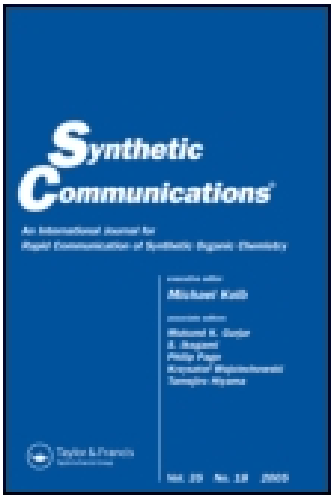

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Microwave-Promoted Synthesis of 3,4-Dihydropyrimidin-2(1H)-(thio)ones Using IL-ONO as Recyclable Base Catalyst Under Solvent-Free Conditions

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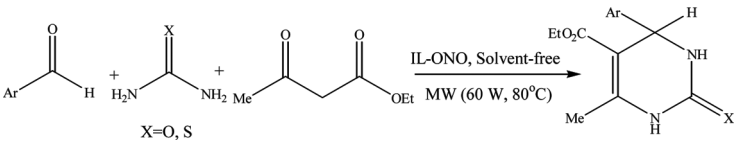
MICROWAVE-PROMOTED SYNTHESIS OF 3,4-DIHYDROPYRIMIDIN-2(1 H)-(THIO)ONES USING IL-ONO AS RECYCLABLE BASE CATALYST UNDER SOLVENT-FREE CONDITIONS

Mortaza Mirzai and Hassan Valizadeh

Department of Chemistry, Faculty of Sciences, Islamic Azad University, Myianeh Branch, Myianeh, Iran

GRAPHICAL ABSTRACT



Abstract *A mild, efficient, and solvent-free microwave (MW)–promoted Biginelli reaction for the synthesis of 3,4-dihydropyrimidin-2(1H)-(thio)ones in nitrite ionic liquid (IL-ONO) is described. This ionic liquid is a weak Lewis base catalyst, which can be easily recovered and reused in several runs. The satisfactory results were obtained with good yields and short reaction time, using a simple experimental procedure.*

Keywords Biginelli; dihydropyrimidinone; microwave; nitrite ionic liquid; solvent-free

INTRODUCTION

Biginelli reported the synthesis of 3,4-dihydropyrimidin-2(1H)-ones via the very simple one-pot condensation reaction of an aldehyde, β-ketoester, and urea in ethanol in 1893. This reaction is known as the Biginelli reaction. Dihydropyrimidinones have attracted increasing interest because of their significant pharmaceutical and therapeutic properties,[1] such as antiviral, antitumor, antibacterial, and anti-inflammatory activities. These compounds can be used as integral backbones of several calcium channel blockers, antihypertensive agents,[2] and α-1a-antagonists.[3] In addition, the dihydropyrimidinone-5-carboxylate motifs that exist in several marine alkaloids show interesting biological activities.[4]

Room-temperature ionic liquids (RTILs) have attracted chemists' interest because of their particular properties, such as undetectable vapor pressure, wide liquid range, as well as the ease of recovery and reuse. RTILs are used as solvents

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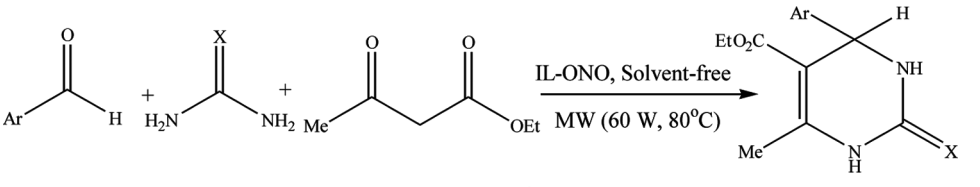
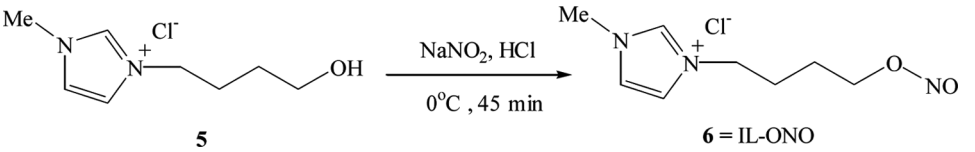


