

## Electronic Supplementary Information (ESI)

### Green and recyclable glycine nitrate (GlyNO<sub>3</sub>) ionic liquid triggered multicomponent Biginelli reaction for the efficient synthesis of dihydropyrimidinones.

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#### Table of contents:-

1. Experimental Section	
1.1. Materials and instrumentation.....	SI-2
1.2. Preparation of amino acid ionic liquid (AAIL).....	SI-3
2. NMR data recorded for compounds.....	SI-4-11
3. NMR spectra of some compounds.....	SI-12-16

### 1.1. Materials and instrumentation

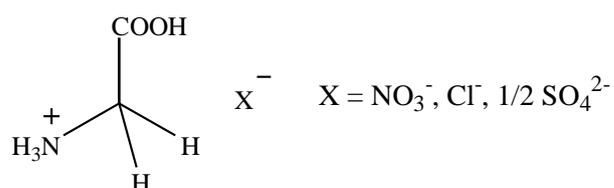
All reagents were obtained from commercial sources (Merck or Acros or HiMedia). The phenylpropenes were purified from natural sources following the reported procedure.<sup>1</sup> The solvents used for isolation/purification of compounds were obtained from Merck and used without further purification. Melting points were obtained manually by capillary methods and are uncorrected. <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75.4 MHz) NMR spectra were recorded on a Bruker Avance-300 spectrometer. TMS was used as internal reference for NMR. HRMS-ESI spectra were determined using Micromass Q-TOF Ultima spectrometer. Column chromatography was done on silica gel (60-100 mesh). Thin layer chromatography (TLC) was performed on silica TLC plates and compounds visualized in iodine or under UV lamp. CEM Discover<sup>®</sup> focused microwave (2450 MHz, 300W) was used wherever mentioned. The temperature of reactions in microwave experiments was measured by an inbuilt infrared temperature probe that determined the temperature on the surface of reaction flask. The sensor is attached in a feedback loop with an on-board microprocessor to control the temperature rise rate. In the case of conventional heating, the temperature of reaction mixture was monitored by thermometer.

HPLC analysis was performed using a Shimadzu HPLC (Model LC-20AT pump, DGU-20A5 degasser) equipped with auto sampler (SIL-20AC), photo diode array detector (CBM-20A; Shimadzu, Kyoto, Japan) and interfaced with IBM Pentium 4 personal computer. The separation was performed on a Purospher star RP-18e column (150 x 4.6 mm id, 5 μM; Merck) at 30°C. The mobile phase consisted of (A) 0.05% TFA (Trifluoroacetic acid) in H<sub>2</sub>O and (B) methanol/acetonitrile (in 70/30; v/v) with gradient elution (0–5 min, 40–70% B; 5–10 min, 70–100% B; 10–12 min, 100–40% B; 12–20 min, 40% B) with a flow rate of 1 mL/min. Analysis wavelength was set at 280 nm.

- [1] a) N. Sharma, U. K. Sharma, R. Salwan, R. C. Kasana and A. K. Sinha, *Catal. Lett.*, 2011, **141**, 616-622; b) R. C. Kasana, U. K. Sharma, N. Sharma and A. K. Sinha, *Curr. Microbiol.*, 2007, **54**, 457-461.

## 1.2. Preparation of amino acid ionic liquids (glycine nitrate (GlyNO<sub>3</sub>), glycine sulphate (GlySO<sub>4</sub>) and glycine chloride (GlyCl))

7.5 g (0.1 mol) of glycine was dissolved in 20 mL water. One mole equivalent of nitric acid or hydrochloric acid or 0.5 mol equivalent of sulfuric acid was added drop wise. The reaction mixture was then warmed to 60°C for 24 h. After evaporating in vacuo at 60°C and lyophilization, the resulting white solid was collected and recrystallized from methanol/ether. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded and matched with reported values.<sup>2</sup>



### Glycine nitrate (GlyNO<sub>3</sub>)

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$  8.11 (s, 3H), 3.68 (s, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75.4 MHz)  $\delta$  169.1, 39.7.

### Glycine sulphate (GlySO<sub>4</sub>)

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$  8.08 (s, 3H), 3.64 (s, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75.4 MHz)  $\delta$  168.7, 38.8

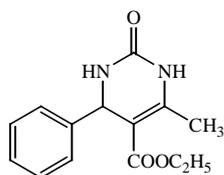
### Glycine chloride (GlyCl)

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$  8.12 (s, 3H), 3.67 (s, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75.4 MHz)  $\delta$  169.0, 39.6.

[2] G. H. Tao, L. He, N. Sun and Y. Kou, *Chem. Commun.*, 2005, 3562-3564.

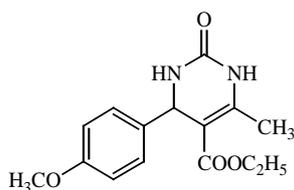
## 2. NMR data recorded for compounds

### Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 1b)



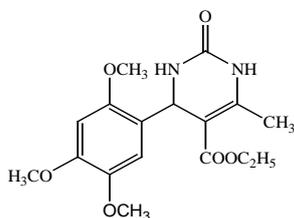
White solid (Yield 92%) m.p. 206-207°C,  $^1\text{H}$  NMR (DMSO- $d_6$ , 300 MHz):  $\delta$  9.21 (1H, s), 7.75 (1H, s), 7.35-7.23 (5H, m), 5.16 (1H, d,  $J = 3.08$  Hz), 4.02 (2H, q,  $J = 7.07$  Hz), 2.25 (3H, s), 1.12 (3H, t,  $J = 7.06$  Hz);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75.4 MHz);  $\delta$  166.2, 153.0, 149.2, 145.7, 129.2, 128.1, 127.1, 100.1, 60.0, 54.8, 18.6 and 14.9. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3$  calculated 261.1370; observed 261.1374. The spectral data matched well with the reported values.<sup>3a</sup>

### Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 2b)



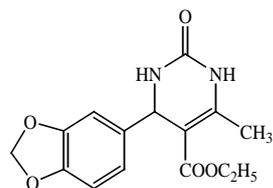
White solid (Yield 88%) m.p. 201-202°C,  $^1\text{H}$  NMR (DMSO- $d_6$ , 300 MHz):  $\delta$  9.17 (1H, s), 7.68 (1H, s), 7.17 (2H, d,  $J = 8.66$  Hz), 6.89 (2H, d,  $J = 8.69$  Hz), 5.10 (1H, d,  $J = 3.17$  Hz), 4.01 (2H, q,  $J = 7.07$  Hz), 3.72 (3H, s), 2.24 (3H, s), 1.13 (3H, t,  $J = 7.07$  Hz);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75.4 MHz);  $\delta$  166.2, 159.3, 153.0, 148.9, 137.9, 128.3, 114.6, 100.4, 60.0, 55.9, 54.2, 18.6 and 14.9. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4$  calculated 291.1520; observed 291.1528. The spectral data matched well with the reported values.<sup>3a</sup>

