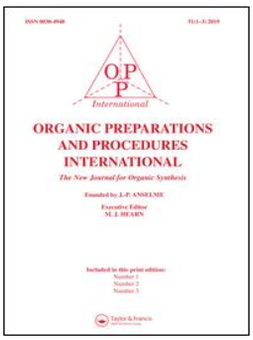

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EXPERIMENTAL PAPER

Green Synthesis and Structural Characterization of *C*6-Phenyl Substituted 3,4-Dihydropyrimidinones

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Dihydropyrimidinones and their derivatives (DHPMs) possess extensive and important biological and pharmacological activities such as antiviral, antibacterial, anticancer and antitumor properties.[1–3] Multifunctionalized DHPMs can be used as calcium channel blockers and α1a-antagonists,[4] antioxidants[5] and antituberculosis drugs.[6] The classical synthesis method is the Biginelli reaction, which involves the one-pot three-component condensation of an aromatic aldehyde, ethyl acetoacetate and urea catalyzed by HCl.[7] With the continuing study on DHPMs, researchers focused their attention on the selection of catalysts, the optimization of reaction conditions, and the scope of starting materials. Therefore, synthetic routes and the diversity of product structures have been improved. In the meantime, many novel multifunctional DHPMs have been obtained.[8–13]

In recent years, we carried out research on the Biginelli reaction to prepare novel products and develop green synthetic methods. Various derivatives such as *C*6-methyl substituted 3,4-dihydropyrimidinones[14] and *N*1-alkyl/aryl substituted 3,4-dihydropyrimidinones[14,15] were synthesized using metal organic sulfonates as catalysts. We found that metal organic sulfonates possess high catalytic activity, good water-resistance, and recyclability. They showed good catalytic effect on esterifications,[16] tetrahydropyran formation,[17] Mannich reactions,[18] cyclocondensations[19] and diacetylations.[20]

A *β*-dicarbonyl compound is one of the three components of the Biginelli reaction. Acetoacetates are commonly used, giving a methyl group at the *C*6 position of 3,4-dihydropyrimidinones. Recently, a few papers reported that acetoacetates can be replaced with benzoylacetates in this reaction.[21–28] However, only a few products were synthesized. As a further study, we carried out the one-pot three-component reaction of an aromatic aldehyde, ethyl benzoylacetate, and a urea derivative (e.g. urea, thiourea, *N*-methylurea, or *N*-methyl thiourea) in the presence of cerium(III) *p*-toluenesulfonate tetrahydrate ($Ce(p\text{-}CH_3C_6H_4SO_3)_3{\cdot}4H_2O$, abbreviated as CePTS) under solvent-free conditions (Scheme 1).

In order to screen the optimal conditions, we investigated catalysts, reaction temperature, and the molar ratio of starting materials. At first, nine metal *p*-toluenesulfonates (0.3 mmol) were evaluated using the model reaction of benzaldehyde (10 mmol), ethyl benzoylacetate (10 mmol) and methylurea (10 mmol) at 80 °C. As shown in Table 1,

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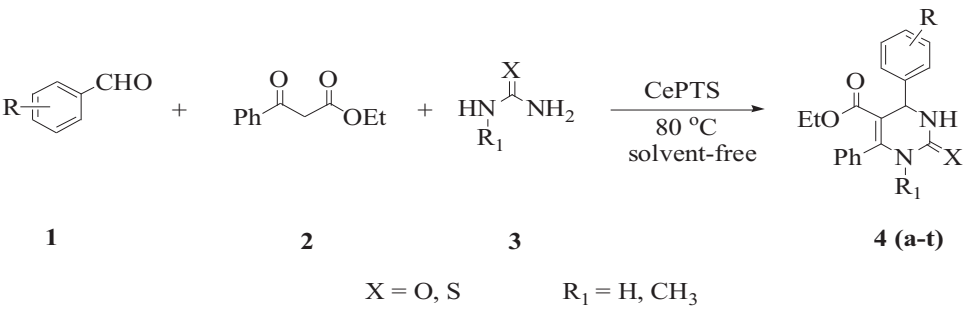


Scheme 1. Three-component synthesis of *C*6-phenyl substituted 3,4-dihydropyrimidinones.

Table 1. Comparison of catalytic effects for different metal *p*-toluenesulfonates.

