Electronic Supplementary Information (ESI)

Efficient and green microwave-assisted multicomponent Biginelli reaction for the synthesis of dihydropyrimidinones catalyzed by heteropolyanion-based ionic liquids under solvent-free conditions

Renzhong Fu, Yang Yang,* Wenchen Lai, Yongfeng Ma, Zhikai

Chen, Jian Zhou, Wen Chai, Quan Wang,* Rongxin Yuan

Jiangsu Laboratory of Advanced Functional Material, School of Chemistry and Materials Engineering,

Changshu Institute of Technology, Changshu, Jiangsu 215500, PR China

E-mail: yangyangirisjs@126.com (Y. Yang), wangquanlzu@gmail.com (Q. Wang); Tel./fax:

+86-512-52251842.

Table of Contents

General information	S2
Synthetic procedure for HPAILs	S3
Synthetic procedure for dihydropyrimidinones	S3
Characterization data of all products	S4
NMR spectra of all products	S15

General Information

Reagent grade solvents were used for extraction, recrystallization and flash chromatography. All other commercial reagents were used as received without additional purification. The progress of reactions were checked by analytical thin-layer chromatography (TLC, silica gel 60 F-254 plates). The plates were visualized first with UV illumination followed by iodine or phosphomolybdic acid hydrate. Column chromatography was performed using silica gel (200-300 mesh). NMR spectra were obtained using BRUKER AVANCE III instrument. ^1H NMR spectra were recorded at 300 MHz and are reported in parts per million (ppm) on the δ scale relative to tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were recorded at 75 MHz and are reported in parts per million (ppm) on the δ scale relative to CDCl_3 (δ 77.16) and $\text{DMSO}-d_6$ (δ 39.52). Multiplicities are indicated as the following : s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doubled doublet; td, tripled doublet; br, broad. Coupling constants (J values) where noted are quoted in hertz. Mass spectra were obtained using Agilent 1260-6120 (ESI) instrument. The melting point was uncorrected.

Synthetic procedure for HPAILs

Methylimidazole (0.11 mol) and 1,3-propane sulfone (0.10 mol) were dissolved in toluene (30 mL) and stirred for 24 h at 50 °C under a nitrogen atmosphere. A white precipitate (MIMPS) formed, which was filtered, washed with diethyl ether three times, then dried in a vacuum. MIMPS (0.09 mol) was added to an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.03 mol), and then the mixture was stirred at room temperature for 24 h. Water was removed in vacuum to give the product $[\text{MIMPS}]_3\text{PW}_{12}\text{O}_{40}$ as a solid. Thus $[\text{MIMPS}]_3\text{PMo}_{12}\text{O}_{40}$, $[\text{PyPS}]_3\text{PW}_{12}\text{O}_{40}$, $[\text{PyPS}]_3\text{PMo}_{12}\text{O}_{40}$, $[\text{TEAPS}]_3\text{PW}_{12}\text{O}_{40}$ and $[\text{TEAPS}]_3\text{PMo}_{12}\text{O}_{40}$ were prepared using according starting materials.

Synthetic procedure for dihydropyrimidinones

To a mixture of aldehyde (3 mmol), 1,3-dicarbonyl compound (3.0 mmol) and urea / thiourea (4.5 mmol) in a 10 mL round bottomed flask was added $[\text{PyPS}]_3\text{PW}_{12}\text{O}_{40}$ (314 mg, 0.09 mmol). The reaction mixture was stirred at 120 °C under MWI (700 W). The progress of the reaction was monitored by TLC. On completion, the mixture was diluted with hot ethyl acetate (20 mL) with stirring for 30 min. The insoluble catalyst was recovered by filtration. The filtrate was evaporated and the residue in almost pure form. Recrystallization or column chromatography could be used for further purification.

Characterization data of all products

5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 1).^[1]

White solid. Mp: 201.1-203.6 °C; IR (KBr): 3244, 3109, 2933, 1710, 1650, 1222, 1089 cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 9.20 (s, 1H), 7.74 (s, 1H), 7.35-7.30 (m, 2H), 7.25-7.21 (m, 3H), 5.15 (d, $J = 3.0$ Hz, 1H), 3.98 (q, $J = 7.0$ Hz, 2H), 2.25 (s, 3H), 1.09 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 165.4, 152.2, 148.4, 144.9, 128.4, 127.3, 126.3, 99.3, 59.2, 54.0, 17.8, 14.1; HRMS Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_3$ ($\text{M} + \text{H}^+$): 261.1234; Found: 261.1238.