### Ethyl 6-methyl-2-oxo-4-(2,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 3b)



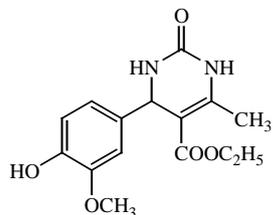
White solid (Yield 84%) m.p. 207-209°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  8.66 (1H, s), 6.64 (1H, s), 6.52 (1H, s), 5.78 (1H, s), 5.68 (1H, s), 4.10 (2H, q,  $J = 7.05$  Hz), 3.88 (3H, s), 3.85 (3H, s), 3.76 (3H, s), 2.42 (3H, s), 1.14 (3H, t,  $J = 7.09$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  166.3, 154.2, 151.7, 149.9, 148.4, 143.2, 122.3, 112.1, 98.9, 97.8, 60.2, 57.3, 56.6, 50.3, 18.8 and 14.6. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_6$  calculated 351.1820; observed 351.1829. The spectral data matched well with the reported values.<sup>3b</sup>

**Ethyl 4-(1,3-benzodioxol-5-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 4b)**



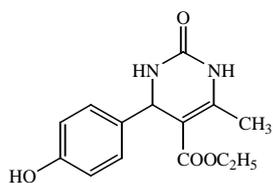
White solid (Yield 80%) m.p. 180-181°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  9.18 (1H, s), 7.69 (1H, s), 6.86-6.69 (3H, m), 5.98 (2H, s), 5.08 (1H d,  $J = 2.85$  Hz), 4.03 (2H, q,  $J = 7.01$  Hz), 2.25 (3H, s), 1.13 (3H, t,  $J = 7.05$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  166.2, 152.9, 149.1, 148.1, 147.2, 139.7, 120.2, 108.9, 107.5, 101.8, 100.2, 60.1, 54.5, 18.6 and 14.9. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_5$  calculated 305.1358; observed 305.1361.

**Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 5b)**



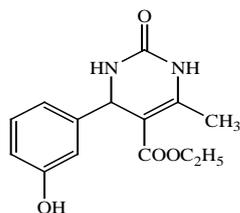
White solid (Yield 80%) m.p. 146-148°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  9.11 (1H, s), 8.91 (1H, s), 7.64 (1H, d,  $J = 2.66$  Hz), 6.80 (1H, d,  $J = 8.09$  Hz), 6.63-6.60 (2H, m), 5.07 (1H, d,  $J = 3.19$  Hz), 4.03 (2H, q,  $J = 7.07$  Hz), 3.72 (3H, s), 2.23 (3H, s), 1.14 (3H, t,  $J = 7.21$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  166.3, 153.1, 148.7, 148.1, 146.7, 136.8, 119.2, 116.1, 11.8, 100.4, 59.9, 56.9, 54.4, 18.6 and 15.0. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_5$  calculated 307.1514; observed 307.1521.

**Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 6b)**



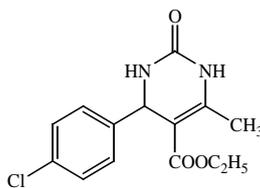
White solid (Yield 75%) m.p. 232-234°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  9.34 (1H, s), 9.12 (1H, s), 7.63 (1H, s), 7.04 (2H, d,  $J = 7.99$  Hz), 6.70 (2H, d,  $J = 7.97$  Hz), 5.05 (1H, s), 4.01 (2H, q,  $J = 6.71$  Hz), 2.23 (3H, s), 1.12 (3H, t,  $J = 6.92$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  165.4, 156.5, 152.2, 147.7, 135.4, 127.4, 114.9, 99.8, 59.1, 53.4, 17.7 and 14.1. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4$  calculated 277.1364; observed 277.1374.

**Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**  
(Table 3, compound 7b)



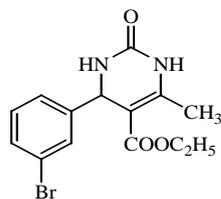
White solid (Yield 76%) m.p. 179-182°C, <sup>1</sup>H NMR (DMSO, 300 MHz): δ 8.46 (1H, s), 8.23 (1H, s), 6.76 (1H, s), 6.18 (1H, t, *J* = 8.12 Hz), 5.77-5.72 (3H, m), 4.15 (1H, d, *J* = 3.17 Hz), 3.09 (2H, q, *J* = 7.10 Hz), 1.32 (3H, s), 0.22 (3H, t, *J* = 7.12 Hz); <sup>13</sup>C NMR (DMSO, 75.4 MHz); δ 166.3, 158.2, 153.1, 148.9, 147.1, 130.1, 117.8, 115.0, 113.9, 100.3, 60.1, 54.7, 18.6 and 14.9. HRMS-ESI: *m/z* [M+H]<sup>+</sup> for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> calculated 277.1364; observed 277.1372. The spectral data matched well with the reported values.<sup>3c</sup>

**Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**  
(Table 3, compound 8b)



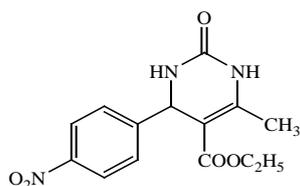
White solid (Yield 86%) m.p. 213-214°C, <sup>1</sup>H NMR (DMSO, 300 MHz): δ 9.25 (1H, s), 7.78 (1H, s), 7.41 (2H, d, *J* = 8.41 Hz), 7.26 (2H, d, *J* = 8.43 Hz), 5.15 (1H, s), 4.01 (2H, q, *J* = 7.05 Hz), 2.25 (3H, s), 1.12 (3H, t, *J* = 7.09 Hz); <sup>13</sup>C NMR (DMSO, 75.4 MHz); δ 165.2, 151.9, 148.7, 143.8, 131.8, 128.4, 128.2, 98.8, 59.2, 53.4, 17.8 and 14.0. HRMS-ESI: *m/z* [M+H]<sup>+</sup> for C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>3</sub> calculated 295.5819; observed 295.5823. The spectral data matched well with the reported values.<sup>3a</sup>

**Ethyl 4-(3-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**  
(Table 3, compound 9b)



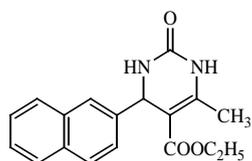
White solid (Yield 88%) m.p. 187-189°C, <sup>1</sup>H NMR (DMSO, 300 MHz): δ 9.27 (1H, s), 7.80 (1H, s), 7.47-7.23 (4H, m), 5.15 (1H, d, *J* = 2.85 Hz), 4.02 (2H, q, *J* = 7.07 Hz), 2.26 (3H, s), 1.13 (3H, t, *J* = 7.01 Hz); <sup>13</sup>C NMR (DMSO, 75.4 MHz); δ 166.0, 152.8, 149.8, 148.3, 131.7, 130.9, 130.0, 126.1, 122.4, 99.5, 60.2, 54.5, 18.7 and 14.9. HRMS-ESI: *m/z* [M+H]<sup>+</sup> for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>Br calculated 340.0332; observed 340.0338. The spectral data matched well with the reported values.<sup>3a</sup>

**Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**  
(Table 3, compound 10b)



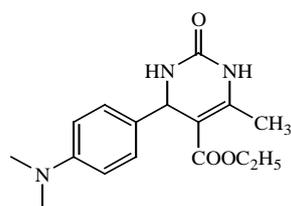
Creamish solid (Yield 85%) m.p. 220-225°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  9.38 (1H, s), 8.15 (2H, d,  $J = 8.31$  Hz), 7.91 (1H, s), 7.72 (2H, d,  $J = 8.38$  Hz), 5.31 (1H, d,  $J = 2.89$  Hz), 4.05 (2H, q,  $J = 7.18$  Hz), 2.28 (3H, s), 1.13 (3H, t,  $J = 7.13$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  165.9, 152.6, 150.3, 148.6, 147.9, 133.8, 131.1, 123.2, 121.9, 99.2, 60.2, 54.4, 18.7 and 14.9. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_5$  calculated 306.1411; observed 306.1417. The spectral data matched well with the reported values.<sup>3a</sup>

**Ethyl 6-methyl-4-(naphthalen-2-yl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**  
(Table 3, compound 11b)



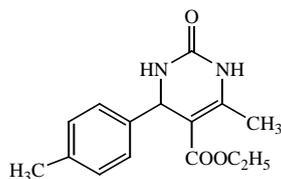
White solid (Yield 85%) m.p. 257-258°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  9.24 (1H, s), 7.93 (1H, s), 7.86 (1H, d,  $J = 7.88$  Hz), 7.79 (1H, s), 7.56-7.43 (5H, m), 6.07 (1H, d,  $J = 3.01$  Hz), 3.83 (2H, q,  $J = 7.59$  Hz), 2.37 (3H, s), 0.84 (3H, t,  $J = 7.07$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  165.6, 151.9, 148.9, 140.7, 133.7, 130.3, 128.7, 126.3, 126.0., 125.9, 124.5, 123.9, 99.4, 59.3, 50.1, 18.0 and 14.1. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3$  calculated 311.1526; observed 311.1534. The spectral data matched well with the reported values.<sup>3c</sup>

**Ethyl 4-[4-(*N,N*-dimethylamino)phenyl]-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**  
(Table 3, compound 12b)



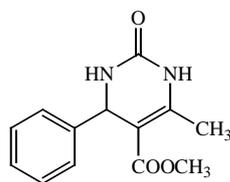
Creamish solid (Yield 84%) m.p. 252-255°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  9.09 (1H, s), 7.60 (1H, s), 7.05 (2H, d,  $J = 8.38$  Hz), 6.67 (2H, d,  $J = 8.42$  Hz), 5.04 (1H, d,  $J = 2.18$  Hz), 4.01 (2H, q,  $J = 6.86$  Hz), 2.85 (6H, s), 2.23 (3H, s), 1.14 (3H, t,  $J = 7.02$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  165.2, 151.9, 149.4, 147.2, 132.3, 126.6, 111.9, 99.6, 58.8, 53.0, 17.39 and 13.8. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_3$  calculated 304.1791; observed 304.1796. The spectral data matched well with the reported values.<sup>3d</sup>

**Ethyl 6-methyl-4-(4-methylphenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 13b)**



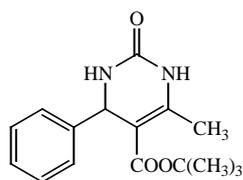
White solid (Yield 87%) m.p. 206-208°C, <sup>1</sup>H NMR (DMSO, 300 MHz): δ 9.12 (1H, s), 7.67 (1H, s), 7.11 (3H, s), 5.12 (1H, d, *J* = 2.67 Hz), 3.98 (2H, d, *J* = 7.07 Hz), 2.25 (6H, s), 1.11 (3H, t, *J* = 7.07 Hz); <sup>13</sup>C NMR (DMSO, 75.4 MHz); δ 166.3, 153.2, 148.9, 142.7, 137.3, 129.8, 126.9, 100.4, 60.0, 54.5, 21.4, 18.6 and 14.9. HRMS-ESI: *m/z* [M+H]<sup>+</sup> for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub> calculated 275.1526; observed 275.1533. The spectral data matched well with the reported values.<sup>3c</sup>

**Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 14b)**



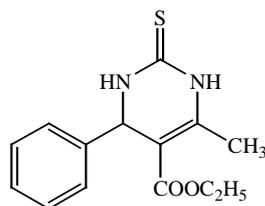
White solid (Yield 84%) m.p. 205-210°C, <sup>1</sup>H NMR (DMSO, 300 MHz): δ 9.22 (1H, s), 7.76 (1H, s), 7.35-7.30 (2H, m), 7.26-7.23 (3H, m), 5.16 (1H, d, *J* = 3.28 Hz), 3.53 (3H, s), 2.26 (3H, s); <sup>13</sup>C NMR (DMSO, 75.4 MHz); δ 166.7, 153.0, 149.5, 145.5, 129.3, 128.1, 127.0, 99.9, 54.7, 51.6 and 18.7. HRMS-ESI: *m/z* [M+H]<sup>+</sup> for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> calculated 247.0714; observed 247.0725. The spectral data matched well with the reported values.<sup>3a</sup>

***tert*-Butyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 15b)**



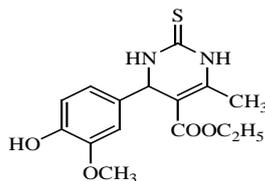
White solid (Yield 89%) m.p. 220-222°C, <sup>1</sup>H NMR (DMSO, 300 MHz): δ 9.04 (1H, s), 7.64 (1H, s), 7.34-7.30 (2H, m), 7.27 (3H, d, *J* = 7.49 Hz), 5.10 (1H, d, *J* = 2.67 Hz), 2.22 (3H, s), 1.28 (9H, s); <sup>13</sup>C NMR (DMSO, 75.4 MHz); δ 165.7, 153.0, 148.1, 145.8, 129.1, 128.1, 127.1, 101.5, 55.2, 49.4, 28.6 and 18.5. HRMS-ESI: *m/z* [M+H]<sup>+</sup> for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub> calculated 289.1682; observed 289.1694. The spectral data matched well with the reported values.<sup>3e</sup>

**Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 16b)**



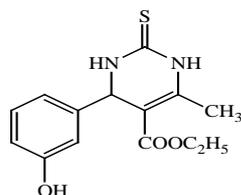
White solid (Yield 80%) m.p. 202-206°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  9.61 (1H, s), 8.93 (1H, s), 6.67-6.53 (5H, m), 4.50 (1H, d,  $J = 3.60$  Hz), 3.35 (2H, q,  $J = 7.10$  Hz), 1.60 (3H, s), 0.43 (3H, t,  $J = 7.03$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  175.2, 165.9, 145.8, 144.3, 129.3, 128.5, 127.2, 101.6, 60.4, 54.9, 17.9 and 14.7. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$  calculated 277.2036; observed 277.2047. The spectral data matched well with the reported values.<sup>3a</sup>

**Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4 tetrahydropyrimidine-5-carboxylate (Table 3, compound 17b)**



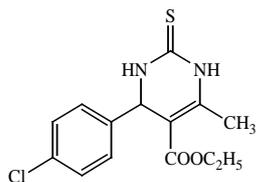
White solid (Yield 80%) m.p. 203°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  10.25 (1H, s), 9.56 (1H, d,  $J = 1.74$  Hz), 9.01 (1H, s), 6.63-6.60 (3H, m), 5.09 (1H, d,  $J = 3.57$  Hz), 4.04 (2H, q,  $J = 7.03$  Hz), 3.73 (3H, s), 2.28 (3H, s), 1.15 (3H, t,  $J = 7.08$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  174.9, 166.1, 148.2, 147.8, 145.4, 153.4, 119.4, 116.3, 111.8, 101.9, 60.4, 56.4, 54.5, 17.9 and 14.9. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$  calculated 323.2180; observed 323.2194.

**Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 3, compound 18b)**



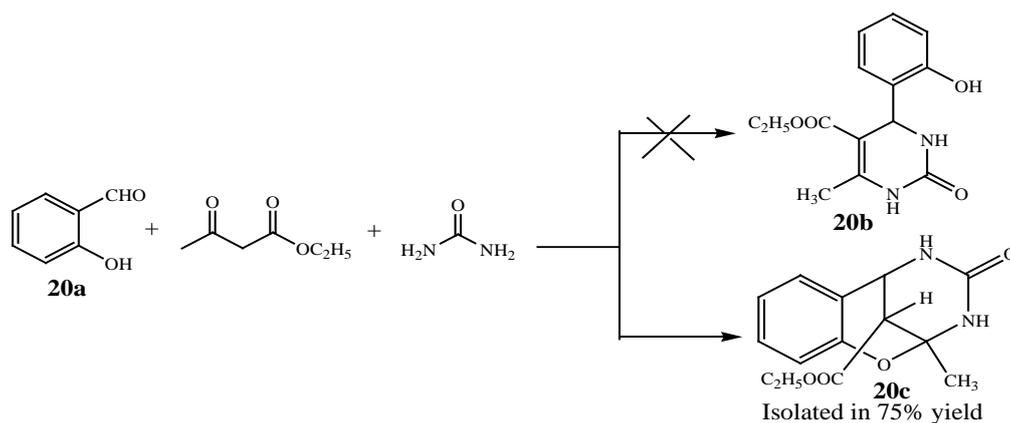
White solid (Yield 74%) m.p. 179-182°C,  $^1\text{H}$  NMR (DMSO, 300 MHz):  $\delta$  9.37 (1H, s), 9.17 (1H, s), 7.70 (1H, s), 7.12 (1H, t,  $J = 7.92$  Hz), 6.68-6.61 (3H, m), 5.06 (1H, s), 4.03 (2H, q,  $J = 6.97$  Hz), 2.24 (3H, s), 1.19 (3H, t,  $J = 7.09$  Hz);  $^{13}\text{C}$  NMR (DMSO, 75.4 MHz);  $\delta$  165.4, 157.3, 152.2, 148.1, 146.3, 129.3, 116.9, 114.2, 113.1, 99.4, 59.2, 53.8, 17.8 and 14.1. HRMS-ESI:  $m/z$   $[\text{M}+\text{H}]^+$  for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$  calculated 293.2030; observed 293.2051. The spectral data matched well with the reported values.<sup>3f</sup>

**Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**  
(Table 3, compound 19b)



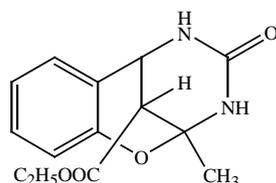
White solid (Yield 83%) m.p. 172-178°C, <sup>1</sup>H NMR (DMSO, 300 MHz): δ 10.38 (1H, s), 9.66 (1H, s), 7.44 (2H, d, *J* = 8.43 Hz), 7.24 (2H, d, *J* = 8.43 Hz), 5.18 (1H, d, *J* = 3.60 Hz), 4.04 (2H, q, *J* = 7.02 Hz), 2.29 (3H, s), 1.12 (3H, t, *J* = 7.08 Hz); <sup>13</sup>C NMR (DMSO, 75.4 MHz): δ 175.1, 165.9, 146.2, 143.2, 133.1, 129.4, 129.2, 101.2, 60.5, 54.3, 18.0 and 14.9. HRMS-ESI: *m/z* [M+H]<sup>+</sup> for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>SCl calculated 311.6485; observed 311.6491. The spectral data matched well with the reported values.<sup>3f</sup>

[3] a) H. N. Karade, M. Sathe, M. P. Kaushik, *Molecules* 2007, 12, 1341-1351; b) Ş. Beşoluk, M. Küçükislamoğlu, M. Zengin, M. Arslan, M. Nebioğlu, *Turk. J. Chem.* 2010, 34, 411-416; c) J. Xin, L. Chang, Z. Hou, D. Shang, X. Liu, X. Feng, *Chem. Eur. J.* 2008, 14, 3177-3181; d) J. S. Yadav, B. V. S. Reddy, K. B. Reddy, K. S. Raj, A. R. Prasad, *J. Chem. Soc. Perkin Trans.* 2001, 1, 1939-1941; e) S. F. Falsone, C. O. Kappe, *Arkivoc* 2001, ii, 122-134; f) D. Dallinger, C. O. Kappe, *Nat. Protoc.* 2007, 2, 317-321



