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RESEARCH PAPER

Fe_3O_4 Nanoparticles as an Efficient and Magnetically Recoverable Catalyst for the Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones under Solvent-Free Conditions

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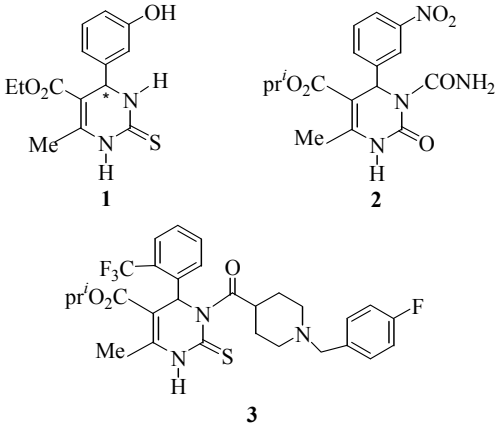
Abstract: The catalytic activity of Fe_3O_4 nanoparticles (NPs) in a one-pot three component condensation reaction consisting of an aromatic aldehyde, urea or thiourea, and a β-dicarbonyl under solvent-free conditions was investigated. This reaction affords the corresponding dihydropyrimidinones (thiones) in high to excellent yields. Compared with the classical Biginelli reactions this method consistently gives a high yield, easy magnetic separation, a short reaction time, and catalyst reusability.

Key words: dihydropyrimidinones; dihydropyrimidinthiones; ferroferric oxide nanoparticle; one-pot condensation; solvent-free

As green chemistry is currently a major concern for organic chemists, reactions under solvent-free conditions with a solid catalyst have received much attention [1]. Green chemistry approaches hold significant potential for the reduction of by-products, a reduction in the amount of waste produced, lower energy costs, and enhanced selectivity. Additionally, the development of new methodologies toward the synthesis of previously unobtainable materials using existing technologies is of interest [2].

Dihydropyrimidinones and dihydropyrimidinthiones are important classes of heterocycles that have attracted much synthetic interest and their derivatives have pharmacological and biological properties such as antihypertensive activity, calcium channel blocking, alpha-1a-antagonism, neuropeptide Y (NPY) antagonism, antitumor, antibacterial, and anti-inflammatory activity [3–6]. Notably, monastrol (**1**) is the only cell-permeable molecule that blocks normal bipolar spindle assembly in mammalian cells causing cell cycle arrest [7] and is considered a lead for the development of new anticancer drugs [8] while appropriately functionalized DHPM analogs have emerged as orally active antihypertensive agents (**2**, **3**) [6] (Scheme 1).

Because of the importance of these compounds as synthons in organic synthesis, many synthetic methods for the preparation of these compounds have been developed based on the Biginelli reaction [9]. The simple and direct method originally reported by Biginelli in 1893 involved a three-component condensation reaction between an aldehyde, urea, and a



Scheme 1. Dihydropyrimidine antagonists.

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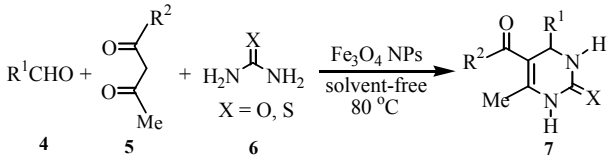
β-ketoester under acidic conditions [10]. One major drawback of this reaction, however, is the low to moderate yields that are frequently obtained when using substituted aromatic or aliphatic aldehydes [11]. This has led to the development of more complex multistep strategies that produce somewhat higher overall yields but lack the simplicity of the one-pot Biginelli protocol [11,12]. Thus, Biginelli's reaction for the synthesis of dihydropyrimidinone has received renewed interest and several improved procedures have recently been reported [13–16] although some of these methods involve the use of strong Lewis acids such as BF_3 [14], $Bi(NO_3)_3$ [15], and $Ln(OTf)_3$ [16], protic acids such as AcOH [14], and additives [14]. However, there are several disadvantages associated with the reported methodologies including unsatisfactory yields, long conversion times, difficult handling of reagents, toxic and inflammable organic solvents, and incompatibility with other functional groups in the molecules that limit these methods to small-scale synthesis. Thus, the development of facile and environmentally friendly synthetic methods for the preparation of dihydropyrimidinones and dihydropyrimidinthiones are in demand.