Scheme 1. MW-assisted synthesis of dihydropyrimidinones in the presence of IL-ONO.

or catalysts in synthetic organic chemistry.[5–9] They usually consist of poorly coordinating ion pairs, and a classical example is the readily accessible 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4].[10] Recent advance in ionic liquid research provided another route for achieving task-specific ionic liquids (TSILs) in which a functional group is covalently tethered to the cation or anion of the ionic liquid, especially to the two N atoms of the imidazole ring. TSILs have been used increasingly as solvents and reagents or catalysts because of their specific properties.[5,7,11–13] Palladium-catalyzed Heck reaction was carried out using TSIL as Lewis base, ligand, and reaction medium.[8] Paun et al. reported the basic ionic liquid–catalyzed Knoevenagel condensation reaction.[14] Tajik and coworkers reported the nitration of phenols using acidic ionic liquid under mild conditions.[15] Bhosale et al. synthesized the flavones in [bmim]BF_4, ionic liquid.[16] Hajipour and coworkers reported a convenient method for the preparation of aldoximes in the presence of in situ prepared ionic liquids.[17] Many protocols for Knoevenagel condensations have been reported in the literature. However, many of those procedures require the use of large amounts of different organic solvents as reaction media, long reaction times, and harsh reaction conditions, which prompt chemical researchers to further develop more environmentally benign, efficient, operationally simple Knoevenagel protocols.[18–27] Recently we used the TSIL-$OPPh_2$ as a weak Lewis base catalyst and reaction medium for the Biginelli and Knoevenagel reactions and also in the synthesis of nitrones.[28–30] We also used task-specific phosphinite ionic liquid as reagent and reaction medium for the one-pot Horner–Wadsworth–Emmons-type reaction under microwave irradiation.[31] Very recently, we reported the nitrozation of aromatic compounds using nitrite ionic liquid (IL-ONO) in aqueous media.[32] We now introduce a new nitrite ionic liquid (IL-ONO) that can act as a weak Lewis basic catalyst for the efficient synthesis of dihydropyrimidinones via the Biginelli reaction under microwave (MW)–assisted solvent-free conditions (Scheme 1).

RESULTS AND DISCUSSIONS

The IL-OH, 1-(4-hydroxybutyl)-3-methylimidazolium chloride **5**, is prepared by the efficient reaction of 3-methylimidazole with 4-chlorobutanole at 80 °C in 92% yield.



5 6 = IL-ONO

Scheme 2. Preparation of nitrite ionic liquid (IL-ONO).

The resulting ionic liquid, when left in contact with 3 M $NaNO_2$ and HCl (1:1) solution at 0°C, prepared nitrous ester-ionic liquid **2** in 87% yield (Scheme 2). This ionic liquid is air and water stable. Synthesis of nitrite ionic liquid **6** can be confirmed by its Fourier transform–infrared (FT-IR) spectrum. The broad band at 3510 cm^{-1} arising from O-H stretching vibration in compound **5** disappeared and a new band emerged around 1605 cm^{-1}, which can be ascribed to the asymmetrical stretching of the nitrite ester group, characteristic of the nitrite esters group.