Entry	Catalyst	Time (h)	Yield (%)
1	$Ce(p\text{-}CH_3C_6H_4SO_3)_3{\cdot}4H_2O$	0.7	91
2	$Nd(p\text{-}CH_3C_6H_4SO_3)_3{\cdot}2H_2O$	0.8	87
3	$Al(p\text{-}CH_3C_6H_4SO_3)_3{\cdot}5H_2O$	1.2	84
4	$Cu(p\text{-}CH_3C_6H_4SO_3)_2{\cdot}6H_2O$	1.5	66
5	$La(p\text{-}CH_3C_6H_4SO_3)_3{\cdot}2H_2O$	1.5	61
6	$Zn(p\text{-}CH_3C_6H_4SO_3)_2{\cdot}5H_2O$	2.0	60
7	$Ca(p\text{-}CH_3C_6H_4SO_3)_2$	2.0	55
8	$Co(p\text{-}CH_3C_6H_4SO_3)_2{\cdot}4H_2O$	2.0	50
9	$Mg(p\text{-}CH_3C_6H_4SO_3)_2{\cdot}6H_2O$	2.5	44
10	None	6.0	12

CePTS possesses the best catalytic activity. It afforded the desired product in 91% yield within 0.7 h (Entry 1, Table 1). In the absence of catalyst, a poor yield of product was obtained, even after a prolonged reaction time (Entry 10, Table 1).

The effect of the molar ratio of the starting materials on the reaction results was also examined in Table 2. We found that product yields improved slightly as the amount of methylurea increased. However, we determined that the optimal molar ratio of aromatic aldehyde, ethyl benzoylacetate and methyl urea was 1.0:1.0:1.0 (Entry 1, Table 2) in order to minimize both the cost of reagents and the amount of waste generated.

Finally, the effect of the catalyst loading and the reaction temperature were investigated (Table 3). The results showed the preferable conditions were 3 mol% catalyst and 80 °C (Entry 3, Table 3). The recyclability of CePTS was also studied (Entry 3, Table 3). When the reaction was complete, the crude product was washed with cold water. The catalyst remained in the aqueous phase and could be recovered by evaporating the filtrate. We found that after the catalyst was used three times, the yield of the product decreased slightly.

A series of *C*6-phenyl substituted 3,4-dihydropyrimidinones were synthesized using the optimized conditions described above (Table 4). In order to further explore the scope of this reaction, the uses of urea, thiourea, *N*-methylurea, and *N*-methylthiourea were investigated, and all proved to be effective in this transformation. All of the corresponding target products were obtained within short reaction times, which demonstrated that CePTS has good catalytic effect and a wide scope across different substrates.

In order to confirm the identity of the products and examine the orientation of groups in space, a crystal structure of compound **4i** was obtained (Figure 1).

Table 2. The effect of starting material ratios on product yields.[a]

Entry	$n_{\text{aromatic aldehyde}} : n_{\text{ethyl benzoylacetate}} : n_{\text{methyl urea}}$	Time (h)	Yield (%)
1	1.0 : 1.0 : 1.0	0.7	91
2	1.0 : 1.0 : 1.1	0.7	92
3	1.0 : 1.0 : 1.2	0.8	92
4	1.0 : 1.0 : 1.3	0.9	93

[a]Reaction conditions: benzaldehyde (10 mmol), ethyl benzoylacetate (10 mmol), CePTS (0.3 mmol), solvent-free, 80 °C.

Table 3. The effect of catalyst loading and reaction temperature on product yields.[a]

Entry	Catalyst (mmol)	Temperature (°C)	Time (h)	Yield (%)
1	0.1	80	3.0	87
2	0.2	80	1.0	90
3	0.3	80	0.7	91, 87, 82[b]
4	0.4	80	0.6	89
5	0.3	60	1.1	84
6	0.3	70	1.0	86
7	0.3	90	0.7	88

[a]Reaction conditions: benzaldehyde (10 mmol), ethyl benzoylacetate (10 mmol), methylurea (10 mmol).
[b]CePTS was reused three times, successively.