Recently, the application of nanoparticles (NPs) as catalysts has attracted worldwide attention because of their high catalytic activity and improved selectivity [17]. Although the nanocatalysts have several advantages over conventional catalyst systems the isolation and recovery of these nanocatalysts is difficult. To overcome this problem the use of magnetically recoverable nanocatalysts is of interest [18]. This type of nanocatalyst can be easily separated from the reaction mixture using an external magnetic field. Fe_3O_4 NPs have been used as an efficient and magnetically recoverable nanocatalyst in the three-component coupling of an aldehyde, an alkyne, and an amine [19]. Also, the application of Fe_3O_4 NPs as nanocatalysts in a C-C coupling reaction by the Sonogashira-Hagihara reaction has been investigated [20].

Because of their inherent properties like environmental friendliness, greater selectivity, operational simplicity, non-corrosive nature, moisture insensitivity, and ease of isolation, it is of interest to determine the behavior of this catalytic system for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones (thiones).

Following our interest in producing 3,4-dihydropyrimidine-2(1H)-ones [21,22], a study to revisit this reaction in a parallel combinatorial fashion using the Fe_3O_4 NPs solvent-free synthesis approach was initiated (Scheme 2).



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Scheme 2. Synthesis of 3,4-dihydropyrimidin-2(1H)-ones (thiones) using Fe_3O_4 NPs.

1 Experimental

1.1 Preparation of the Fe_3O_4 NPs

The Fe_3O_4 NPs were prepared as reported in the literature [23]. Typically, to prepare Fe_3O_4 NPs 5.2 g of $FeCl_3$ and 2.0 g of $FeCl_2$ were successively dissolved in 25 ml of distilled water containing 0.85 ml of 12.1 mol/L HCl. The resulting solution was added dropwise into 250 ml of a 1.5 mol/L NaOH solution under vigorous stirring. The last step generated an instant black precipitate. The precipitate was isolated in a magnetic field and the supernatant was removed from the precipitate by decantation.

1.2 Synthesis of 3,4-dihydropyrimidin-2(1H)-ones

All the chemicals were purchased from Merck, Fluka and Sigma-Aldrich. The reactions were monitored by thin layer chromatography (TLC). The products were isolated and identified by comparing their physical and spectral data with authentic samples. Infrared (IR) spectra were recorded on FT-IR JASCO-680, ^{1}H-NMR spectra were obtained on a Bruker DPX-300 MHz and melting points were determined on a Barnstead Electrothermal (BI 9300) apparatus.

In a typical procedure for the preparation of 5-(ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (**7a**), a mixture of benzaldehyde (1 mmol), ethylacetoacetate (1 mmol), urea (1.5 mmol), and Fe_3O_4 NPs (0.046 g) was stirred at 80 °C for 16 min. After the completion of the reaction as determined by TLC, 5 ml of ethanol was added to the reaction mixture, stirred and heated for 5 min. The reaction mixture was filtered and washed with hot ethanol. The hot filtrate was poured onto crushed ice and the solid product collected by filtration and washed with cold ethanol and a mixture of ethanol-water. The solid product was recrystallized from ethanol. The products were characterized by IR, ^{1}H NMR, and by a comparison of their melting points with the reported melting points.

5-Ethoxycarbonyl-6-methyl-4-(2-chloro-6-flourophenyl)-3,4-dihydropyrimidin-2(1H)-one (**7g**). mp: 246–248 °C; R_f = 0.33 (*n*-hexane:ethyl acetate = 2:1); IR (KBr, cm^{-1}): 3349, 3122, 2983, 1698, 1636, 1520, 1454, 1230; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, 3H, J = 7.0 Hz), 2.19 (s, 3H), 3.88 (q, 2H, J = 6.8 Hz), 5.86 (s, 1H), 7.16 (dd, J = 8.2 and J = 21.6 Hz, 1H), 7.3 (m, 2H), 7.63 (s, 1H), 9.3 (s, 1H); Anal. Calcd. for $C_{14}H_{14}ClFN_2O_3$: C, 53.77; H, 4.51; Cl, 11.34; F, 6.08; N, 8.96; O, 15.35; Found: C, 53.8; H, 4.6; N, 9.0.