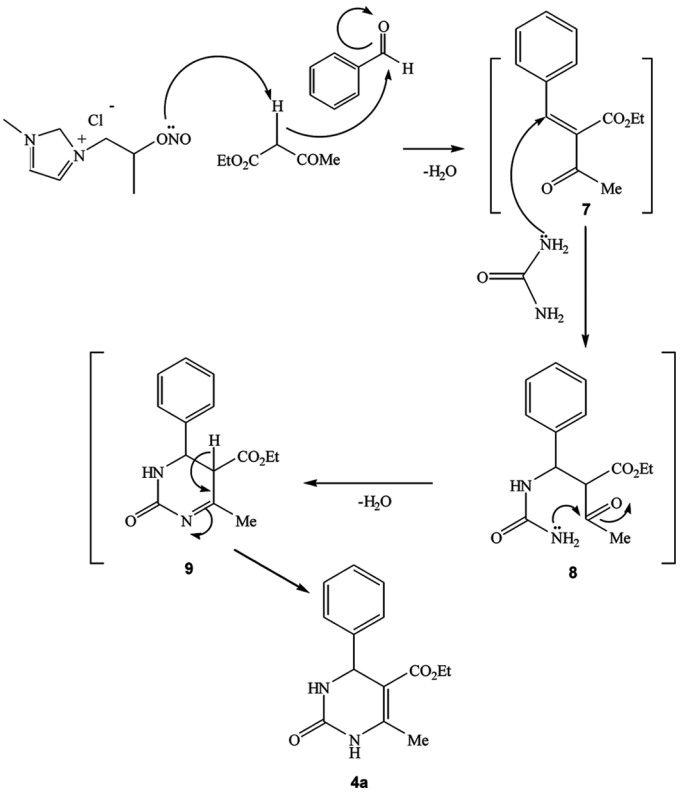
The new nitrite IL was used for the synthesis of dihydropyrimidinone derivatives under MW irradiation. Irradiation of the mixture of benzaldehyde, urea **2a**, and ethylacetoacetate in IL-ONO lead to the formation of related dihydropyrimidinone **4a** in 85% yield. At first, the reaction mixture was irradiated by 100 W microwaves at 100 °C. Next, to improve the yields, we performed the reaction using different conditions and found that the 60 W and 80 °C are the best conditions. The best results were obtained with a 1:1:1.25:1.5 ratio of aldehyde, urea, β-ketoester, and IL-ONO. Dihydropyridinone **4a** was prepared in 90% yield in 3.5 min under optimized conditions. Several DHPMs were successfully synthesized in good yields by following this method. The products could be separated from the IL system by simple extraction with ether and ethylacetate in all examined cases. The results of the transformation of differently substituted arylaldehydes to DHPM derivatives **4a–j** are gathered together in Table 1. All products are known compounds, characterized by mp, IR, ^1H NMR spectra, and elemental analysis.

To exhibit the catalytic effect of IL-ONO, the condensation of two arylaldehydes (2-nitrobenzaldehyde and 4-chlorobenzaldehyde) and ethylacetoacetate was studied respectively with urea and thiourea by using different imidazolium-based

Table 1. MW-assisted synthesis of dihydropyrimidin-2(H)-ones and thiones in IL-ONO

					Mp (°C)		
Entry	X	Ar	Product	Time (min)	Found	Reported[Ref.]	Yield[a] (%)
1	O	Ph	**4a**	3.5	205–208	206–208[33]	90
2	O	4-NO_2-Ph	**4b**	4	210–213	211–213[34]	89
3	O	2-NO_2-Ph	**4c**	5	220–221	221[35]	88
4	O	3-NO_2-Ph	**4d**	3.5	228–230	229–231[36]	90
5	O	4-MeO-Ph	**4e**	4	202–203	202–204[36]	91
6	O	2-Furyl	**4f**	5	206–209	206–208[37]	89
7	S	Ph	**4g**	4.5	204–208	205–206[38]	87
8	S	4-MeO-Ph	**4h**	4	148–149	150–152[36]	90
9	S	4-Cl-Ph	**4i**	5	179–182	180–182[38]	89
10	S	3-NO_2-Ph	**4j**	4.5	206–209	206–207[33]	88

[a]Isolated yields of products.