Table 4. The synthesis of C6-phenyl substituted 3,4-dihydropyrimidinones.[a]

Product	R	R_1	X	Yield (%) (Time (h))	Mp (°C) Found	Mp (°C) Reported
4a	H	Me	O	91 (0.7)	175-177	171[29]
4b	2-Cl	Me	O	74 (0.8)	144-146	–
4c	4-Cl	Me	O	93 (0.3)	200-202	203-205[23]
4d	2,4-Cl_2	Me	O	79 (0.7)	145-147	–
4e	4-CH_3	Me	O	92 (0.3)	222-224	223-225[23]
4f	2-CH_3O	Me	O	91 (1.2)	179-181	–
4g	4-CH_3O	Me	O	94 (1.0)	169-171	–
4h	3-NO_2	Me	O	93 (1.0)	182-184	–
4i	4-NO_2	Me	O	87 (0.9)	194-196	190-192[23]
4j	3-OH	Me	O	95 (1.7)	139-141	–
4k	H	Me	S	87 (1.5)	118-120	–
4l	4-Cl	Me	S	94 (0.6)	162-164	–
4m	4-NO_2	Me	S	84 (0.5)	191-193	–
4n	3-OH	Me	S	90 (0.6)	179-181	–
4o	H	H	S	91 (2.3)	192-193	192[30]
4p	4-Cl	H	S	92 (2.6)	184-186	185-188[25]
4q	4-CH_3O	H	S	92 (1.0)	167-169	171-174[25]
4r	4-CH_3	H	S	90 (1.0)	177-179	177-180[25]
4s	H	H	O	61 (2.7)	158-160	157-159[27]
4t	3-NO_2	H	O	64 (3.0)	230-232	233-235[28]

[a]Reaction conditions: aromatic aldehyde (10 mmol), ethyl benzoylacetate (10 mmol), urea (10 mmol), CePTS (0.3 mmol), 80 °C.

A possible mechanism for the reaction is shown in Scheme 2.[31] First, the aldehyde reacts with a (thio)urea to form an acylimine intermediate. Addition of the β-ketoester to the acylimine forms an open-chain urea derivative, which then undergoes cyclization and dehydration to form the target product.

In summary, numerous *C6*-phenyl substituted 3,4-dihydropyrimidinones were synthesized by a three-component condensation of equimolar amounts of an aromatic aldehyde, ethyl benzoylacetate, and a urea using CePTS as a catalyst at 80 °C. Advantages of the method include: operational simplicity, mild reaction conditions, formation of diverse product structures, and green chemistry. Finally, the CePTS exhibits high

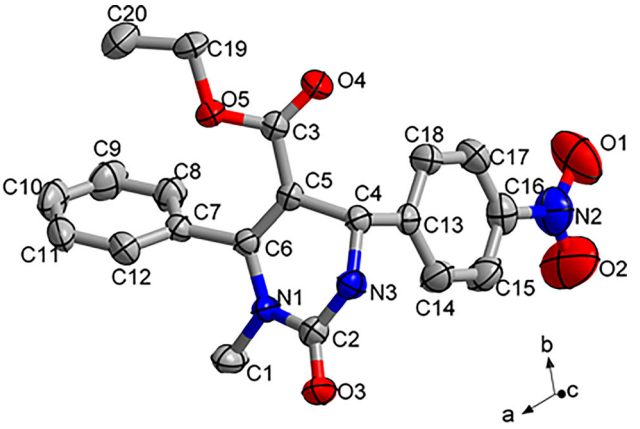
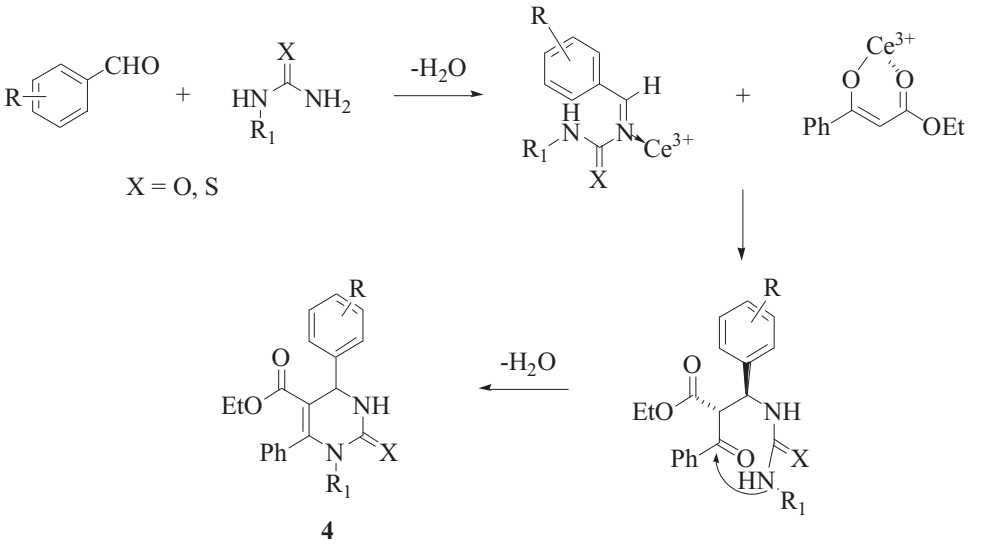


Figure 1. X-ray molecular structure of compound **4i**, showing thermal displacement ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.