5-Ethoxycarbonyl-6-methyl-4-(2-hydroxy-3-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (**7k**). mp: 221–223 °C; R_f = 0.3 (*n*-hexane:ethyl acetate = 2:1). IR (KBr, cm^{-1}): 3450, 3352, 2938, 1677, 1625, 1529, 1479, 1274. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (t, J = 7.1 Hz, 3H), 2.01 (s, 3H), 3.19 (s, 1H), 3.89 (s, 3H), 4.28 (q, J = 7.1 Hz, 2H), 4.66 (s, 1H), 5.7 (s, 1H),

5.78 (s, 1H), 6.76–6.94 (m, 3H). Anal. Calcd. for $C_{15}H_{18}N_2O_5$: C, 58.82; H, 5.92; N, 9.15; O, 26.12; Found: C, 58.9; H, 5.8; N, 9.2.

5-Methoxycarbonyl-6-methyl-4-(5-bromo-2-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (**7n**). mp: 260–262 °C; R_f = 0.23 (*n*-hexane:ethyl acetate = 2:1). IR (KBr, cm^{-1}): 3234, 3090, 2960, 1753, 1701, 1579, 1473, 1247. ^{1}H NMR (500 MHz, DMSO): δ1.92 (s, 3H), 3.83 (s, 3H), 4.71 (s, 1H), 6.78 (s, 1H), 7.08 (brs, 2H), 7.33–7.38 (m, 3H). Anal. Calcd. for $C_{13}H_{13}BrN_2O_4$: C, 45.77; H, 3.84; Br, 23.42; N, 8.21; O, 18.76; Found: C, 45.8; H, 3.9; N, 8.3.

5-Methylcarbonyl-6-methyl-4-(2-thienyl)-3,4-dihydropyrimidin-2(1H)-one (**7r**). mp: 202–204 °C; R_f = 0.31 (*n*-hexane:ethyl acetate = 2:1). IR (KBr, cm^{-1}): 3332, 3265, 2941, 1679, 1600, 1527, 1424. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.11 (s, 3H), 2.24 (s, 3H), 5.58 (s, 1H), 6.8–7.09 (m, 3H), 6.98 (s, 1H), 7.29 (s, 1H). Anal. Calcd. for $C_{11}H_{12}N_2O_2S$: C, 55.91; H, 5.12; N, 11.86; O, 13.54; S, 13.57; Found: C, 56.1; H, 5.2; N, 11.8.

5-Methoxycarbonyl-6-methyl-4-(2-thienyl)-3,4-dihydropyrimidin-2(1H)-thione (**7y**). mp: 230–232 °C; R_f = 0.38 (*n*-hexane:ethyl acetate = 2:1). IR (KBr, cm^{-1}): 3384, 3276, 2959, 1615, 1415, 1083. ^{1}H NMR (500 MHz, $CDCl_3$): δ2.38 (s, 3H), 3.74 (s, 3H), 5.71 (s, 1H), 6.93–7.26 (m, 3H), 7.42 (s, 1H), 7.93 (s, 1H). Anal. Calcd. for $C_{11}H_{12}N_2O_2S_2$: C, 49.23; H, 4.51; N, 10.44; O, 11.92; S, 23.90; Found: C, 49.3; H, 4.6; N, 10.5.

5-Methoxycarbonyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1H)-thione (**7z**). mp: 202–204 °C; R_f = 0.33 (*n*-hexane:ethyl acetate = 2:1). IR (KBr, cm^{-1}): 3334, 3200, 2970, 1669, 1570, 1470, 1183. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.36 (s, 3H), 3.65 (s, 3H), 5.36 (s, 1H), 7.16 (dd, J = 17.6 and J = 8.0 Hz, 2H), 7.34 (dd, J = 16.7 and J = 7.8 Hz, 2H), 7.44 (s, 1H), 8.08 (s, 1H). Anal. Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14; O, 11.58; S, 11.60; Found: C, 60.8; H, 5.9; N, 10.2.