Scheme 3. Plausible mechanism for the formation of the selected product **4a** in the presence of IL-ONO.

ILs including [bmim]Cl, [bmim]Br, and [bmim]BF_4 at 80 °C under microwave irradiation (MWI). It was found that [bmim]Cl and [bmim]Br were no more effective, and the reactions were carried out in [bmim]BF_4 to afford the related products in lower yields and longer reaction times in comparison with IL-ONO.

A plausible mechanism for the formation of the selected product **4a** in the presence of IL-ONO as a weak base catalyst is outlined in Scheme 3. Intermediate **7** apparently results from the initial Knoevenagel condensation of ethylacetoacetate with benzaldehyde in the presence of IL-ONO as Lewis base catalyst. Michael addition of urea to the **7** yields the intermediate **8**, which cyclizes to cyclic imine **9** via the intramolecular condensation reaction. Compound **9** is converted to a stable enamine product.

In the present study, the recyclability of IL-ONO as catalyst for the preparation of products **4a**, **4f**, and **4j** was investigated. After removal of the mixture of product, possible impurities, and unreacted materials, the remaining IL was reused for five consecutive cycles without loss in efficiency (Table 2).

CONCLUSION

Task-specific Lewis basic ionic liquid IL-ONO has been shown to facilitate the Biginelli condensation reaction of a range of arylaldehydes under MW-assisted

Table 2. Comparison of efficiency of IL-ONO in synthesis of Biginelli products **4a**, **4f**, and **4j** after five times

	Yield[a] (%)		
Run	**4a**	**4f**	**4j**
1	90	89	88
2	88	88	86
3	89	87	87
4	87	86	87
5	87	86	86

[a]Isolated yields of product.

solvent-free conditions. 3,4-Dihydropyrimidin-2(1H)-(thio)ones were prepared in good yields in very short reaction time. In addition, IL-ONO can be easily recycled and reused with the same efficacy for five cycles. The merit of this methodology is that it is simple, mild, and efficient.

EXPERIMENTAL

All chemicals were purchased from Merck and used as received. ^{1}H NMR spectra (400 MHz) were recorded on a Bruker Avance spectrometer using tetramethylsilane (TMS) as internal standard. IR spectra were recorded in KBr and were determined on a Perkin-Elmer FT-IR spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer and are reported in percentage of atomic abundance. MW experiments were conducted in a Milestone MicroSynth apparatus. All melting points are uncorrected and measured in open glass capillaries using a Stuart melting-point apparatus.

Synthesis of 1-(4-Hydroxybutyl)-3-methylimidazolium Chloride 5

1-Methylimidazole (20 mL, 0.25 mol) and 4-chloro-1-butanol (27 mL, 0.27 mol) was stirred at 80 °C for 4 h. The unreacted materials were washed by diethyl ether (8 ml × 3). The diethyl ether was removed under reduced pressure at room temperature, followed by heating under high vacuum, to yield a colorless liquid that became more viscous upon extensive drying but did not solidify. Isolated yield was 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (2H, m, CH_2), 1.41 (m, 2H, CH_2), 2.92 (s, 3H, N–CH_3), 3.84 (t, 2H, N–CH_2), 4.15 (dt, 2H, CH_2-OH), 5.56 (t, 1H, OH), 7.76, 7.78 [two singlets, 2H, C(4,5)–H], 9.09 [s, 1H, C(2)–H]. ^{13}C NMR (100 MHz, $CDCl_3$) 21.75 (-CH_2), 26.31 (-CH_2), 35.83 (N–CH_3), 39.54 (N–CH_2), 64.88 [CH_2(OH)], 123.16 [C(4 or 5)], 124.09 [C(4 or 5)], 137.00 [C(2)].

