

# Supporting Information

for

## Multicomponent versus domino reactions: One-pot free-radical synthesis of $\beta$ -amino-ethers and $\beta$ -amino-alcohols

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Analytical data and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds **1a–p**

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**4-Methyl-N-(2-(tetrahydrofuran-2-yl)propan-2-yl)aniline (1a):** Purification by FCC (Hex:AcOEt 7:3) afforded a yellow oil (63% isolated yield). FTIR (liquid film)  $\nu_{\text{max}}$  3390, 2980, 2881, 1615, 15133, 1110, 811  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\text{CDCl}_3$   $\delta$  (ppm): 1.24-1.25 (m, 6H, 2CH<sub>3</sub>); 1.83-1.95 (m, 4H, 2CH<sub>2</sub>, Cyc), 2.28 (s, 3H, 1CH<sub>3</sub>), 3.62 (sbr, 1H, NH), 3.78-3.85 (m, 2H, 1CH<sub>2</sub>, Cyc), 3.89-3.95 (m, 1H, 1CH, Cyc), 6.78-6.80 (m, 2H, 2CH, Ar), 6.98-7.00 (m, 2H, 2CH, Ar);  $^{13}\text{C}$   $\text{CDCl}_3$   $\delta$  (ppm): 20.6, 23.7, 24.8, 26.4, 26.5, 56.7, 68.7, 86.1, 120.7, 129.2, 129.4, 144.2; GC/MS: 148 (100), 219 (3.3), 106 (6.7). HMRS calcd for C<sub>14</sub>H<sub>21</sub>NO: 219.1623; found 219.1627.

**4-Methyl-N-(1-(tetrahydrofuran-2-yl)cyclohexyl)aniline (1b):** Purification by FCC (Hex:CH<sub>2</sub>Cl<sub>2</sub> 5:5) afforded a brown oil (64% isolated yield). FTIR (liquid film)  $\nu_{\text{max}}$  2929, 2856, 1615, 1513, 1064, 811  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\text{CDCl}_3$   $\delta$  (ppm): 1.26-1.32 (m, 1H, 1CH, Cyc); 1.47-1.63 (m, 7 H, 7CH, Cyc), 1.76-1.91 (m, 6H, 6CH, Cyc), 2.24 (s, 3H, 1CH<sub>3</sub>), 3.73-3.84 (m, 2H, 1CH, Cyc), 3.97 (m, 1H, 1CH, Cyc), 6.77-6.79 (m, 2H, 2CH, Ar), 6.94-6.96 (m, 2H, 2CH, Ar);  $^{13}\text{C}$   $\text{CDCl}_3$   $\delta$  (ppm): 20.4, 21.4, 21.5, 25.8, 26.0, 26.3, 31.1, 32.8, 58.4, 68.2, 84.2, 119.0, 127.9, 129.3, 144.1; ESI-MS  $m/z$  260 [ $\text{M}^+$  + H], 282 [ $\text{M}^+$  + Na]; HMRS calcd for C<sub>17</sub>H<sub>25</sub>NO: 259.1936; found 259.1940

**4-Methyl-N-(2-(tetrahydrofuran-2-yl)pentan-2-yl)aniline (mixture 1:1 diastereoisomer A and B) (1c):** Purification by FCC (Hex:AcOEt 6:4) afforded a yellow oil (57% isolated yield). FTIR (liquid film)  $\nu_{\text{max}}$  3382, 2958, 2870, 1513, 1067, 809  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\text{CDCl}_3$   $\delta$  (ppm): 0.91 (t, 3H, 1 CH<sub>3</sub>); 0.93 (t, 6H, 2 CH<sub>3</sub>); 1.20 (s, 3H, 1 CH<sub>3</sub>), 1.37-1.51 (m, 4H, 2CH<sub>2</sub>), 1.58-1.65 (m, 3H, 1CH+1CH<sub>2</sub>), 1.69-1.77 (m, 1H, CH), 1.80-1.93 (m, 8H, 4CH<sub>2</sub>, Cyc), 2.26 (s, 6H, 2CH<sub>3</sub>), 3.75-3.83 (m, 2H, 2CH, Cyc), 3.86-3.94 (m, 4H, 4CH, Cyc), 6.72-6.74 (2m, 4H, 4CH, Ar), 6.96-6.98 (m, 4H, 4CH, Ar);  $^{13}\text{C}$   $\text{CDCl}_3$   $\delta$  (ppm): 14.8, 14.9, 17.1, 17.3, 20.6, 21.8, 22.0, 26.3, 26.3, 26.4, 26.5, 40.0, 40.3, 58.9, 59.0, 68.5, 68.7, 84.3, 84.9, 119.2, 119.5, 128.2, 128.5, 129.5, 144.3, 144.75; GC/MS: 176 (100), 247 (3.3), 106 (6.7). HMRS calcd for C<sub>16</sub>H<sub>25</sub>NO: 247.1936; found 247.1934