5-Ethoxycarbonyl-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 2).^[1]

White solid. Mp: 203.1-205.7 °C; IR (KBr): 3243, 3111, 2930, 1709, 1649, 1223, 1089 cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 9.16 (s, 1H), 7.67 (s, 1H), 7.15 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 5.10 (d, $J = 3.0$ Hz, 1H), 3.97 (q, $J = 7.0$ Hz, 2H), 3.71 (s, 3H), 2.24 (s, 3H), 1.10 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 165.4, 158.5, 152.2, 148.1, 137.1, 127.5, 113.7, 99.6, 59.2, 55.1, 53.4, 17.8, 14.2; HRMS Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_4$ ($\text{M} + \text{H}^+$): 291.1339; Found: 291.1337.

5-Ethoxycarbonyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 3).^[1]

Yellow solid. Mp: 216.1-217.1 °C; IR (KBr): 3231, 3094, 2916, 1701, 1649, 1456, 1285, 1219, 1082, 777 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.16 (s, 1H), 7.69 (s, 1H), 7.12 (s, 4H), 5.10 (d, *J* = 2.1 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.26 (s, 3H), 2.24 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.4, 152.2, 148.2, 142.0, 136.4, 128.9, 126.2, 99.4, 59.2, 53.6, 20.7, 17.8, 14.1; HRMS Calcd for C₁₅H₁₉N₂O₃ (M + H⁺): 275.1390; Found: 275.1394.

5-Ethoxycarbonyl-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 4).^[2]

Yellow solid. Mp: 214.8-216.6 °C; IR (KBr): 3245, 3119, 2972, 1650, 1487, 1471, 1287, 1220, 1084, 778, 484 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.32 (s, 1H), 9.11 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.14 (d, *J* = 3.3 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.2, 152.0, 148.7, 143.8, 131.8, 128.4, 128.2, 98.8, 59.3, 53.4, 17.8, 14.1; HRMS Calcd for C₁₄H₁₆ClN₂O₃ (M + H⁺): 295.0844; Found: 295.0841.

5-Ethoxycarbonyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 5).^[2]

Yellow solid. Mp: 201.1-202.7 °C; IR (KBr): 3230, 3109, 2977, 1701, 1641, 1591, 1520 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.37 (s, 1H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.90 (s, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 5.27 (d, *J* = 3.0 Hz, 1H), 3.98 (q, *J* = 6.9 Hz, 2H), 2.26 (s, 3H), 1.09 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.1, 152.0, 151.8, 149.4, 146.7,

127.7, 123.9, 98.2, 59.4, 53.7, 17.9, 17.8, 14.1; HRMS Calcd for C₁₄H₁₆N₃O₅ (M + H⁺): 306.1084; Found: 306.1086.

5-Ethoxycarbonyl-6-methyl-4-(4-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one
(table 2, entry 6).^[2]

Yellow solid. Mp: 198.4-200.1 °C; IR (KBr): 3520, 3230, 3150, 1705, 1690 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.25 (s, 1H), 7.78 (s, 1H), 7.62 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 5.04 (d, *J* = 2.7 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.4, 156.5, 152.2, 147.8, 135.5, 127.4, 115.0, 99.7, 59.1, 53.4, 17.8, 14.1; HRMS Calcd for C₁₄H₁₇N₂O₄ (M + H⁺): 277.1183; Found: 277.1186.

5-Ethoxycarbonyl-6-methyl-4-(2-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one
(table 2, entry 7).^[2]

White solid. Mp: 223.1-224.5 °C; IR (KBr): 3354, 3268, 1683, 1597 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.57 (brs, 1H), 9.09 (s, 1H), 7.10 (s, 1H), 7.05 (td, *J* = 7.5, 1.5 Hz, 1H), 6.97 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.79 (dd, *J* = 7.5, 0.6 Hz, 1H), 6.71 (td, *J* = 7.5, 0.6 Hz, 1H), 5.46 (d, *J* = 3.0 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.5, 154.7, 152.4, 148.6, 129.9, 128.3, 127.3, 118.8, 115.4, 97.8, 59.1, 49.2, 17.8, 14.1; HRMS Calcd for C₁₄H₁₇N₂O₄ (M + H⁺): 277.1183; Found: 277.1186.