2 Results and discussion

2.1 Characterization of Fe_3O_4 NPs

Table 1 Catalyst effects in the synthesis of 5-(ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-ones (thiones) from benzaldehyde, ethylacetoacetate, and urea or thiourea under solvent-free conditions

Fe_3O_4 NPs	Dihydropyrimidinone		Dihydropyrimidinthione	
(mol%)	Time (min)	Yield[a] (%)	Time (min)	Yield[a] (%)
5	34	90	88	88
10	25	92	60	90
15	22	94	57	92
20	16	95	48	94
25	16	93	48	92

[a]Isolated yields.

Figure 1(a) shows the XRD pattern of the Fe_3O_4 NPs. A number of prominent Bragg reflections reveal that the resultant NPs are Fe_3O_4 with a spinel structure [24]. The size of the Fe_3O_4 NPs was also determined from X-ray line broadening using the Debye-Scherrer formula ($D = 0.9\lambda/\beta\cos\theta$, where D is the average crystalline size, λ is the X-ray wavelength used, β is the angular line width at half maximum intensity, and θ is the Bragg's angle). For the (311) reflection the average size of the Fe_3O_4 NPs was estimated to be around 13 nm. Transmission electron microscopy (TEM) analyses were used for characterization (Fig. 1(b)). The TEM image reveals spherical Fe_3O_4 NPs with an average size of 20–30 nm.

2.2 Effect of catalyst concentration

The catalyst concentration was varied over a range of 5–25 mol% iron oxide nanoparticles on the basis of the total volume of the reaction mixture. Table 1 shows the effect of catalyst concentration on the reaction of benzaldehyde, ethylacetoacetate, and urea or thiourea. The yield of the corresponding dihydropyrimidinone or dihydropyrimidinthione increased with an increase in the catalyst concentration from 5 to 20 mol%. A further addition of catalyst had no noticeable effect on the yield. This was due to the fact that beyond a certain concentration more catalyst sites exist than that required by the reactant molecules and, hence, the additional amount of catalyst does

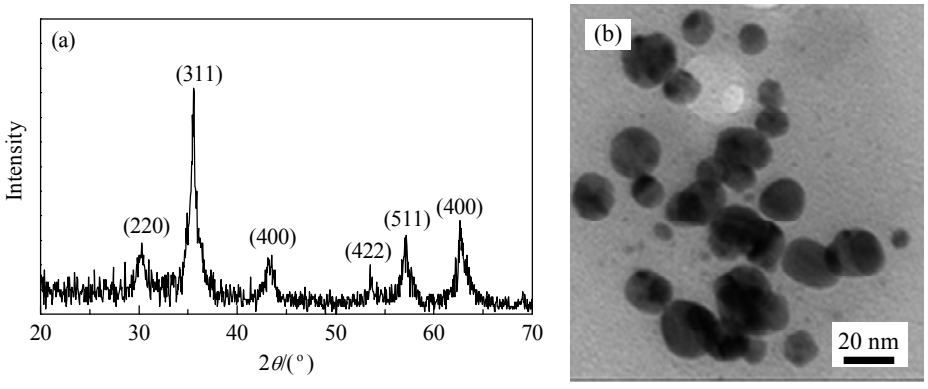


Fig. 1. Powder X-ray diffraction pattern of the Fe_3O_4 NPs (a) and the TEM image showing spherical Fe_3O_4 NPs of 20-30 nm in size (b).

not increase the rate of the reaction. Therefore, in all further reactions 20 mol% of the catalyst was used.

2.3 Synthesis of 3,4-dihydropyrimidin-2(1H)-ones (thiones) upon catalysis by Fe_3O_4 NPs

The results from the reaction of β-dicarbonyl, urea (or thiourea), and various aldehydes in the presence of optimized Fe_3O_4 NPs are shown in Table 2. We extended these reaction conditions to a series of aryl aldehydes under solvent-free conditions. Both aromatic aldehydes bearing either activating or deactivating groups reacted well with β-dicarbonyl to yield the corresponding dihydropyrimidinones (thiones) in high to excellent yields (entries 1–29). All the reactions were complete within 15–40 min.

