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A simple and efficient synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones via Biginelli reaction catalyzed by nanomagnetic-supported sulfonic acid

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ABSTRACT

Nanomagnetic-supported sulfonic acid is found to be a new, powerful, and reusable heterogeneous catalyst for the rapid synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones under conventional heating and microwave irradiation. This is the first example of combination of magnetic iron nanoparticles and microwave technique for the multicomponent reaction. The optical behaviors of the 3,4-dihydropyrimidin-2-(1*H*)-ones have been investigated by UV–vis spectroscopy.

1. Introduction

Catalysis lies at the heart of countless chemical protocols, from academic research laboratories to the chemical industry. With the birth of nanocatalysts, the diffusion limitations associated with porosity and transport of reactants and/or products to and from the catalytic sites, present in bulk materials, can be overcome; however, isolation and recovery of these nanocatalysts from the reaction mixture is not so easy. Conventional filtration is not efficient because of the nano size of the catalyst. This limitation hampers the economics and sustainability of these nanocatalytic protocols. To overcome this issue, the use of magnetic nano-supports has emerged as one of the best solutions; their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the reaction mixture with an external magnet.[1–6] Exploring newer and better experimental techniques to carry out chemical transformations has been an important premise of chemical synthesis. Microwave-assisted organic synthesis has been one such technique, as it helps in minimizing the energy consumption required for heating as well as time required for the reaction. The unique combination of solid catalysts with microwave activation resulted in several beneficial features. (i) First, most solid catalysts absorb microwave irradiation, thus they can serve as an internal heat source for the reactions. As all heterogeneous catalytic reactions occur on the surface of catalysts, it is the most direct and selective heating that one can provide. (ii) The catalyst itself can serve as a heat source and as a medium for reactions, eliminating the need to apply a solvent for these reactions. .(iii) Based on a broad array of literature data heterogeneous catalytic microwave-assisted reactions occur much more rapidly than their conventionally heated counterparts, thus the time factor is another advantage.[7,8] Organic synthesis performed through multicomponent reactions have become a significant area of research in organic chemistry since such processes improve atom economy.[9] From an environmental and economic perspective, multicomponent reactions (MCRs) have emerged as valuable tools for the preparation of structurally diverse drug-like compounds. One prominent MCR that produces an interesting class of nitrogen heterocycles is the venerable Biginelli reaction providing 3,4-dihydropyrimidin-2-(1*H*)-ones (DHPMs). DHPM derivatives exhibit a wide range of biological and pharmacological properties, such as antiviral, antimitotic, anticarcinogenic, antihypertensive and most importantly, as calcium channel modulators.[10–13]

2. Results and discussion

At the onset of this study, no example of the combination of magnetic iron nanoparticles and microwave technique had been reported for the multicomponent reactions. Herein we describe an efficient and facile synthesis of 3,4-dihydropyrimidin-2-

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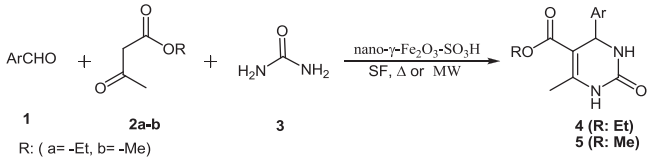
(1*H*)-ones under thermal and microwave conditions catalyzed by nanomagnetic-supported sulfonic acid, nano-γ-Fe_2O_3–SO_3H, (Scheme 1). Nano-γ-Fe_2O_3–SO_3H has been prepared by the reaction of chlorosulfonic acid with nano maghemite previously and was characterized thoroughly and has been used as catalyst in Hantzsch 1,4-dihydropyridines synthesis.[14]



Scheme 1. Synthesis of Biginelli 3,4-dihydropyrimidin-2-(1*H*)-ones catalyzed by nano-γ-Fe_2O_3–SO_3H.