5-Ethoxycarbonyl-6-methyl-4-(furan-2-yl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 8).^[1]

Yellow solid. Mp: 207.2-208.9 °C; IR (KBr): 3364, 3221, 3120, 2970, 1699, 1638, 1457, 1372, 1299, 1229, 1092, 1014, 793, 742, 449 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.24 (s, 1H), 7.76 (s, 1H), 7.55 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.35 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.09 (d, *J* = 3.3 Hz, 1H), 5.21 (d, *J* = 3.6 Hz, 1H), 4.02 (qd, *J* = 7.2, 0.9 Hz, 2H), 2.23 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.1, 156.0, 152.5, 149.4, 142.2, 110.4, 105.3, 96.8, 59.3, 47.8, 17.8, 14.2; HRMS Calcd for C₁₂H₁₅N₂O₄ (M + H⁺): 251.1026; Found: 251.1024.

5-Ethoxycarbonyl-6-methyl-4-(n-hexyl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 9).^[3]

Yellow solid. Mp: 229.8-231.2°C; IR (KBr): 3248, 3121, 2957, 2936, 2855, 1724, 1703, 1647, 1383, 1288, 1223, 1086, 779 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.92 (s, 1H), 7.32 (s, 1H), 4.11-3.99 (m, 3H), 2.15 (m, 3H), 1.38 (m, 10H), 1.18 (t, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.5, 152.8, 148.3, 99.5, 59.1, 50.1, 36.7, 31.3, 28.5, 23.7, 22.1, 17.7, 14.2, 14.0; HRMS Calcd for C₁₄H₂₅N₂O₃ (M + H⁺): 269.1860; Found: 269.1863.

5-Ethoxycarbonyl-6-methyl-4-isopropyl-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 10).^[3]

Yellow solid. Mp: 193.4-194.8 °C; IR (KBr): 3234, 2985, 1710, 1642 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.90 (s, 1H), 7.30 (s, 1H), 4.11-4.00 (m, 2H), 3.94 (t, *J* = 3.6 Hz, 1H), 2.17 (s, 3H), 1.70-1.62 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 1H), 0.81 (d, *J* = 6.9 Hz, 3H), 0.74 (d, *J*

= 6.9 Hz, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 165.8, 153.2, 148.5, 98.1, 59.0, 55.5, 34.6, 18.5, 17.7, 16.0, 14.2; HRMS Calcd for $\text{C}_{11}\text{H}_{19}\text{N}_2\text{O}_3$ ($\text{M} + \text{H}^+$): 227.1390; Found: 227.1387.

5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione (table 2, entry 11).^[1]

Yellow solid. Mp: 200.4-202.5 °C; IR (KBr): 3322, 3466, 3176, 3111, 1670, 1575, 1470, 1277, 1197, 1105, 696 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6) δ 10.34 (s, 1H), 9.65 (s, 1H), 7.37-7.21 (m, 5H), 5.18 (d, $J = 3.6$ Hz, 1H), 4.01 (q, $J = 6.9$ Hz, 2H), 2.29 (s, 3H), 1.10 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 174.2, 165.1, 145.0, 143.5, 128.6, 127.7, 126.4, 100.7, 59.6, 54.1, 17.2, 14.0; HRMS Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$ ($\text{M} + \text{H}^+$): 277.1005; Found: 277.1006.

5-Ethoxycarbonyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1H)-thione (table 2, entry 12).^[4]

Yellow solid. Mp: 192.3-194.1 °C; IR (KBr): 3255, 1659, 1562 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6) δ 10.30 (s, 1H), 9.61 (d, $J = 1.8$ Hz, 1H), 7.16 (m, 4H), 5.13 (d, $J = 3.6$ Hz, 1H), 4.00 (q, $J = 7.2$ Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 1.10 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 174.2, 165.2, 144.9, 140.6, 136.9, 129.1, 126.3, 100.8, 59.6, 53.8, 20.7, 17.2, 14.1; HRMS Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ ($\text{M} + \text{H}^+$): 291.1162; Found: 291.1160.