**Scheme S1** Synthesis of compound **20c**.

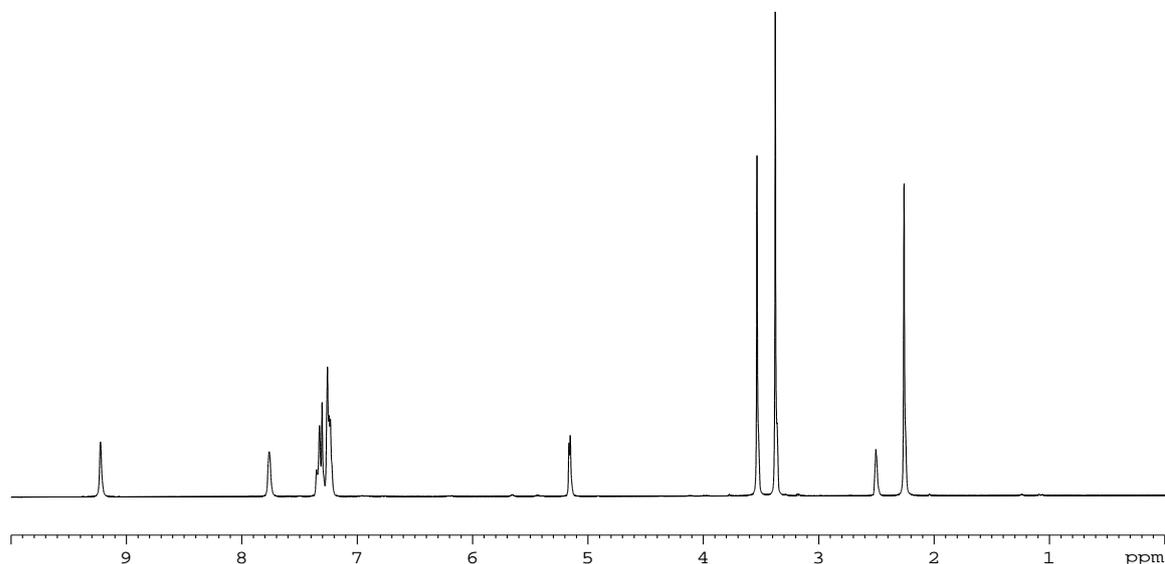
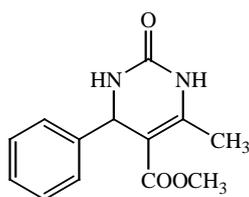
**Ethyl 9-methyl-11-oxo-8-oxa-10,12-diazatricyclo[7.3.1.0<sup>2,7</sup>]trideca-2,4,6-triene-13-carboxylate (Scheme S1, compound 20c)**



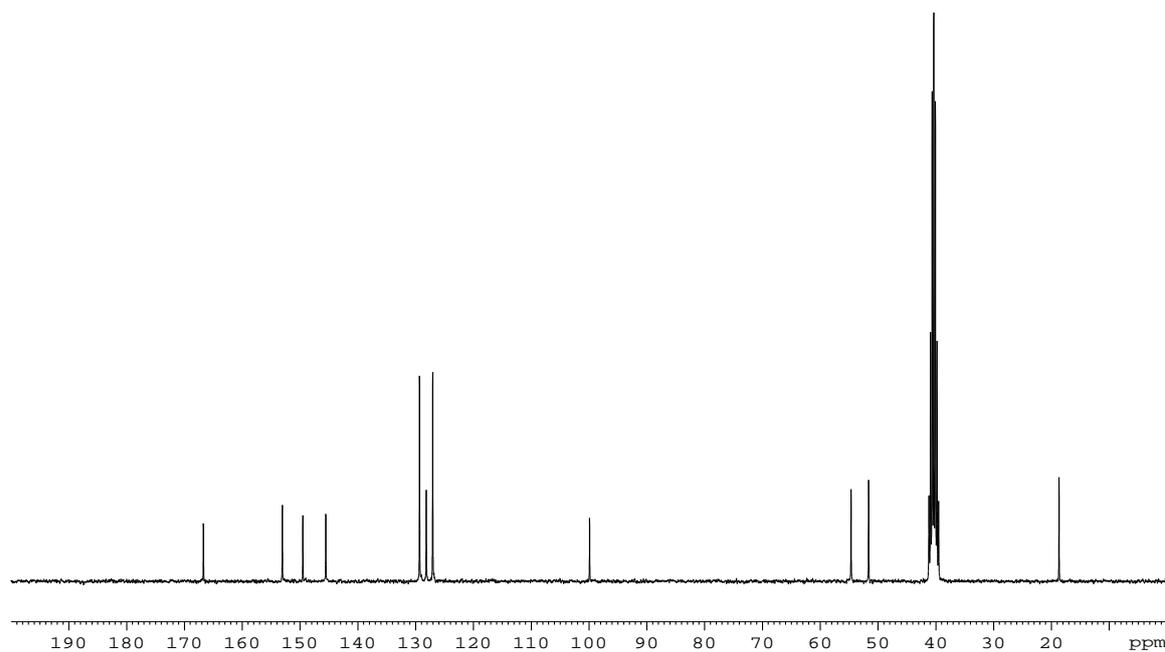
White solid (Yield 75%) m.p. 202-205°C, <sup>1</sup>H NMR (DMSO, 300 MHz): δ 7.60 (1H, s), 7.24-7.17 (3H, m), 6.96-6.88 (1H, m), 6.80 (1H, d, *J* = 8.35 Hz), 4.49 (1H, m), 4.19 (2H, q, *J* = 7.31 Hz), 3.26 (1H, s), 1.74 (3H, s), 1.26 (3H, t, *J* = 7.11 Hz); <sup>13</sup>C NMR (DMSO, 75.4 MHz): δ 168.7, 154.8, 150.9, 129.6, 128.9, 125.7, 120.7, 116.8, 83.4, 60.8, 44.2, 40.6, 24.2 and 14.3. HRMS-ESI: *m/z* [M+H]<sup>+</sup> for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> calculated 277.1364; observed 276.1369. The spectral data matched well with the reported values.<sup>4</sup>

[4] a) A. Kumar, R. A. Maurya, *Tetrahedron Lett.* 2007, 48, 4569-4571; b) E. M. H. Abbas, S. M. Abdallah, M. H. Abdoh, H. A. Tawfik, W. S. El-Hamouly, *Turk. J. Chem.* 2008, 32, 297-304.