First, in order to optimize the conditions, the reaction of benzaldehyde 1, ethyl acetoacetate **2a** and urea **3**, was chosen as a model system under thermal conditions (Table 1). The results listed in Table 1 showed that the conversions were sensitive to the catalyst. Nanomagnetic-supported sulfonic acid proved to be the best catalyst affording the highest yield (Table 1, entries 8, 9). In order to evaluate the effect of the catalyst particle size on the catalytic activity, the results were compared with those obtained using bulk-γ-Fe_2O_3–SO_3H. Utilizing nano-γ-Fe_2O_3–SO_3H or nano-γ-Fe_2O_3@-SiO_2–SO_3H increased the yield from 65% to 95% (Table 1, entries 7, 8, and 9). One reason for this behavior may be related to the number of available active sites, which in turn increases the catalytic activity. No activity was observed in the presence of Fe and pure bulk-Fe_2O_3 (Table 1, entries 1, 4). A trace amount of product also observed when catalyzed by $FeCl_3\cdot6H_2O$, $FeCl_2\cdot4H_2O$, nano-γ-Fe_2O_3, and nano-γ-Fe_2O_3@SiO_2 (entries 2, 3, 5, 6). The reaction was clean and fairly rapid. No side products were detected in these reactions.

Table 1
Iron-based catalyzed Biginelli 3,4-dihydropyrimidin-2-(1*H*)-ones[a]

Entry	Catalyst (0.1 g)	Time (h:min)	Yield (%)[b]
1	Fe	03:00	—
2	$FeCl_2\cdot4H_2O$	03:00	Trace
3	$FeCl_3\cdot6H_2O$	03:00	Trace
4	Bulk-Fe_2O_3	03:00	—
5	Nano-γ-Fe_2O_3	03:00	25
6	Nano-γ-Fe_2O_3@SiO_2	03:00	20
7	Bulk-Fe_2O_3–SO_3H	03:00	65
8	Nano-γ-Fe_2O_3@SiO_2–SO_3H	03:00	95
9	Nano-γ-Fe_2O_3–SO_3H	03:00	95

[a] Benzaldehyde–ethyl acetoacetate–urea=1:2:1.5, Solvent-free, at 60 °C.
[b] Yields refer to isolated products.

Only 0.1 g of nano-γ-Fe_2O_3–SO_3H was required to convert substrates into the corresponding product and higher amounts of the catalyst did not increase the yields significantly. Reaction with 0.09 g of the catalyst required a longer reaction time while the reaction with 0.07 g of nano-γ-Fe_2O_3–SO_3H produced only a 69% yield of the product after 3 h under thermal conditions (Table 2).

Moreover, when the reaction was carried out in solvent-free condition, good conversion was achieved and the results showed that, 'no solvent' is the 'best solvent' and complies with the green chemistry principles (Table 3, entry 4).[15]

Table 2
Influence of the amount of nano-γ-Fe_2O_3–SO_3H on the Biginelli synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones[a]

Entry	Nano-γ-Fe_2O_3–SO_3H (g)	Time (h:min)	Yield (%)[b]
1	0.05	3:00	53
2	0.07	3:00	69
3	0.09	3:50	92
4	0.1	3:00	95
5	0.15	3:00	95

[a] Benzaldehyde–ethyl acetoacetate–urea=1:2:1.5, Solvent-free, at 60 °C.
[b] Yields refer to isolated products.

Table 3
Effect of solvent and temperature on the nano-γ-Fe_2O_3–SO_3H catalyzed synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones[a]

Entry	Solvent	Temp/°C	Time (h:min)	Yield (%)[b]
1	H_2O	Reflux	05:00	15
2	EtOH	Reflux	05:00	91
3	CH_3CN	Reflux	05:00	91
4	—	60	03:00	95
5	—[c]	60[c]	00:03[c]	97

[a] Benzaldehyde–ethyl acetoacetate–urea=1:2:1.5, 0.1 g nano-γ-Fe_2O_3–SO_3H, at 60 °C.
[b] Yields refer to isolated products.
[c] Microwave irradiation.

Using microwave irradiation decreased remarkably the reaction times. So, to further optimize the reaction conditions, the temperature and the MW power were also optimized and the best results were obtained using 0.1 g of nano-γ-Fe_2O_3–SO_3H in solvent-free condition at 250 W. In both methods, 60 °C was the optimum temperature. No increase in yield was observed at higher temperatures, while lowering the temperature below 60 °C reduced the reaction rate.