5-Ethoxycarbonyl-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-thione (table 2, entry 13).^[4]

Colorless solid. Mp: 168.1-169.6 °C; IR (KBr): 3331, 3167, 3105, 2978, 1668, 1570, 1197, 747 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6) δ 10.39 (s, 1H), 9.67 (s, 1H), 7.44-7.40 (m, 2H),

7.25-7.20 (m, 2H), 5.17 (d, $J = 3.6$ Hz, 1H), 4.00 (q, $J = 7.0$ Hz, 2H), 2.29 (s, 3H), 1.09 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 174.3, 165.0, 145.4, 142.4, 132.3, 128.6, 128.3, 100.3, 59.7, 53.5, 17.2, 14.0; HRMS Calcd for $\text{C}_{14}\text{H}_{16}\text{ClN}_2\text{O}_2\text{S}$ ($\text{M} + \text{H}^+$): 311.0616; Found: 311.0619.

5-Ethoxycarbonyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydro-pyrimidin-2-thione (table 2, entry 14).^[4]

Yellow solid. Mp: 200.0-202.1 °C; IR (KBr): 3324, 3173, 2918, 1679, 1655, 1576, 1522, 1466, 1350, 1201, 1176, 1123 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6) δ 10.50 (s, 1H), 9.77 (s, 1H), 8.24 (d, $J = 8.7$ Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 2H), 5.30 (d, $J = 3.6$ Hz, 1H), 4.01 (q, $J = 6.9$ Hz, 2H), 2.31 (s, 3H), 1.10 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 174.4, 164.8, 150.4, 147.0, 146.0, 127.8, 124.0, 99.7, 59.8, 53.7, 17.3, 14.0; HRMS Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_3\text{O}_4\text{S}$ ($\text{M} + \text{H}^+$): 322.0856; Found: 322.0854.

5-Methoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 15).^[1]

Yellow solid. Mp: 211.3-213.7 °C; IR (KBr): 3238, 3117, 2933, 1719, 1645, 1222, 1092 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6) δ 9.23 (s, 1H), 7.77 (s, 1H), 7.35-7.30 (m, 2H), 7.26-7.21 (m, 3H), 5.15 (d, $J = 3.3$ Hz, 1H), 3.53 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 165.9, 152.2, 148.7, 144.7, 128.5, 127.4, 126.2, 99.1, 53.9, 50.9, 17.9; HRMS Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_3$ ($\text{M} + \text{H}^+$): 247.1077; Found: 247.1079.

5-Methoxycarbonyl-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 16).^[2]

Yellow solid. Mp: 192.1-194.2 °C; IR (KBr): 3232, 3104, 3003, 2950, 2837, 1698, 1645, 1609, 1512 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.19 (s, 1H), 7.69 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.09 (d, *J* = 3.0 Hz, 1H), 3.72 (s, 3H), 3.52 (s, 3H), 2.25 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.9, 158.5, 152.2, 148.4, 136.9, 127.3, 113.8, 99.3, 55.1, 53.2, 50.8, 17.8; HRMS Calcd for C₁₄H₁₇N₂O₄ (M + H⁺): 277.1183; Found: 277.1186.

5-Methoxycarbonyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1H)-one

(table 2, entry 17).^[5]

Yellow solid. Mp: 204.0-206.4 °C; IR (KBr): 3175, 1691, 1634 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.19 (s, 1H), 7.71 (s, 1H), 7.11 (s, 4H), 5.11 (d, *J* = 3.3 Hz, 1H), 3.52 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.9, 152.2, 148.5, 141.8, 136.4, 129.0, 126.1, 99.2, 53.5, 50.8, 20.7, 17.8; HRMS Calcd for C₁₄H₁₇N₂O₃ (M + H⁺): 261.1234; Found: 261.1236.

5-Methoxycarbonyl-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-one

(table 2, entry 18).^[1]

Yellow solid. Mp: 204.3-207.1 °C; IR (KBr): 3238, 3114, 2950, 2875, 1702, 1645 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.28 (s, 1H), 7.80 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 5.14 (d, *J* = 3.3 Hz, 1H), 3.53 (s, 3H), 2.25 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.7, 152.0, 149.0, 143.6, 131.9, 128.5, 128.1, 98.6, 53.3, 50.9, 17.9; HRMS Calcd for C₁₃H₁₄ClN₂O₃ (M + H⁺): 281.0687; Found: 281.0689.