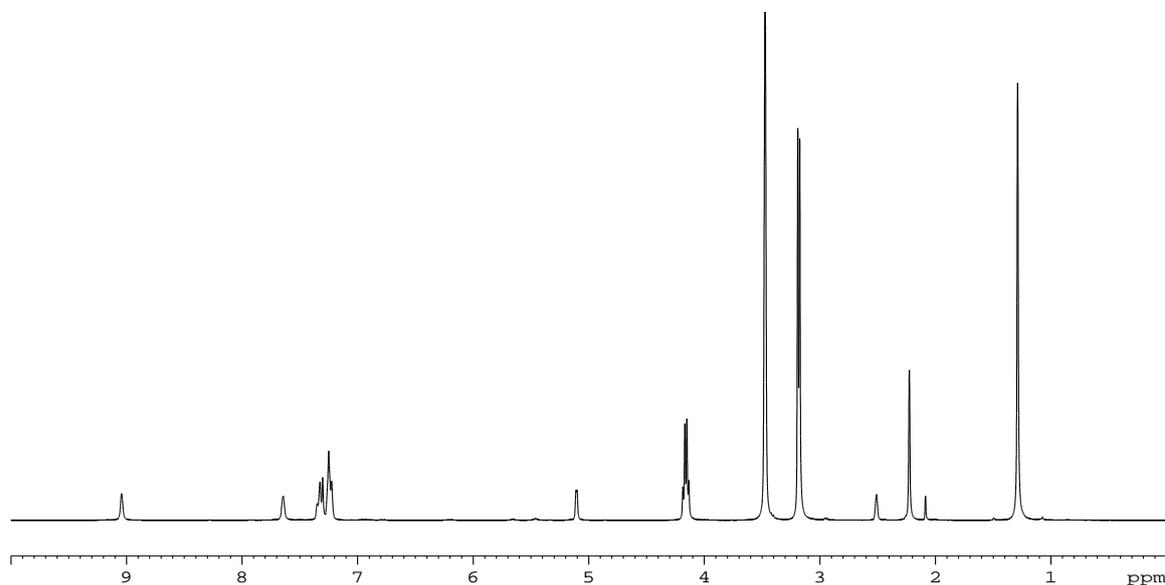
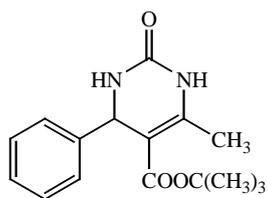
### 3. NMR spectra of some compounds



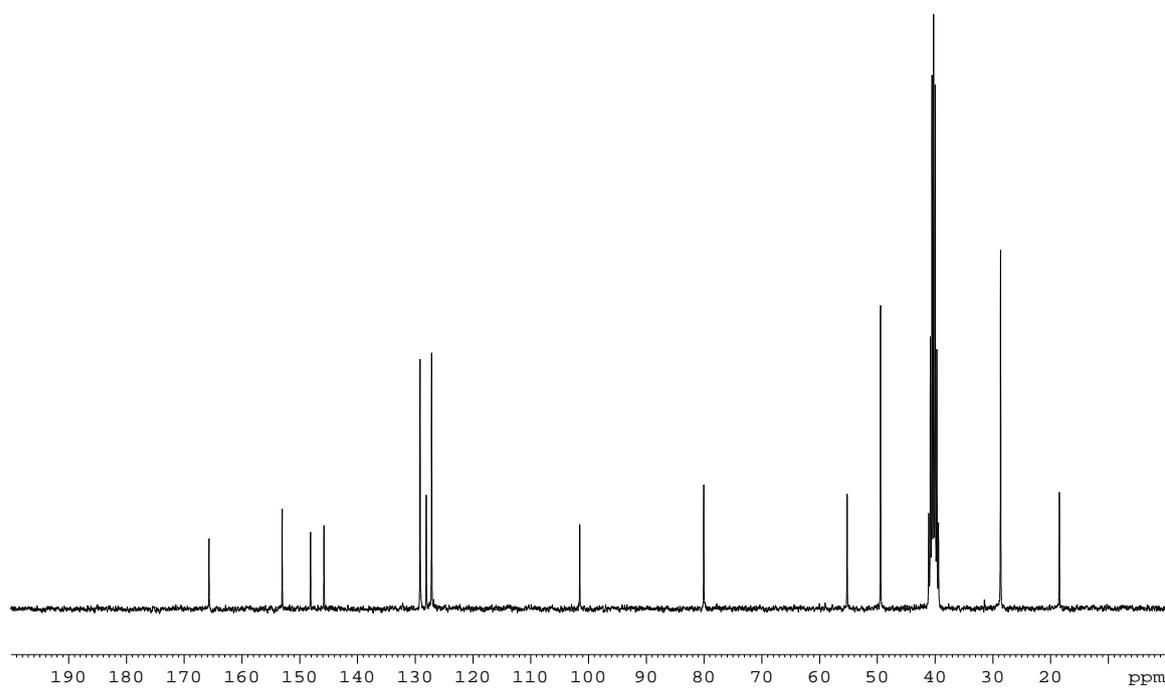
$^1\text{H}$  NMR (in  $\text{DMSO-}d_6$ ) spectrum of Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**14b**, Table 3)



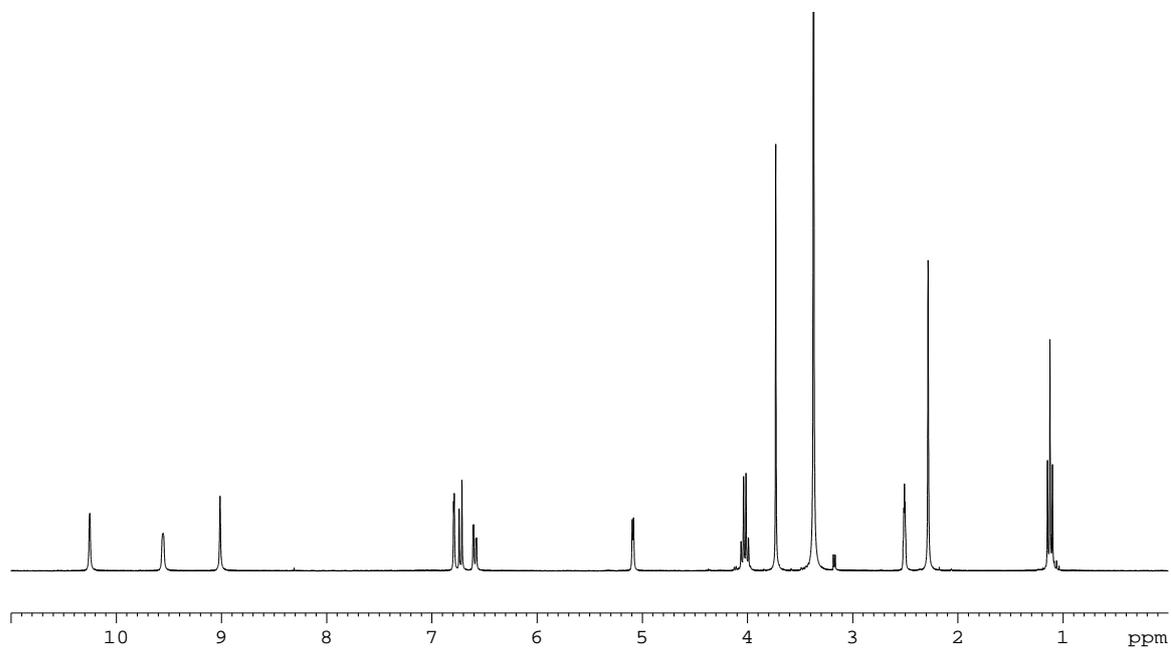
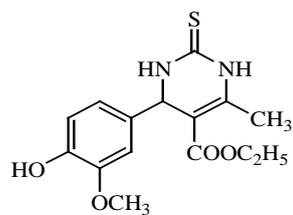
$^{13}\text{C}$  NMR (in  $\text{DMSO-}d_6$ ) spectrum of Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**14b**, Table 3)