As for the efficiency of the catalyst, it can be separated from the reaction mixture using a normal magnet.

To use Fe_3O_4 NPs in large scale synthesis, especially in a chemical laboratory, a typical reaction was performed for the synthesis of **7a** with tenfold amount of reactants and the catalyst with respect to the experiment given in the experimental section. The obtained yield of 90% under these conditions is comparable with that in Table 2.

The reactions of acid-sensitive substrates such as cinnamaldehyde also proceeded well to give the dihydropyrimidinone without any side products (entry 10). However, aliphatic aldehydes such as butanal, as observed previously, reacted over longer times with a reduced yield (entry 8, 70 min time, 43% yield) compared with the aromatic compounds under our reaction conditions [33].

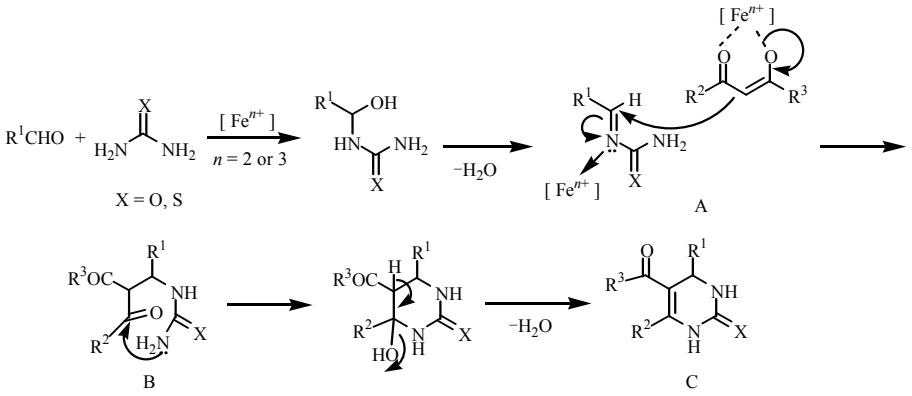
A plausible mechanism for the formation of dihydropyrimidinone is shown in Scheme 3. The reaction may proceed through the acid-catalyzed formation of an acyl imine intermediate or *N*-alkylidene urea formed by a reaction between the aldehyde and urea (A). The interception of the iminium ion by β-dicarbonyl produces an open chain ureide (B), which subsequently cyclizes to the dihydropyrimidinones. Because of the Lewis acidity property of the ferrous or ferric ion, complex (A) can be formed through a coordinative bond and stabilized by a metal cation.

Table 2 Synthesis of dihydropyrimidinones (thiones) catalyzed with Fe_3O_4 NPs under solvent-free condition

Entry	Product[a]	R^1	R^2	X	Time (min)	Yield[b] (%)	Melting point (°C)	
							Found	Reported
1	**7a**	C_6H_5	OEt	O	16	90	203–205	202–203
2	**7b**	4-NO_2-C_6H_4	OEt	O	25	85	206–208	208–209
3	**7c**	4-Cl-C_6H_4	OEt	O	15	93	213–215	215–216
4	**7d**	4-CH_3O-C_6H_4	OEt	O	30	93	200–202	201–202
5	**7e**	2- CH_3O -C_6H_4	OEt	O	30	76	254–256	255–257
6	**7f**	2,4-Cl_2-C_6H_3	OEt	O	30	86	247–249	248–250
7	**7g**	2-Cl-6-F-C_6H_3	OEt	O	35	80	246–248	—
8	**7h**	$CH_3CH_2CH_2$	OEt	O	70	43	179–181	180–182
9	**7i**	2-Thienyl	OEt	O	33	89	214–216	215–217
10	**7j**	C_6H_5-CH=CH	OEt	O	35	74	231–234	232–235
11	**7k**	2-OH-3-CH_3O-C_6H_3	OEt	O	35	96	221–223	—
12	**7l**	C_6H_5-	OMe	O	40	92	210–211	209–211
13	**7m**	2-CH_3O-C_6H_4	OMe	O	24	77	284–286	283–285
14	**7n**	2-OH-5-Br-C_6H_4	OMe	O	25	94	260–262	—
15	**7o**	2-Thienyl	OMe	O	32	90	222–224	225–227
16	**7p**	4-NO_2-C_6H_4	OMe	O	22	90	232–234	235–237
17	**7q**	4-CH_3-C_6H_4	Me	O	33	84	253–255	256–257
18	**7r**	2-Thienyl	Me	O	33	92	202–204	—
19	**7s**	C_6H_5	OEt	S	40	94	205–207	208–210
20	**7t**	4-CH_3-C_6H_4	OEt	S	34	92	193–195	192–194
21	**7u**	4-Cl-C_6H_4	OEt	S	32	95	178–180	180–183
22	**7v**	4-CH_3O-C_6H_4	OEt	S	40	90	147–150	150–152
23	**7w**	C_6H_5-	OMe	S	40	92	222–224	221–222
24	**7x**	2-CH_3O-C_6H_4	OMe	S	35	84	249–252	253–255
25	**7y**	2-Thienyl	OMe	S	30	94	230–232	—
26	**7z**	4-CH_3-C_6H_4	OMe	S	30	94	156–158	155–156
27	**7a'**	C_6H_5	Me	S	30	90	210–212	214–215
28	**7b'**	4-CH_3O-C_6H_4	Me	S	25	95	162–164	161–163
29	**7c'**	4-CH_3-C_6H_4	Me	S	25	90	212–214	215–217