5-Methoxycarbonyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one

(table 2, entry 19).^[2]

Yellow solid. Mp: 235.5-237.3 °C; IR (KBr): 3366, 3233, 3113, 2951, 1703, 1643, 1598, 1520 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.38 (s, 1H), 8.21 (d, *J* = 8.9 Hz, 2H), 7.91 (s, 1H), 7.50 (d, *J* = 8.9 Hz, 2H), 5.27 (d, *J* = 3.3 Hz, 1H), 3.53 (s, 3H), 2.27 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 165.6, 151.8, 151.7, 149.6, 146.7, 127.6, 123.9, 98.0, 53.5, 50.9, 17.9; HRMS Calcd for C₁₃H₁₄N₃O₅ (M + H⁺): 292.0928; Found: 292.0925.

5-Methoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione (table 2, entry 20).^[6]

Yellow solid. Mp: 202.1-204.5 °C; IR (KBr): 3340, 1662, 1600, 1566 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.37 (s, 1H), 9.68 (d, *J* = 1.8 Hz, 1H), 7.38-7.32 (m, 2H), 7.30-7.26 (m, 1H), 7.25-7.21 (m, 2H), 5.18 (d, *J* = 3.6 Hz, 1H), 3.56 (s, 3H), 2.30 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 174.3, 165.7, 145.3, 143.3, 128.7, 127.7, 128.3, 100.5, 53.9, 51.1, 17.3; HRMS Calcd for C₁₃H₁₅N₂O₂S (M + H⁺): 263.0849; Found: 263.0846.

5-Methoxycarbonyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1H)-thione (table 2, entry 21).^[7]

Yellow solid. Mp: 155.3-156.9 °C; IR (KBr): 3334, 3200, 2970, 1669, 1570, 1470, 1183 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.34 (s, 1H), 9.65 (d, *J* = 1.8 Hz, 1H), 7.16-7.08 (m, 4H), 5.13 (d, *J* = 3.6 Hz, 1H), 3.54 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 174.2, 165.7, 145.2, 140.4, 136.9, 129.1, 126.2, 100.5, 53.6, 51.1, 20.7, 17.2; HRMS Calcd for C₁₄H₁₇N₂O₂S (M + H⁺): 277.1005; Found: 277.1001.

5-Methoxycarbonyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-thione

(table 2, entry 22).^[7]

Yellow solid. Mp: 122.2-124.7 °C; IR (KBr): 3178, 3105, 2997, 2952, 1693, 1567, 1516 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.52 (s, 1H), 9.78 (s, 1H), 8.23 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 5.31 (d, *J* = 3.6 Hz, 1H), 3.56 (s, 3H), 2.31 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 174.5, 165.4, 150.2, 147.0, 146.2, 127.8, 124.1, 99.5, 53.6, 51.3, 17.4; HRMS Calcd for C₁₃H₁₄N₃O₄S (M + H⁺): 308.0700; Found: 308.0702.

5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 23).^[3]

Yellow solid. Mp: 238.5-240.9 °C; IR (KBr): 3287, 3241, 2914, 1706, 603, 1466, 1248, 764 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.21 (s, 1H), 7.86 (s, 1H), 7.35-7.30 (m, 2H), 7.26-7.22 (m, 3H), 5.26 (d, *J* = 3.3 Hz, 1H), 3.54 (s, 3H), 2.29 (s, 3H), 2.10 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 194.3, 152.2, 148.2, 144.3, 128.6, 127.4, 126.5, 109.6, 53.9, 30.4, 19.0; HRMS Calcd for C₁₃H₁₅N₂O₂ (M + H⁺): 231.1128; Found: 231.1124.