Synthesis of IL-ONO 6

Freshly prepared 1-(4-hydroxybutyl)-3-methylimidazolium chloride (22 g, 0.1 mol) was added to 15 ml aqueous solution of sodium nitrite (7.59 g, 0.11 mol). While stirring of the mixture at 0 °C, 37% HCl (11 ml) was added slowly. While cold,

the mixture was washed with cold water (20 ml) and dried under vacuum at room temperature. Isolated yield was 87%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.27 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 2.89 (s, 3H, N–CH_3), 3.78 (t, 2H, N–CH_2), 4.23 (t, 2H, CH_2-ONO), 7.75, 7.76 [two singlets, 2H, C(4,5)–H], 9.15 [s, 1H, C(2)–H]. ^{13}C NMR (100 MHz, DMSO-d_6) 19.15 (-CH_2), 25.96 (-CH_2), 37.13 (N–CH_3), 51.50 (N–CH_2), 67.78 [CH_2(ONO)], 124.06 [C(4 or 5)], 124.42 [C(4 or 5)], 136.70 [C(2)].

Synthesis of 3,4-Dihydropyrimidin-2(1H)-(thio)ones (4a–q): General Procedure

A mixture of arylaldehyde (15 mmol), urea or thiourea (15 mmol), 1,3-dicarbonyl compound (18.75 mmol), and IL-ONO (22.5 mmol) was subjected to MWI (60 W) at 80 °C in a solventless system. The reaction was monitored by thin-layer chromatography (TLC) using ethyl acetate/hexane (2:7) as eluent. After cooling to room temperature, the reaction mixtures were extracted with ether and ethylacetate (15 ml × 3). The organic layers were collected and concentrated in vacuum. The residual solid was recrystallized from ethyl acetate or ethanol to afford the pure product.

Recyclability of IL-ONO

After carrying out the reaction, the mixture was extracted with the mixture of ether and ethylacetate (8 mL × 3) to remove all adsorbed organic substrates. Then the remained IL was dried in a vacuum oven and reused in the next cycle directly without further purification.

Selected Spectroscopic Data

5-Ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyrimidine-2(1H)-one 4a. IR (KBr) υ_{max}: 1093, 1223, 1645, 1702, 1725, 3117, 3241 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.10 (t, 3H, $J = 7.1$ Hz), 2.25 (s, 3H), 3.97 (q, 2H, $J = 7.1$ Hz), 5.12 (d, 1H, $J = 3.3$ Hz), 7.20–7.31 (m, 5H, ArH), 7.73 (s, 1H, NH), 9.18 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 15.17, 19.78, 54.95, 60.19, 98.23, 126.25, 127.12, 128.45, 144.80, 148.32, 152.56, 160.33. Anal. calcd. for $C_{14}H_{16}N_2O_3$ (%): C, 64.60; H, 6.20; N, 10.76. Found: C, 64.40; H, 6.15; N, 10.71.

5-Ethoxycarbonyl-(4-nitrophenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-one 4b. IR (KBr) υ_{max}: 1350, 1530, 1646, 1702, 1720, 3121, 3241 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.12 (t, 3H, $J = 7.01$ Hz), 2.30 (s, 3H), 4.01 (q, 2H, $J = 7.01$ Hz), 5.19 (d, 1H, $J = 3.69$ Hz), 7.20–7.29 (m, 4H, ArH), 7.72 (s, 1H, NH), 9.29 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 16.05, 19.25, 54.62, 58.31, 102.28, 114.40, 115.23, 128.13, 144.20, 161.70, 162.33, 165.13. Anal. calcd. for $C_{14}H_{15}N_3O_5$ (%): C, 55.08; H, 4.95; N, 13.76. Found: C, 56.01; H, 4.92; N, 13.52.