Using the optimized reaction conditions (Table 3, entry 5), we explored the generality of this method with different aldehydes to prepare a series of DHPMs (Table 4). In most cases, the reactions

Table 4
Nano-γ-Fe_2O_3–SO_3H catalyzed Biginelli synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones[a]

Entry	Ar	R	Product	Method A		Method B	
				Time (h:min)	Yield (%)[b]	Time (min:sec)	Yield (%)[b]
1	Ph	Et	**4a**	03:00	95	03:00	97[17]
2	*p*-MeC_6H_4	Et	**4b**	03:00	74	03:00	89[18]
3	*p*-ClC_6H_4	Et	**4c**	04:00	65	02:00	96[19]
4	*p*-HOC_6H_4	Et	**4d**	02:30	89	00:30	96[20]
5	*p*-$O_2NC_6H_4$	Et	**4e**	03:30	82	00:30	95[21]
6	*p*-FC_6H_4	Et	**4f**	03:00	69	01:00	93[22]
7	*o*-HOC_6H_4	Et	**4g**	03:00	79	01:10	97[23]
8	3,4-$DiMeOC_6H_4$	Et	**4h**	1:35	91	02:00	94[24]
9	*o*-Cl-C_6H_4	Et	**4i**	03:00	79	05:00	83[25]
10	4-HO-3-EtO-C_6H_3	Et	**4j**	03:00	71	02:00	97[26]
11	*m*-HOC_6H_4	Et	**4k**	03:00	93	00:30	95[27]
12	Ph	Me	**5a**	02:00	84	01:00	93[28]
13	3,4-DiMeO-C_6H_4	Me	**5b**	01:30	97	02:00	92[29]
14	*p*-$O_2NC_6H_4$	Me	**5c**	02:00	90	00:40	98[30]
15	*p*-MeC_6H_4	Me	**5d**	02:45	81	03:10	94[31]
16	*p*-ClC_6H_4	Me	**5e**	03:35	78	02:30	95[31]
17	*p*-HOC_6H_4	Me	**5f**	01:50	94	00:30	97[32]
18	*p*-FC_6H_4	Me	**5g**	03:00	70	01:10	96[33]
19	*o*-HOC_6H_4	Me	**5h**	02:45	85	01:00	97[26]
20	*o*-ClC_6H_4	Me	**5i**	03:00	82	03:00	89[34]
21	4-HO-3-EtO-C_6H_3	Me	**5j**	02:20	80	02:10	98[35]

[a] All products were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopic data, and melting points.
[b] Yields refer to isolated products.

proceeded cleanly. The results obtained by the two different techniques: conventional heating (method A) and MW irradiation (method B), were compared. As shown in Table 4, the microwave-assisted nano-γ-Fe_2O_3–SO_3H catalyzed reactions were superior to those using conventional heating. MW-assisted chemistry was used due to the efficiency of the interaction of MWs with the polar nano-catalyst,[16] as it allows rapid heating of the reaction mixture to required temperatures and the precise control of the reaction temperature. With two methods, the aryl group substitution with different groups and with the same groups located at different positions of the aromatic ring has been shown not to have much effect on the formation of the final product and afford the expected products **4** and **5** in good to high yields. The products were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, and also by comparison with authentic samples.

Importantly, note that the ferromagnetic property of nano-γ-Fe_2O_3–SO_3H made the isolation and reuse of this catalyst very easy. After completion of the reaction, the mixture was triturated with ethyl acetate. Within a few seconds after stirring was stopped, the reaction mixture turned clear and catalyst was deposited on the magnetic bar, which was easily removed using an external magnet. After being washed with acetone and dried in air, the nano-γ-Fe_2O_3–SO_3H can be directly reused without any deactivation even after five rounds of synthesis of product **4a** (Table 5). The characterization of the nano-γ-Fe_2O_3–SO_3H before and after reuse five times showed the same particle size by transmission electron microscopy (TEM; Fig. 1b) and the same crystal structure by XRD.

Table 5
Caption reuse of nano-γ-Fe_2O_3–SO_3H in the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones[a]

Run	Yield (%)[a]	
	Method A	Method B
1	95	97
2	95	97
3	95	96
4	93	96
5	93	94

[a] Isolated yield.