5-Acetyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 24).^[6]

Yellow solid. Mp: 204.2-206.5 °C; IR (KBr): 3288, 3120, 2920, 1699, 1616, 1236, 1139, 765, 561 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.16 (s, 1H), 7.78 (s, 1H), 7.13 (s, 4H), 5.22 (d, *J* = 3.0 Hz, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 2.08 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 194.4, 152.2, 148.0, 141.3, 136.5, 129.1, 126.4, 109.6, 53.6, 30.3, 20.7, 18.9; HRMS Calcd for C₁₄H₁₇N₂O₂ (M + H⁺): 245.1285; Found: 245.1288.

5-Acetyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (table 2, entry 25).^[6]

Yellow solid. Mp: 263.3-264.8 °C; IR (KBr): 3339, 3254, 3138, 1709, 1672, 1607, 1514, 1445, 1348, 1236, 1103, 762 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.34 (s, 1H), 9.20 (d, *J* = 8.7 Hz, 2H), 7.99 (s, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 5.38 (d, *J* = 3.6 Hz, 1H), 2.31 (s, 3H), 2.18 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 193.9, 152.0, 151.6, 149.1, 146.7, 127.7, 123.8, 109.5, 53.2, 30.7, 19.1; HRMS Calcd for C₁₃H₁₄N₃O₃ (M + H⁺): 276.0979; Found: 276.0981.

5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione (table 2, entry 26).^[3]

Yellow solid. Mp: 228.1-230.3 °C; IR (KBr): 3323, 3180, 2984, 1669, 1578, 1463, 1272, 1201, 758 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.28 (s, 1H), 9.76 (s, 1H), 7.38-7.22 (m, 5H), 5.29 (d, *J* = 3.9 Hz, 1H), 2.33 (s, 3H), 2.16 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 194.8, 174.1, 144.6, 142.9, 128.6, 127.7, 126.6, 110.5, 53.8, 30.4, 18.3; HRMS Calcd for C₁₃H₁₅N₂OS (M + H⁺): 247.0900; Found: 247.0901.

5-Acetyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1H)-thione (table 2, entry 27).

Yellow solid. Mp: 215.7-217.3 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.25 (s, 1H), 9.72 (s, 1H), 7.16-7.09 (m, 4H), 5.25 (d, *J* = 3.9 Hz, 1H), 2.32 (s, 3H), 2.26 (s, 3H), 2.13 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 194.8, 174.0, 144.4, 140.0, 137.0, 129.2, 126.5, 110.4, 53.6, 30.3, 20.7, 18.2; HRMS Calcd for C₁₄H₁₇N₂OS (M + H⁺): 261.1056; Found: 261.1059.

5-Acetyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-thione (table 2, entry 28).

Yellow solid. Mp: 207.3-209.5 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.46 (s, 1H), 9.89 (d, *J* = 2.4 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 5.41 (d, *J* = 3.9 Hz, 1H), 2.36 (s, 3H), 2.23 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 194.6, 174.6, 150.0, 146.9, 145.6, 127.8, 124.0, 110.3, 53.1, 30.8, 18.5; HRMS Calcd for C₁₃H₁₄N₃O₃S (M + H⁺): 292.0750; Found: 292.0753.

NMR spectra of all products

References

1. Salim, S. D.; Akamanchi, K. G. *Catal. Commun.* **2011**, *12*, 1153-1156.
2. Mandhane, P. G.; Joshi, R. S.; Nagargoje, D. R.; Gill, C. H. *Tetrahedron Lett.* **2010**, *51*, 3138–3140.
3. Ma Y.; Qian, C.; Wang, L.; Yang, M. J. *Org. Chem.* 2000, *65*, 3864-3868.
4. Konkala, K.; Sabbavarapu, N. M.; Katla, R.; Durga, N. Y. V.; Reddy T, V. K.; Bethala L. A. P. D.; Rachapudi B. N. P. *Tetrahedron Lett.* 2012, *53*, 1968-1973.
5. Rajack, A.; Yuvaraju, K.; Praveen, C.; Murthy, Y. L. N. *Journal of Molecular Catalysis A: Chemical* 2013, *370*, 197-204.
6. Salehi, P.; Dabiri, M.; Zolfigol, M. A.; Fard, M. A. B. *Tetrahedron Lett.* 2003, *44*, 2889-2891.
7. Fang, D.; Luo, J.; Zhou, X.; Ye, Z.; Liu, Z. *Journal of Molecular Catalysis A: Chemical* 2007, *274*, 208-211