[a]All products were characterized by ^{1}H NMR and IR spectroscopy and compared with those reported in the literature [25–32].

[b]Isolated yield.



Scheme 3. Plausible mechanism for dihydropyrimidinone synthesis using Fe_3O_4 NPs.

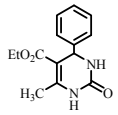
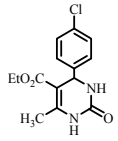
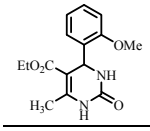
2.4 Comparison of Fe_3O_4 NPs with bulk Fe_3O_4 during the synthesis of 3,4-dihydropyrimidin-2(1H)-ones

To show the ability of the Fe_3O_4 NPs with respect to bulk Fe_3O_4, some comparative results are summarized in Table 3. The yields and reaction times in the presence of Fe_3O_4 NPs are better than using bulk Fe_3O_4.

2.5 Catalyst reusability

The reusability of the catalyst is important for large scale operations and an industrial point of view. Therefore, the reusability of the catalysts was examined in the reaction between ethylacetoacetate, urea, and benzaldehyde. Since the catalyst can be separated from the reaction mixture using an external magnetic field it was recovered with a simple magnet after the dilution of the reaction mixture with EtOH. The recovered catalysts were dried and weighed. Afterwards, according to the amount of catalyst the required amount of fresh ethylacetoacetate, urea, and benzaldehyde were added. The results showed that the catalyst can be reused four consecutive times without a noticeable loss in activity (Table 4)

Table 3 Comparative synthesis of 3,4-dihydropyrimidin-2(1H)-ones in the presence of Fe_3O_4 NPs or bulk Fe_3O_4

Product	Fe_3O_4 bulk		Fe_3O_4 NPs	
	Time (min)	Yield[a] (%)	Time (min)	Yield[a] (%)
	40	90	16	95
	25	90	15	93
	60	70	35	80

[a]Isolated yield.

Table 4 Reusability of Fe_3O_4 NPs for the reaction between benzaldehyde, ethylacetoacetate, and urea

Run	Time (min)	Yield[a] (%)
1	16	90
2	18	88
3	18	86
4	20	85

[a]Isolated yield.

3 Conclusions

We found an efficient, inexpensive and straightforward procedure for the one-pot synthesis of dihydropyrimidinones (thiones) using Fe_3O_4 NPs as a catalyst. We also found that the performance of the catalytic system is greatly facilitated when used without solvents, which is important from the view point of green chemistry. Moreover, the catalysts are nonhygroscopic and inexpensive, which are advantages of this transformation.