5-Ethoxycarbonyl-(2-nitrophenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-one 4c. IR (KBr) υ_{max}: 1354, 1531, 1648, 1705, 1724, 3120, 3238 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ: 1.09 (t, 3H, $J = 7.35$ Hz, CH_3), 2.26 (s, 3H, CH_3), 3.86 (q, 2H, $J = 7.35$ Hz, OCH_2), 5.51 (d, 1H, $J = 2.88$ Hz, CH), 7.01 (d, 1H, $J = 7.92$ Hz, CH),

7.14 (m, 1H, CH), 7.19 (d, 1H, $J = 6.23$ Hz, CH), 7.29 (m, 1H, CH), 7.31 (br s, 1H, NH), 9.09 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6): 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. Anal. calcd. for $C_{14}H_{15}N_3O_5$ (%): C, 55.08; H, 4.95; N, 13.76. Found: C, 56.08; H, 4.91; N, 13.50.

5-Ethoxycarbonyl-(2-chlorophenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-one 4d. IR (KBr) υ_{max}: 1650, 1711, 1719, 3118, 3243 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 1.10 (t, 3H, $J = 7.12$ Hz, CH_3), 2.20 (s, 3H, CH_3), 3.81 (q, 2H, $J = 7.12$ Hz, OCH_2), 5.54 (d, 1H, $J = 2.89$ Hz, CH), 6.99 (d, 1H, $J = 8.52$ Hz, CH), 7.13 (m, 1H, CH), 7.20 (d, 1H, $J = 6.19$ Hz, CH), 7.26 (m, 1H, CH), 7.32 (br s, 1H, NH), 8.89 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ: 164.35, 155.69, 149.87, 148.32, 132.52, 127.96, 126.65, 117.78, 109.98, 100.21, 55.11, 48.64, 19.45, 16.53. Anal. calcd. for $C_{14}H_{15}ClN_2O_3$ (%): C, 57.05; H, 5.13; N, 9.50. Found: C, 58.01; H, 5.12; N, 9.35.

5-Ethoxycarbonyl-(2-methylphenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-one 4e. IR (KBr) υ_{max}: 1661, 1702, 1713, 3122, 3245 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ: 1.08 (t, 3H, $J = 7.15$ Hz, CH_3), 2.12 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.81 (q, 2H, $J = 7.15$ Hz, OCH_2), 5.61 (d, 1H, $J = 2.78$ Hz, CH), 6.98 (d, 1H, $J = 8.43$ Hz, CH), 7.05 (m, 1H, CH), 7.18 (d, 1H, $J = 6.23$ Hz, CH), 7.25 (m, 1H, CH), 7.33 (br s, 1H, NH), 9.01 (br s, 1H, NH). ^{13}C NMR (DMSO-d): δ: 159.02, 151.09, 148.37, 146.97, 130.02, 125.90, 122.15, 116.10, 108.90, 101.20, 58.01, 47.35, 45.04, 17.41, 14.03. Anal. calcd. for $C_{15}H_{18}N_2O_3$ (%): C, 65.68; H, 6.61; N, 10.21. Found: C, 66.02; H, 6.60; N, 10.18.

5-Ethoxycarbonyl-(2-furyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-one 4f. IR (KBr) υ_{max}: 1664, 1701, 1715, 3120, 3241 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 1.05 (t, 3H, $J = 7.46$ Hz, CH_3). 2.19 (s, 3H, CH_3), 3.78 (q, 2H, $J = 7.46$ Hz, OCH_2), 5.64 (d, 1H, $J = 2.35$ Hz, CH), 6.78 (dd,1H, $J = 7.23$, 2.38 Hz, CH), 7.03 (dd, 1H, $J = 7.23$, 7.36 Hz, CH), 7.18 (dd, 1H, $J = 2.38$, 7.36 Hz, CH), 7.36 (br s, 1H, NH), 9.77 (br s, 1H, NH), ^{13}C NMR (DMSO-d_6): δ: 161.02, 154.21, 133.23, 131.23, 127.11, 124.17, 104.19, 102.96, 98.35, 59.65, 42.04, 14.03. Anal. calcd. for $C_{12}H_{14}N_2O_4$ (%): C, 57.59; H, 5.64; N, 11.19. Found: C, 58.12; H, 5.65; N, 11.13.

