3), 4.02 (q, J= 7.10 Hz, 2H, CH3CH2-), 5.85 (s, 1H, CH-), 5.87 (s, 1H, NH), 7.17-7.56 (m, 4H, Ar-H), 8.85 (s, 1H, NH). 13C-NMR (62.9 MHz, CDCl3): δ= 13.97, 18.28, 52.10, 59.95, 98.82, 127.52, 127.99, 129.26, 129.77, 132.56, 139.52, 148.48, 153.24, 165.31. IR (KBr): 3232, 3112, 2920, 1701, 1643 cm-1.

Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 4)

White solid, m.p. 215-216 ◦C. 1H-NMR (250 MHz, CDCl3): δ= 1.09 (t, J= 7.12 Hz, 3H, CH3CH2-), 2.33 (s, 3H, CH3), 4.06 (m, CH3CH2-), 5.36 (s, 1H, CH-), 5.87 (s, 1H, NH), 7.27 (4H, Ar-H), 8.38 (s, 1H, NH). 13C-NMR (62.9 MHz, CDCl3): δ= 14.13, 18.68,

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55.02, 60.05, 127.79, 128.51, 128.65, 141.93, 146.18, 152.92, 158.86, 165.15. IR (KBr): 3244, 3116, 2927, 1705, 1651 cm-1.

Ethyl 6-methyl-4-(2-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 5)

White solid, m.p. 222-223 ◦C. 1H NMR (250 MHz, DMSO-d6): δ= 1.09 (t, 3H, J=7.35 Hz, CH3, CH3CH2-), 2.26 (s, 3H, CH3), 3.86 (q, 2H, J=7.35 Hz, OCH2), 5.51 (d, 1H, J= 2.88 Hz, CH-), 7.01 (d, 1H, J=7.92 Hz, Ar-H), 7.14 (m, 1H, Ar-H), 7.19 (d, 1H, J= 6.23 Hz, Ar-H), 7.29 (m, 1H, Ar-H), 7.31 (s, 1H, NH), 9.09 (s, 1H, NH). 13C NMR (62.9 MHz, DMSO-d6): δ: 165.79, 156.54, 151.25, 150.13, 133.10, 128.11, 127.02, 119.32, 110.65, 97.10, 54.71, 49.13, 18.01, 17.04. IR (KBr): 3238, 3120, 2931, 1724, 1648, 1531, 1354 cm-1.

Ethyl 6-methyl-4-(3-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 6)

Pale-yellow solid, m.p. 227-228 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.07 (t, J= 7.0 Hz, 3H, CH3CH2-), 2.48 (s, 3H, CH3), 3.96 (q, J= 1.8 Hz, 2H, CH3CH2-), 5.28 (s, 1H, CH-), 7.66 (m, 2H, Ar-H), 7.87 (s, 1H, NH), 8.11 (m, 2H, Ar-H), 9.33 (s, 1H, NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 13.91, 17.78, 53.46, 59.34, 98.26, 120.94, 122.29, 130.16, 132.93, 146.89, 147.64, 149.36, 151.74, 164.99. IR (KBr): 3328, 3101, 2931, 1708, 1627, 1527 cm-1.

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Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 7)

White solid, m.p. 210 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.07 (m, 3H, CH3CH2-), 2.24 (s, 3H, CH3), 3.95 (m, 2H, CH3CH2-), 5.25 (s, 1H, CH-), 7.49 (m, 2H, Ar-H), 7.87 (s. 1H, NH), 8.21 (m, 2H, Ar-H), 9.33 (s, 1H, NH). 13C-NMR (62.9 MHz, CDCl3): δ= 19.23, 23.05, 58.85, 64.602, 103.36, 129.03, 132.85, 151.78, 154.58, 156.94, 157.16, 170.25. IR (KBr): 3232, 3117, 2916, 1705, 1647 cm-1.

Ethyl 4-(2-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 9)

White solid, m.p. 262-263 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.00 (t, J= 7.04 Hz, 3H, CH3CH2-), 2.47 (s, 3H, CH3), 3.76 (s, 3H, -OCH3), 3.90 (m, 2H, CH3CH2-), 5.46 (s, 1H, CH-), 6.81-7.23 (m, 5H, Ar-H, NH), 9.08 (s, 1H, NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 13.94, 17.63, 48.80, 55.29, 58.93, 111.04, 120.07, 127.00, 128.63, 146.17, 156.45, 167.41. IR (KBr): 3251, 2958, 1724, 1701, 1635 cm-1.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 10)

White solid, m.p. 200-201◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.07 (m, 3H, CH3CH2-), 2.22 (s, 3H, CH3), 3.69 (s, 3H, -OCH3), 3.91 (m, 2H, CH3CH2-), 5.08 (s, 1H, CH-), 6.75 (m, 2H, Ar-H), 7.11 (m, 2H, Ar-H), 7.65 (s, 1H, NH), 9.14 (s, 1H, NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 14.03, 17.69, 53.27, 54.97, 59.08, 99.49, 113.62,

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DOI: 10.1039/C4RA09929J

127.33, 136.99, 147.94, 152.11, 158.37, 165.30. IR (KBr): 3251, 3112, 2923, 1705, 1651 cm-1.