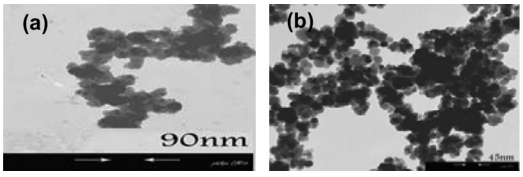


Fig. 1. TEM pictures of nano-γ-Fe_2O_3–SO_3H before use (a) and after reuse five times (b).

Because of extended conjugation with inbuilt 3,4-dihydropyrimidin-2-(1*H*)-one ring, these compounds are expected to show optical behavior. Therefore the UV–vis absorption spectra were recorded in different solvents (Table 6).

In acetonitrile UV–vis absorption spectra appeared around 251–281 nm range, in ethanol UV–vis absorption spectra appeared around 268–280 nm and in acetone absorption bands appeared around 208–210 nm range. Comparatively in acetonitrile and ethanol solutions 3,4-dihydropyrimidin-2-(1*H*)-ones exhibited relatively higher absorption than the acetone solution, also the results couldn't be classified according to the substituents on the phenyl ring.

Table 6
UV–vis data of the some of 3,4-dihydropyrimidin-2-(1*H*)-ones

Compound (4)	λ_{max}^{nm}		
Aryl	Acetone	Ethanol	Acetonitrile
Ph (**4a**)	208	279	279
p-MeC_6H_4 (**4b**)	210	278	275
p-ClC_6H_4 (**4c**)	210	279	280
p-FC_6H_4 (**4f**)	210	273	251
o-ClC_6H_4 (**4i**)	210	278	281
p-$O_2NC_6H_4$ (**4e**)	—	278	—
3,4-MeO–C_6H_4 (**4h**)	210	268	275
4-HO–3-EtO-C_6H_3 (**4j**)	210	280	275

3. Results and discussion

In conclusion, an efficient, sustainable and green procedure for synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones has been developed using a magnetically separable and easily recyclable nano-γ-Fe_2O_3–SO_3H catalyst in solvent-free medium under thermal or microwave conditions. Easy magnetic separation of the catalyst eliminates the requirement of catalyst filtration after completion of the reaction, which is an additional greener attribute of this reaction.

4. Experimental section

4.1. Instrumentation, analysis, and starting materials

All chemicals were purchased from Merck, Fluka or Acros companies and used without any further purification. Nano-γ-Fe_2O_3–SO_3H was prepared with the reported method.[14] Microwave LG oven MG 555f model was used. NMR spectra were recorded with a Bruker Avance 300 spectrometer (^{1}H NMR 300 MHz and ^{13}C NMR 75 MHz) in pure deuterated chloroform with tetramethylsilane (TMS) as the internal standard. Presented UV–vis spectra were obtained as ethanol solutions (10^{-5} M) on a Shimadzu UV-1650PC spectrophotometer.

4.2. General procedure for the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones under conventional heating method (method A)

A mixture of aldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), urea (1.5 mmol) and nano-γ-Fe_2O_3–SO_3H (0.1 g) was heated at 60 °C. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and triturated with ethyl acetate (5 mL). In the presence of a magnetic stirrer bar, nano-γ-Fe_2O_3–SO_3H moved onto the stirrer bar steadily and the reaction mixture turned clear within 10 s. The catalyst can be isolated by simple decantation. After evaporation of the solvent, the crude product was recrystallized from EtOH/H_2O to give a pure product.

4.3. General procedure for the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones under microwave irradiation method (method B)

A mixture of aldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), urea (1.5 mmol), and nano-γ-Fe_2O_3–SO_3H was placed in a microwave reaction vial. The LG microwave oven MG 555f was programmed to 250 W at 60 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, ethyl acetate (5 mL) was added and the catalyst was separated by applying an external magnet. The solvent was evaporated and the residue was

recrystallized from EtOH/H_2O to give a pure product, which gave satisfactory spectroscopic data (^{1}H NMR, ^{13}C NMR, and IR) and melting point, compared to data with those of samples synthesized by reported procedures.