Scheme 2. Proposed mechanism for the 3-component coupling reaction.

catalytic activity, reusability, and wide substrate scope, furnishing several novel 3,4-dihydropyrimidinones.

Experimental section

Melting points were determined using an RD-II micromelting point apparatus (Tianjin Tianguang Optical Instrument Limited Company, China). Infrared spectra were recorded on a Varian Scimitar 2000 infrared spectrometer (Agilent Technologies Inc., USA) using potassium bromide pellets. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent 400-NMR spectrometer (Agilent Technologies Inc., USA) in DMSO-d_6 using TMS as an internal standard (δ 0.00 ppm). Elemental analyses (C, H, N) were carried out using a Perkin Elmer Elemental Analyser EA 2400II. Crystallographic data for

compound **4i** were collected using a Bruker Smart Apex II diffractometer (Bruker Corporation, Germany) with Mo Kα radiation (λ = 0.71069 Å) at 296 K using the ω-scan technique. The diffraction data were integrated by using the SAINT program, which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption corrections were applied using the SADABS program. Structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on F2 by the full-matrix least-squares technique using the SHELXTL crystallographic software package. Thin layer chromatography was performed on Merck Silica gel 60 F_{254} plates using a mixture of ethyl acetate/petroleum ether (v/v = 3:7) as the mobile phase. Metal *p*-toluenesulfonates were synthesized according to a reported literature procedure.[32] All other reagents were commercially available (Shanghai Chemical Reagent Company, China) and were used without further purification.

Preparation of C6-phenyl substituted 3,4-dihydropyrimidinones (4)

A mixture of aromatic aldehyde (10 mmol), ethyl benzoylacetate (10 mmol), urea (10 mmol) and CePTS (0.3 mmol) was stirred at 80 °C on an oil bath until the reaction was determined to be complete by TLC. The reaction mixture was cooled to room temperature, and ice water was added. The crude products were obtained by filtration and drying and were purified by recrystallization from hot ethanol. All of the products were characterized by IR, $^{1}H/^{13}C$ NMR and elemental analysis. The spectral data of the new products are as follows:

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(2-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-one (4b)

White solid, mp 144-146 °C; IR (KBr, cm^{-1}): ν 3335, 3230, 3089, 2988, 1688, 1636, 762; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (s, 1H, NH), 7.61 (d, J = 7.6 Hz, 1H, ArH), 7.48 (d, J = 6.4 Hz, 4H, ArH), 7.43 (t, J = 7.2 Hz, 2H, ArH), 7.35 (t, J = 7.6 Hz, 2H, ArH), 5.75 (d, J = 3.2 Hz, 1H, CH), 3.63 (q, J = 6.8 Hz, 2H, $O\underline{CH_2}CH_3$), 2.72 (s, 3H, NCH_3), 0.67 (t, J = 6.8 Hz, 3H, $OCH_2\underline{CH_3}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.03, 151.93, 151.24, 140.16, 134.51, 131.71, 129.36, 129.07, 128.47, 128.42, 128.27, 128.03, 127.88, 127.65, 127.12, 101.98, 58.84, 50.52, 31.54, 12.92.

Anal. Calcd. for $C_{20}H_{19}N_2O_3Cl$: C, 64.78; H, 5.16; N, 7.55. Found: C, 64.66; H, 5.14; N, 7.56.

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(2,4-dichlorophenyl)-3,4-dihydropyrimidin-2(1H)-one (4d)

White solid, mp 145-147 °C; IR (KBr, cm^{-1}): ν 3350, 3227, 3086, 2976, 1685, 1626, 787; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.15 (s, 1H, NH), 7.62 (t, J = 8.4 Hz, 2H, ArH), 7.48 (t, J = 4.0 Hz, 4H, ArH), 7.41 (s, 1H, ArH), 7.31 (s, 1H, ArH), 5.69 (d, J = 3.6 Hz, 1H, CH), 3.61 (q, J = 6.4 Hz, 2H, $O\underline{CH_2}CH_3$), 2.69 (s, 3H, NCH_3), 0.65 (t, J = 6.4 Hz, 3H, $OCH_2\underline{CH_3}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.08, 147.87, 147.56, 135.57, 130.56,

128.81, 128.74, 126.21, 124.84, 124.46, 124.17, 123.97, 123.25, 97.70, 55.03, 46.38, 27.72, 9.07.