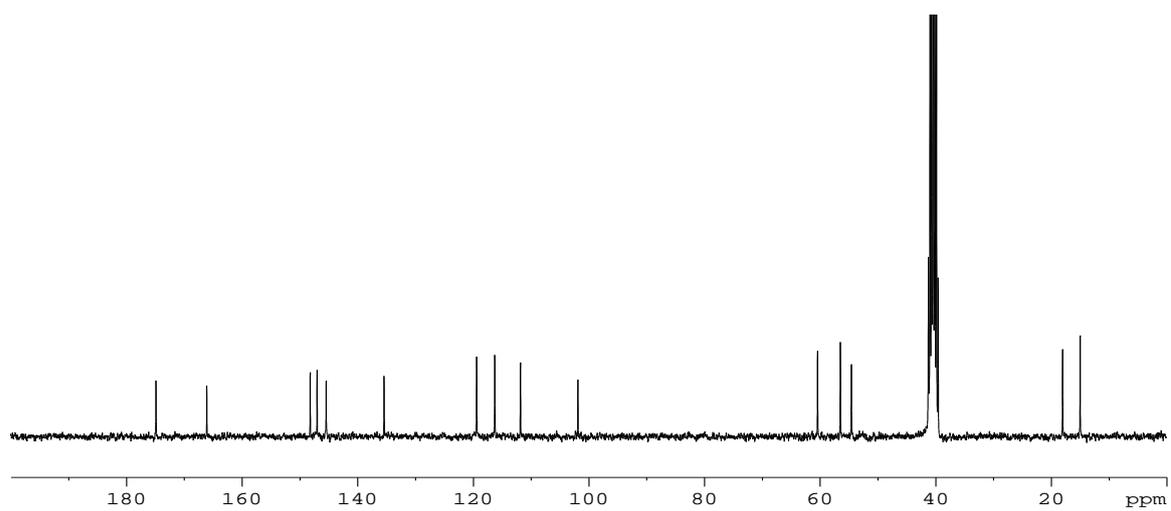
$^1\text{H}$  NMR (in  $\text{DMSO-}d_6$ ) spectrum of *tert*-Butyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**15b**, Table 3)



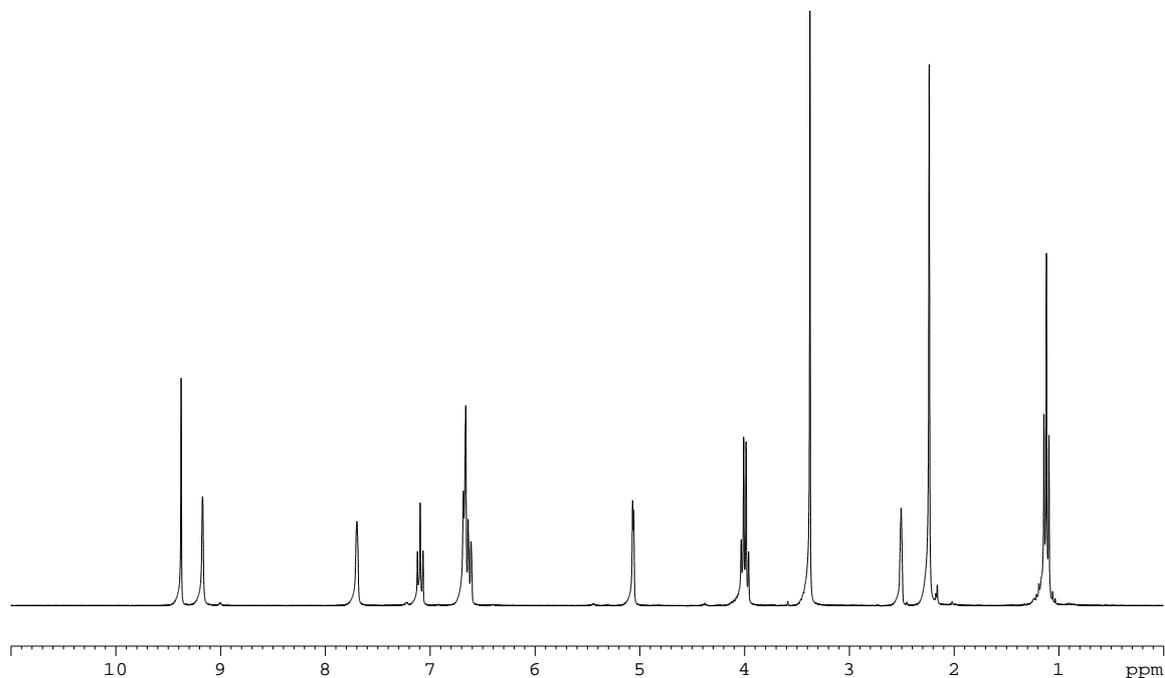
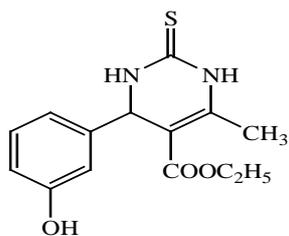
$^{13}\text{C}$  NMR (in  $\text{DMSO-}d_6$ ) spectrum of *tert*-Butyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**15b**, Table 3)



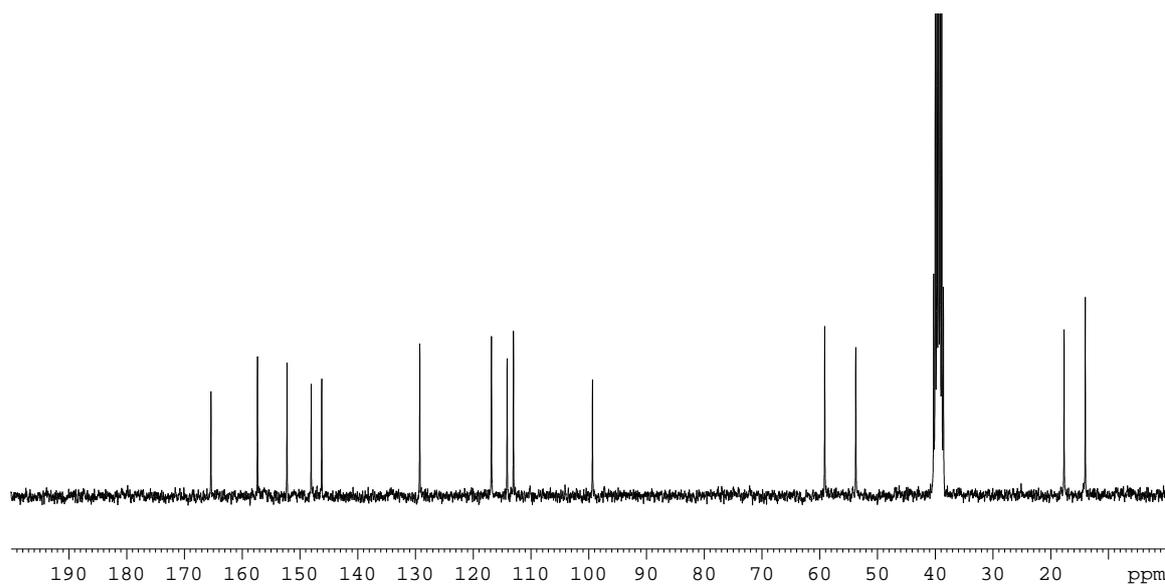
<sup>1</sup>H NMR (in DMSO-*d*<sub>6</sub>) spectrum of Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4 tetrahydropyrimidine-5-carboxylate (**17b**, Table 3)