4.4. Spectral data of some products

*4.4.1. 5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (**4a**).* Mp: 202–204 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.62 (s, 1H, NH), 7.24–7.31 (m, 5H, ArH), 6.1 (s, 1H, NH), 5.38 (s, 1H, CH), 4.03 (q, 2H, OCH_2CH_3), 2.32 (s, 3H, CH_3), 1.13 (t, 3H, OCH_2CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 14.12, 18.55, 55.59, 59.97, 101.23, 126.56, 127.88, 128.66, 143.73, 146.48, 153.73, 165.65.

IR (KBr) cm^{-1}: 3247.90, 3116.75, 2977.89, 1720.39, 1643.24.

*4.4.2. 5-(Ethoxycarbonyl)-6-methyl-4-(p-tolyl)-3,4-dihydropyrimidin-2(1H)-one (**4b**).* Mp: 216–218 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.75 (s, 1H, NH), 7.09–7.21 (m, 4H, ArH), 6.22 (s, 1H, NH), 5.34 (s, 1H, CH), 4.04 (q, 2H, OCH_2CH_3), 2.3 (s, 3H, CH_3), 1.15 (t, 3H, OCH_2CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 14.16, 18.50, 21.09, 55.18, 59.93, 101.35, 126.45, 129.30, 137.52, 140.91, 146.41, 153.99, 165.74.

IR (KBr)cm^{-1}: 3245.97, 3114.82, 2979.82, 1724.24, 1649.02.

*4.4.3. 5-(Ethoxycarbonyl)-4-(4-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**4c**).* Mp: 214–216 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.44 (s, 1H, NH), 7.22–7.29 (m, 4H, ArH), 6.1 (s, 1H, NH), 5.36 (s, 1H, CH), 4.04 (q, 2H, OCH_2CH_3), 2.32 (s, 3H, CH_3), 1.15 (t, 3H, OCH_2CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 14.15, 18.63, 55.02, 60.14, 101.02, 127.99, 128.84, 133.69, 142.19, 146.54, 153.48, 165.45.

IR (KBr)cm^{-1}: 3240.19, 3116.75, 2977.89, 1704.96, 1650.95.

*4.4.4. 5-(Ethoxycarbonyl)-6-methyl-4-(3,4-dimethoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (**4h**).* Mp: 178 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 9.15 (s, 1H, NH), 7.68 (s, 1H, NH),5.09 (s, 1H, CH), 3.95 (q, 2H, OCH_2CH_3), 3.37 (s, 3H, CH3), 3.95 (q, 2H, OCH_2CH_3), 2.24 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 14.15, 17.76, 53.49, 55.4, 55.52, 59.19, 99.39, 110.45, 111.72, 117.9, 137.35, 148.06, 148.15, 148.48, 152.29, 165.43.

IR (KBr) cm^{-1}: 3247.90, 3116.75, 1712.67, 1650.95.

*4.4.5. 5-(Ethoxycarbonyl)-4-(2-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**4i**).* Mp: 222–224 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 9.08 (s, 1H, NH), 7.19–7.37 (m, 4H, ArH), 5.98 (s, 1H, NH), 5.86 (s, 1H, CH), 3.97 (q, 2H, OCH_2CH_3), 2.41 (s, 3H, CH_3), 1.02 (t, 3H, OCH_2CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 13.97, 18.23, 52.06, 59.93, 98.8, 127.51, 128.03, 129.23, 129.75, 132.55, 139.58, 148.56, 153.42, 165.33.

IR (KBr) cm^{-1}: 3234.40, 3110.97, 1701.10, 1645.17.

*4.4.6. 5-(Ethoxycarbonyl)-4-(3-ethoxy-4-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**4j**).* Mp: 193–195 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.27 (s, 1H, NH), 6.79 (s, 1H, NH), 5.31 (s, 1H, CH),4.75(s, 1H, OH) 4.03 (q, 2H, OCH_2CH_3), 2.33 (s, 3H, CH_3), 1.39 (t, 3H, OCH_2CH_3), 1.15 (t, 3H, OCH_2CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 14.13, 14.77, 17.74, 53.55, 59.15, 63.93, 99.64, 112.3, 115.38, 118.45, 135.9, 146.13, 146.32, 147.84, 152.31, 165.47.

IR (KBr) cm^{-1}: 3417, 3263, 2985.60, 1704.96, 1650.95.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.10.085.

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