Ethyl 4-(furan-2-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 11)

Black solid, m.p. 205-206 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.14 (t, J= 5.27 Hz, 3H, CH3CH2-), 2.20 (s, 3H, CH3), 4.02 (q, J= 7.04 Hz, 2H, CH3CH2-), 5.19 (s, 1H, CH), 6.06-6.12 (m, 1H, Ar-H), 6.24-6.34 (m, 1H, Ar-H), 7.35 (m, 1H, Ar-H), 7.72 (s, 1H, NH), 9.21 (s, 1H, NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 13.88, 14.07, 53.20, 59.15, 105.20, 110.27, 113.58, 142.06, 143.56, 150.50, 156.41, 158.67. IR (KBr): 3201, 3250, 2896, 2850, 1693 cm-1.

Ethyl 6-methyl-2-oxo-4-(thiophen-2-yl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 12)

White solid, m.p. 210-211 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.17 (m, 3H, CH3CH2-), 2.20 (s, 3H, CH3), 4.04 (q, J= 7.05 Hz, 2H, CH3CH2-), 5.39 (s, 1H, CH-), 6.87-6.93 (m, 2H, Ar-H), 7.17.(m, 1H, Ar-H), 7.88.(s, 1H, NH), 9.48 (s, 1H, NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 14.08, 17.61, 49.28, 59.30, 99.71, 123.44, 124.56, 126.60, 148.59, 148.70, 152.19, 164.95. IR (KBr): 3332, 3240, 3116, 2981, 1701, 1647, 1230, 1095 cm-1.

Ethyl 6-methyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 13)

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Pale- yellow solid, m.p. 223-224 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.15-1.27 (m, 3H, CH3CH2-), 2.47 (s, 3H, CH3), 4.04-4.13 (m, 2H, CH3CH2-), 4.70 (d, J= 2.8 Hz, 1H, CH), 6.13-6.21 (dd, J= 5.8, 5.95 Hz, 1H, CH=C-H), 6.38 (d, J=15.8, 1H, H-C=CH), 7.44-7.26 (m, 5H, Ar-H), 7.54 (s, 1H, NH), 9.15 (s, 1H, NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 14.18, 17.69, 51.82, 59.15, 97.70, 126.26, 127.51, 127.74, 128.04, 129.89, 136.16, 148.49, 152.57, 165.14. IR (KBr): 3241, 1704, 1650, cm-1.

5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (Table 2, entry 15)

Pale- yellow solid, m.p. 235-236 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 2.08 (s, 3H, CH3), 2.27 (s, 3H, CH3CO-), 5.23 (s, 1H, CH-), 7.21-7.33 (m, 5H, Ar-H), 7.80 (s, 1H, NH), 8.97 (s, 1H, NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 18.84, 30.24, 53.74, 109.53, 126.35, 127.28, 128.46, 144.15, 148.07, 152.09, 194.24. IR (KBr): 3294, 3116, 2920, 1701, 1616 cm-1.

Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 16)

White solid, m.p. 211 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.08 (m, 3H, CH3CH2-), 2.27 (s, 3H, CH3), 3.99 (m, 2H, CH3CH2-), 5.09 (s, 1H, CH-), 6.89 (m, 2H, Ar-H), 7.09-7.30 (m, 2H, Ar-H), 9.58 (s, 1H, NH), 10.27 (s, 1H,NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 13.96, 17.07, 55.01, 59.47, 100.88, 113.79, 127.55, 135.64, 144.68, 158.66, 165.09, 173.94. IR (KBr): 3328, 3174, 1670, 1573 cm-1.

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Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 17)

White solid, m.p. 179-180 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.09 (m, 3H, CH3CH2), 2.27 (s, 3H, CH3), 3.97 (m, 2H, CH3CH2-), 5.14 (s, 1H, CH-), 7.16- 7.23 (m, 2H, Ar-H), 7.38-7.42 (m, 2H, Ar-H), 9.65 (s, 1H, NH), 10.59 (s, 1H, NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 13.93, 17.12, 53.38, 59.59, 100.21, 128.25, 128.53, 132.20, 142.31, 145.32, 164.92, 174.17. IR (KBr): 3325, 3178, 2985, 1674, 1573, 1195 cm-1.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimid- ine -5-carboxylate (Table 2, entry 19)

Yellow solid, m.p. 153 ◦C. 1H-NMR (250 MHz, DMSO-d6): δ= 1.05 (m, 3H, CH3CH2-), 2.27 (s, 3H, CH3), 3.69 (s, 3H, -OCH3), 3.99 (m, 2H, CH3CH2-), 5.09 (s, 1H, CH-), 6.86 (m, 2H, Ar-H), 7.13 (m, 2H, Ar-H), 9.58 (s, 1H, NH), 10.27 (s, 1H,NH). 13C-NMR (62.9 MHz, DMSO-d6): δ= 19.21, 22.32, 58.63, 60.26, 64.73, 106.13, 119.04, 132.80, 140.89, 149.93, 163.92, 170.34, 179.19. IR (KBr): 3313, 3170, 1666, 1573 cm-1.

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