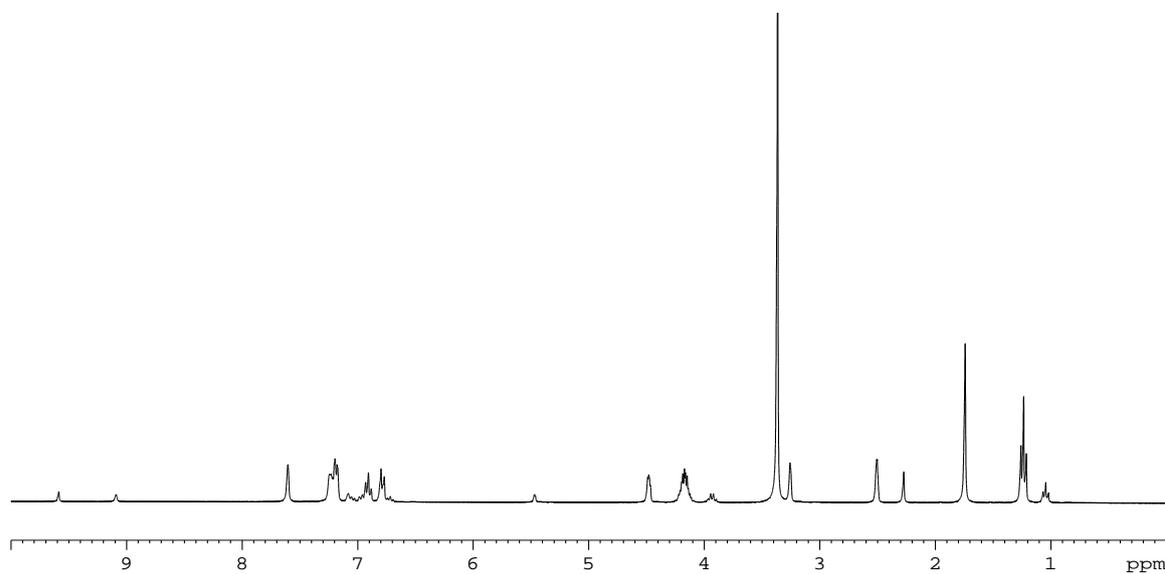
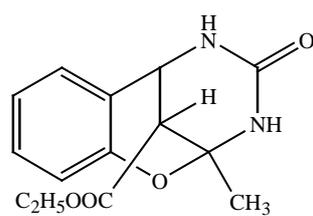
<sup>13</sup>C NMR (in DMSO-*d*<sub>6</sub>) spectrum of Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4 tetrahydropyrimidine-5-carboxylate (**17b**, Table 3)



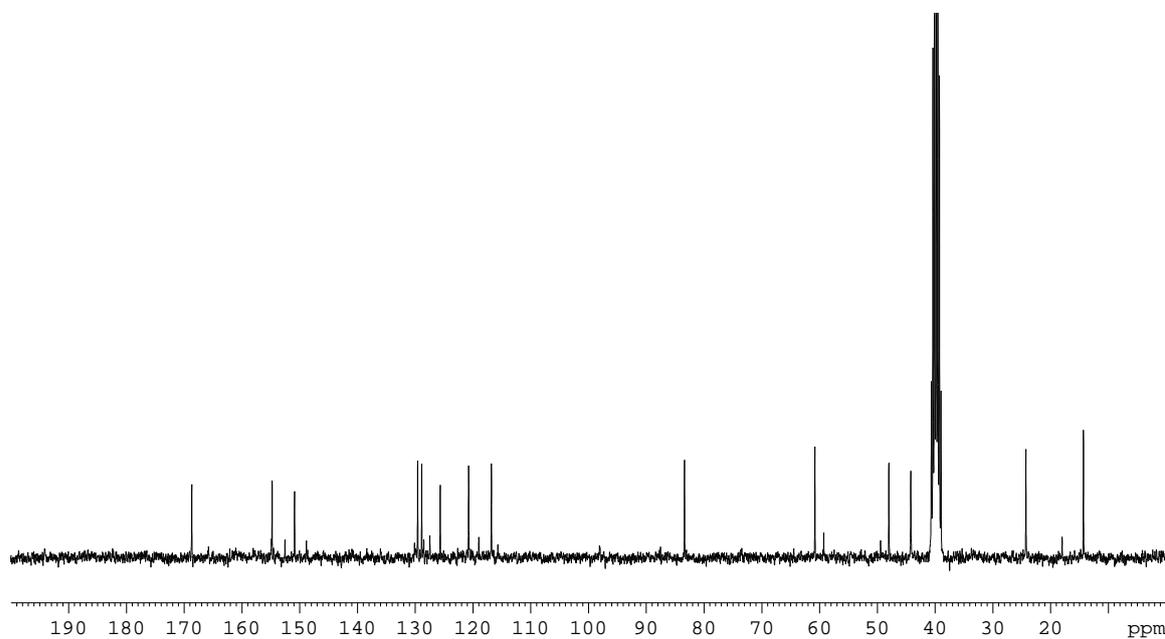
$^1\text{H}$ NMR (in  $\text{DMSO-}d_6$ ) spectrum of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**18b**, Table 3)



$^{13}\text{C}$ NMR (in  $\text{DMSO-}d_6$ ) spectrum of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**18b**, Table 3)



$^1\text{H}$ NMR (in  $\text{DMSO-}d_6$ ) spectrum of Ethyl 9-methyl-11-oxo-8-oxa-10,12-diazatricyclo[7.3.1.0<sup>2,7</sup>]trideca-2,4,6-triene-13-carboxylate (**20c**, Scheme S1)



$^{13}\text{C}$ NMR (in  $\text{DMSO-}d_6$ ) spectrum of Ethyl 9-methyl-11-oxo-8-oxa-10,12-diazatricyclo[7.3.1.0<sup>2,7</sup>]trideca-2,4,6-triene-13-carboxylate (**20c**, Scheme S1)