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References

1 Tanaka K, Toda F. *Chem Rev*, 2000, **100**: 1025
2 Cave G W V, Raston C L, Scott J L. *Chem Commun*, 2001: 2159
3 Rovnyak G C, Kimball S D, Beyer B, Cucinotta G, Dimarco J D, Gougoutas J, Hedberg A, Malley M, McCarthy J P, Zhang R, Moreland S. *J Med Chem*, 1995, **38**: 119
4 Kappe C O, Fabian W M F, Semones M A. *Tetrahedron*, 1997, **53**: 2803
5 Atwal K S, Swanson B N, Unger S E, Floyd D M, Moreland S, Hedberg A, O'Reilly B C. *J Med Chem*, 1991, **34**: 806
6 Grover G J, Dzwonczyk S, McMullen D M, Normadin D E, Parham S G, Sleph P G, Moreland S. *J Cardiovasc Pharmacol*, 1995, **26**: 289

7 Gartner M, Sunder-Plassmann N, Seiler J, Utz M, Vernos I, Surrey T, Giannis A. *ChemBioChem*, 2005, **6**: 1173
8 Kappe C O, Shishkin O V, Uray G, Verdino P. *Tetrahedron*, 2000, **56**: 1859
9 Mitra A K, Banerjee K. *Synlett*, 2003, 1509
10 Biginelli P. *Gazz Chim Ital*, 1893, **23**: 360
11 Atwal K S, Rovnyak G C, O'Reilly B C, Schwartz J. *J Org Chem*, 1989, **54**: 5898
12 O' Reilly B C, Atwal K S. *Heterocycles*, 1987, **26**: 1185
13 Kappe C O. *Tetrahedron*, 1993, **49**: 6937
14 Hu E H, Sidler D R, Dolling U H. *J Org Chem*, 1998, **63**: 3454
15 Khodaei M M, Khosropour A R, Beygzadeh M. *Synth Commun*, 2004, **34**: 1551
16 Huang Y, Yang F, Zhu C. *J Am Chem Soc*, 2005, **127**: 16386
17 Wang S, Wang Z, Zha Z. *Dalton Trans*, 2009: 9363
18 Firouzabadi H, Iranpoor N, Ghaderi A, Ghavami M, Hoseini S J. *Bull Chem Soc Jpn*, 2011**, 84**: 100
19 Polshettiwar V, Luque R, Fihri A, Zhu H, Bouhrara M, Basset J M. *Chem Rev*, 2011, **111**: 3036
20 Firouzabadi H, Iranpoor N, Gholinejad M, Hoseini S J. *Adv Synth Catal*, 2011, **353**: 125
21 Nasr-Esfahani M, Karami B, Montazerozohori M, Abdi K. *J Heterocycl Chem*, 2008, **45**: 1183
22 Nasr-Esfahani M, Khosropour A R. *Bull Korean Chem Soc*, 2005, **26**: 1331
23 Kang Y S, Rishbud S, Rabolt J F, Stroeve P. *Chem Mater*, 1996, **8**: 2209
24 Park J, An K, Hwang Y, Park J G, Noh H J, Kim J Y, Park J H, Hwang N M, Hyeon T. *Nature Mater*, 2004, **3**: 891
25 Khabazzadeh H, Saidi K, Sheibani H. *Bioorg Med Chem Lett*, 2008, **18**: 278
26 Yu Y, Liu D, Liu C, Luo G. *Bioorg Med Chem Lett*, 2007, **17**: 3508
27 Ramalingan C, Kwak Y -W. *Tetrahedron*, 2008, **64**: 5023
28 Rodríguez-omínguez J C, Bernardi D, Kirsch G. *Tetrahedron Lett*, 2007, **48**: 5777
29 Salehi P, Dabiri M, Zolfigol M A, Bodagh Fard M A. *Tetrahedron Lett*, 2003, **44**: 2889
30 Varala R, Alam M M, Adapa S R. *Synlett*, 2003: 67
31 Reddy K R, Reddy C V, Mahesh M, Raju P V K, Reddy V V N. *Tetrahedron Lett*, 2003, **44**: 8173
32 Litvic M, Vecenaj I, Ladisic Z M, Lovric M, Vinkovic V, Filipan-Litvic M. *Tetrahedron*, 2010, **66**: 3463
33 Bose D S, Kumar R K, Fatima L. *Synlett*, 2004: 279