5-Ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyrimidine-2(1H)-thione 4g. IR (KBr) υ_{max}: 1645, 1678, 1702, 3110, 3248 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.12 (t, 3H, $J = 7.11$ Hz,), 2.27 (s, 3H), 3.99 (q, 2H, $J = 7.11$ Hz), 5.21 (d, 1H, $J = 3.24$ Hz), 7.24–7.35 (m, 5H, ArH), 7.77 (s, 1H, NH), 8.87 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 158.25, 145.56, 139.11, 138.25, 125.56, 124.98, 122.85, 100.54, 61.75, 53.43, 20.12, 14.52. Anal. calcd. for $C_{14}H_{16}N_2O_2S$ (%): C, 60.85; H, 5.84; N, 1014. Found: C, 60.89; H, 5.85; N, 10.11.

5-Ethoxycarbonyl-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-thione 4h. IR (KBr) υ_{max}: 1646, 1702, 1720, 3121, 3241 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.18 (t, 3H, $J = 7.13$ Hz), 2.26 (s, 3H, Me), 3.85 (s, 3H, OMe), 3.98 (q, 2H, $J = 7.13$ Hz), 5.15 (d, 1H, $J = 3.51$ Hz), 7.11–7.20 (m, 4H, ArH), 7.69 (s, 1H, NH), 8.98 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 163.21, 155.42, 151.12, 142.52, 127.89, 113.63, 107.45, 101.52, 60.78, 59.11, 57.75,

20.10, 13.63. Anal. calcd. for $C_{15}H_{18}N_2O_3S$ (%): C, 58.80; H, 5.92; N, 9.14. Found: C, 58.85; H, 5.90; N, 9.12.

5-Ethoxycarbonyl-(4-chlorophenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-thione 4i. IR (KBr) υ_{max}: 1641, 1714, 1685, 3116, 3247 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz) δ: 1.06 (t, 3H, $J = 7.43$ Hz), 2.18 (s, 3H), 3.89 (q, 2H, $J = 7.43$ Hz), 5.24 (d, 1H, $J = 3.05$ Hz), 7.24 (d, 2H, $J = 7.13$ Hz), 7.27 (d, 2H, $J = 7.09$ Hz), 7.82 (s, 1H, NH), 9.08 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 159.98, 156.42, 153.32, 141.25, 125.65, 111.08, 109.56, 100.23, 60.23, 57.41, 20.06, 12.38. Anal. calcd. for $C_{14}H_{15}ClN_2O_2S$ (%): C, 54.10; H, 4.86; N, 9.01. Found: C, 55.09; H, 4.88; N, 8.98.

5-Ethoxycarbonyl-(3-nitrophenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-thione 4j. IR (KBr) υ_{max}: 1354, 1531, 1648, 1705, 1724, 3120, 3238 cm^{-1}. ^1H NMR (DMSO-d_6): δ: 1.21 (t, 3H, $J = 7.15$ Hz), 2.21 (s, 3H), 3.86 (q, 2H, $J = 7.15$ Hz), 5.65 (d, 1H, $J = 2.58$ Hz), 7.11 (dd, 1H, $J = 2.75$, 2.09 Hz), 7.19 (m, 1H), 7.21 (dd, 1H, $J = 6.53$, 7.01 Hz, CH), 7.39 (m, 1H, CH), 7.28 (br s, 1H, NH), 9.01 (br s, 1H, NH), ^{13}C NMR (DMSO-d_6): δ: 163.79, 151.50, 148.25, 142.13, 130.18, 126.01, 125.67, 119.82, 112.09, 99.00, 58.71, 47.13, 16.01, 14.04. Anal. calcd. for $C_{14}H_{15}N_3O_4S$ (%): C, 52.33; H, 4.70; N, 13.08. Found: C, 52.35; H, 4.73; N, 13.05.

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