Anal. Calcd. for $C_{20}H_{18}N_2O_3Cl_2$: C, 59.27; H, 4.48; N, 6.91. Found: C, 59.35; H, 4.47; N, 6.90.

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(2-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (4f)

Pale yellow solid, mp 179-181 °C; IR (KBr, cm^{-1}): ν 3361, 3231, 3098, 2984, 1687, 1631, 756; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.65 (s, 1H, NH), 7.43 ~ 7.24 (m, 7H, ArH), 7.01 (d, J = 8.0 Hz, 1H, ArH), 6.92 (t, J = 7.2 Hz, 1H, ArH), 5.47 (d, J = 3.6 Hz, 1H, CH), 3.80 (s, 3H, OCH_3), 3.58 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 2.62 (s, 3H, NCH_3), 0.61 (t, J = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.15, 157.40, 153.47, 151.63, 135.55, 130.75, 129.39, 128.91, 128.65, 127.79, 120.67, 111.67, 102.32, 59.45, 55.85, 49.43, 32.30, 13.70.

Anal. Calcd. for $C_{21}H_{22}N_2O_4$: C, 68.84; H, 6.05; N, 7.65. Found: C, 68.92; H, 6.04; N, 7.62.

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (4g)

Pale yellow solid, mp 169-171 °C; IR (KBr, cm^{-1}): ν 3334, 3224, 3088, 2979, 1696, 1635, 752; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (d, J = 4.0 Hz, 1H, NH), 7.45 (t, J = 2.4 Hz, 3H, ArH), 7.32-7.26 (m, 4H, ArH), 6.95 (d, J = 8.4 Hz, 2H, ArH), 5.17 (d, J = 3.6 Hz, 1H, CH), 3.76 (s, 3H, OCH_3), 3.66 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 2.64 (s, 3H, NCH_3), 0.67 (t, J = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.30, 159.01, 153.54, 151.08, 136.25, 135.29, 129.33, 128.98, 128.73, 128.59, 127.81, 114.34, 104.48, 59.59, 55.48, 52.54, 32.36, 13.72.

Anal. Calcd. for $C_{21}H_{22}N_2O_4$: C, 68.84; H, 6.05; N, 7.65. Found: C, 68.75; H, 6.07; N, 7.67.

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(3-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (4h)

Pale yellow solid, mp 182-184 °C; IR (KBr, cm^{-1}): ν 3348, 3228, 3089, 2981, 1678, 1624, 787; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.35 (d, J = 3.6 Hz, 1H, NH), 8.26 (s, 1H, ArH), 8.20 (d, J = 8.4 Hz, 1H, ArH), 7.89 (d, J = 7.6 Hz, 1H, ArH), 7.74 (t, J = 7.6 Hz, 1H, ArH), 7.47 (s, 3H, ArH), 7.30 (d, J = 13.2 Hz, 2H, ArH), 5.39 (d, J = 3.6 Hz, 1H, CH), 3.69 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 2.66 (s, 3H, NCH_3), 0.67 (t, J = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.61, 148.66, 147.70, 143.68, 141.64, 130.32, 128.69, 126.33, 124.61, 124.55, 124.18, 124.11, 123.32, 118.42, 116.97, 98.64, 55.24, 48.01, 27.93, 9.06.

Anal. Calcd. for $C_{20}H_{19}N_3O_5$: C, 62.99; H, 5.02; N, 11.02. Found: C, 63.10; H, 5.03; N, 10.99.

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(3-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (4j)

Pale yellow solid, mp 139-141 °C; IR (KBr, cm^{-1}): ν 3350, 3222, 3093, 2985, 1687, 1621, 784; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.43 (s, 1H, ArOH), 8.07 (d, J = 3.6 Hz, 1H, NH), 7.42 (t, J = 2.4 Hz, 3H, ArH), 7.23 (q, J = 3.6 Hz, 2H, ArH), 7.13 (t, J = 8.0 Hz, 1H, ArH), 6.78 (d, J = 8.0 Hz, 2H, ArH), 6.63 (m, 1H, ArH), 5.10 (d, J = 3.6 Hz, 1H, CH), 3.63 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 2.59 (s, 3H, NCH_3), 0.63 (t, J = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.29, 157.90, 153.58, 151.25, 145.51, 135.28, 130.02, 129.01, 117.25, 114.81, 113.34, 104.23, 59.63, 52.94, 32.38, 13.71.

Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.27; H, 5.70; N, 7.93.

5-Ethoxycarbonyl-1-methyl-4,6-phenyl-3,4-dihydropyrimidin-2(1H)-thione (4k)

White solid, mp 118-120 °C; IR (KBr, cm^{-1}): ν 3193, 3064, 2981, 1732, 754; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.71 (s, 1H, NH), 7.47-7.30 (m, 9H, ArH), 7.18 (s, 1H, ArH), 4.94 (d, J = 12.0 Hz, 1H, CH), 3.48-3.37 (m, 2H, OCH_2CH_3), 2.90 (s, 3H, NCH_3), 0.54 (t, J = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.98, 166.74, 140.97, 138.10, 128.48, 127.94, 127.86, 127.58, 125.81, 85.50, 59.18, 58.60, 53.30, 36.91, 12.98.

Anal. Calcd. for $C_{20}H_{20}N_2O_2S$: C, 68.16; H, 5.72; N, 7.95. Found: C, 68.08; H, 5.73; N, 7.93.

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-thione (4l)

Pale yellow solid, mp 162-164 °C; IR (KBr, cm^{-1}): ν 3174, 3028, 2993, 1728, 1685, 702; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.09 (d, J = 4.4 Hz, 1H, NH), 7.49 (d, J = 8.4 Hz, 5H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 7.32 (s, 1H, ArH), 7.26 (s, 1H, ArH), 5.26 (d, J = 4.8 Hz, 1H, CH), 3.73 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 3.01 (s, 3H, NCH_3), 0.69 (t, J = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.86, 160.40, 144.49, 136.73, 129.79, 128.28, 125.30, 124.91, 124.63, 124.30, 124.17, 123.95, 123.33, 101.86, 55.66, 47.74, 9.07.

Anal. Calcd. for $C_{20}H_{19}N_2O_2SCl$: C, 62.09; H, 4.95; N, 7.24. Found: C, 61.98; H, 4.96; N, 7.22.

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-thione (4m)

Pale yellow solid, mp 191-193 °C; IR (KBr, cm^{-1}): ν 3192, 3003, 2949, 1720, 1605, 752; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.94 (s, 1H, NH), 8.20 (d, J = 8.4 Hz, 2H, ArH), 7.72 (d, J = 8.8 Hz, 2H, ArH), 7.48-7.27 (m, 5H, ArH), 5.07 (d, J = 11.6 Hz, 1H, CH), 3.50 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 2.89 (s, 3H, NCH_3), 0.55 (t, J = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 175.07, 162.75, 143.06, 141.98, 136.91, 125.83, 123.99, 123.80, 122.08, 119.06, 81.66, 55.58, 53.95, 48.94, 33.07, 9.10.

Anal. Calcd. for $C_{20}H_{19}N_3O_4S$: C, 60.44; H, 4.82; N, 10.57. Found: C, 60.36; H, 4.84; N, 10.61.

5-Ethoxycarbonyl-1-methyl-6-phenyl-4-(3-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione (4n)

White solid, mp 179-181 °C; IR (KBr, cm^{-1}): ν 3295, 3212, 2997, 1728, 1606, 701; ^1H NMR (400 MHz, DMSO-d_6): δ 9.44 (s, 1H, ArOH), 8.65 (s, 1H, NH), 7.42-7.34 (m, 4H, ArH), 7.13 (t, $J = 7.2$ Hz, 2H, ArH), 6.79 (d, $J = 7.2$ Hz, 2H, ArH), 6.68 (d, $J = 8.4$ Hz, 1H, ArH), 4.85 (d, $J = 12.0$ Hz, 1H, CH), 3.51 (q, $J = 7.2$ Hz, 2H, $O\underline{CH_2}CH_3$), 2.89 (s, 3H, NCH_3), 0.57 (t, $J = 7.2$ Hz, 3H, $OCH_2\underline{CH_3}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.93, 166.71, 156.76, 140.96, 139.47, 128.88, 127.91, 127.59, 125.74, 118.37, 114.81, 114.62, 85.43, 59.21, 53.76, 53.19, 36.91, 13.01.

Anal. Calcd. for $C_{20}H_{20}N_2O_3S$: C, 65.20; H, 5.47; N, 7.60. Found: C, 65.36; H, 5.46; N, 7.58.

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