**N-(4-(tert-Butyl)-1-(tetrahydrofuran-2-yl)cyclohexyl)-4-methylaniline (1d):** Purification by FCC (Hex:CH<sub>2</sub>Cl<sub>2</sub> 5:5) afforded a white powder (49% isolated yield), mp 91-93°C. FTIR (liquid film)  $\nu_{\text{max}}$  3410, 2943, 2863, 1615, 1448, 1069, 810  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\text{CDCl}_3$   $\delta$  (ppm): 0.84 (s, 9H, tBu); 1.02 (dt, 1H, CH); 1.18-1.29 (m, 1H, CH); 1.31-1.42 (m, 2H, 2CH); 1.46-1.61 (m, 3H, 3CH); 1.74-1.89 (m, 5H, 5CH); 2.07-2.12 (m, 1H, 1CH); 2.24 (s, 3H, CH<sub>3</sub>), 3.72-3.81 (m, 2H, 2CH, Cyc), 3.90 (m, 1H, 1CH, Cyc), 6.77-6.79 (m, 2H, 2CH, Ar), 6.94-6.96 (m, 2H, 2CH, Ar);  $^{13}\text{C}$   $\text{CDCl}_3$   $\delta$  (ppm): 20.6, 22.0, 22.1, 26.2, 26.4, 27.7, 31.0, 32.6, 32.9, 48.1, 58.3, 68.4, 85.2, 118.4, 127.7, 129.5, 144.3; ESI-MS  $m/z$  316 [ $\text{M}^+$  + H], 338 [ $\text{M}^+$  + Na]; HMRS calcd for C<sub>21</sub>H<sub>33</sub>NO 315.2562; found 315.2560

**4-Methyl-N-(4-phenyl-1-(tetrahydrofuran-2-yl)cyclohexyl)aniline (1e):** Purification by FCC (Hex:CH<sub>2</sub>Cl<sub>2</sub> 6:4) afforded a white powder (40% isolated yield), mp 104-106°C. FTIR (liquid film)  $\nu_{\text{max}}$  2923, 2858, 1614, 1513, 1255, 757, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\text{CDCl}_3$   $\delta$  (ppm): 1.52-1.60 (m, 1H, 1CH, Cyc); 1.65-1.91 (m, 9H, 9 CH); 1.93-1.98 (m, 1 H, 1CH, Cyc), 2.08-2.14 (m, 1H, 1CH, Cyc), 2.22 (s, 3H, 1CH<sub>3</sub>), 2.52

(m, 1H, 1CH, Cyc), 3.70-3.81 (m, 2H, 1CH<sub>2</sub>, Cyc), 3.91 (m, 1H, 1CH, Cyc); 6.78-6.80 (m, 2H, 2CH, Ar), 6.93-6.95 (m, 2H, 2CH, Ar), 7.11-7.16 (m, 1H, CH Ar); 7.18-7.26 (m, 5H, 4CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 20.6, 26.3, 26.4, 28.9, 29.0, 31.2, 32.8, 44.4, 58.4, 68.4, 84.9, 118.9, 126.1, 127.0, 128.3, 128.4, 129.6, 144.2, 147.3; ESI-MS *m/z* 336 [M<sup>+</sup> + H], 358 [M<sup>+</sup> + Na]; HMRS calcd for C<sub>23</sub>H<sub>29</sub>NO: 335.2249; found 335.2253.

**4-Methoxy-N-(2-(tetrahydrofuran-2-yl)propan-2-yl)aniline (1f):** Purification by FCC (Hex:CH<sub>2</sub>Cl<sub>2</sub> 7:3) afforded a yellow oil (57% isolated yield). FTIR (liquid film) *v*<sub>max</sub> 2972, 2868, 1509, 1463, 1241, 1068, 1038, 527 cm<sup>-1</sup>; <sup>1</sup>H NMR CDCl<sub>3</sub> δ (ppm): 1.14 (s, 6H, 2CH<sub>3</sub>); 1.79-1.93 (m, 4 H, 2CH<sub>2</sub>, Cyc), 3.71-3.76 (m, 1H, CH, Cyc), 3.74 (s, 3H, OCH<sub>3</sub>), 3.76-3.81 (m, 1H, CH, Cyc), 3.85-3.91 (m, 1H, CH, Cyc); 6.73-6.75 (m, 2H, 2CH, Ar), 6.83-6.85 (m, 2H, 2CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 23.4, 24.8, 26.4, 26.6, 55.6, 57.1, 68.7, 85.8, 114.2, 123.9, 139.5, 154.8; ESI-MS *m/z* 236 [M<sup>+</sup> + H], 258 [M<sup>+</sup> + Na]; HMRS calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>2</sub>: 235.1572; found 235.1575.

**4-Chloro-N-(2-(tetrahydrofuran-2-yl)propan-2-yl)aniline (1g):** Purification by FCC (Hex:AcOEt 8:2) afforded a light brown powder (69% isolated yield), mp 48-50°C. FTIR (liquid film) *v*<sub>max</sub> 3381, 2973, 2869, 1597, 1491, 1069, 817 cm<sup>-1</sup>; <sup>1</sup>H NMR CDCl<sub>3</sub> δ (ppm): 1.24 (s, 3H, CH<sub>3</sub>); 1.26 (s, 3H, CH<sub>3</sub>); 1.77-1.93 (m, 4 H, 2CH<sub>2</sub>, Cyc), 3.74-3.82 (m, 2H, 2CH, Cyc), 3.87-3.92 (m, 1H, 1CH, Cyc), 6.74-6.76 (m, 2H, 2CH, Ar), 7.08-7.11 (m, 2H, 2CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 23.5, 24.7, 26.3, 26.5, 56.7, 68.8, 86.1, 120.4, 124.2, 128.8, 145.5; ESI-MS *m/z* 240 [M<sup>+</sup> + H], 262 [M<sup>+</sup> + Na]; HMRS calcd for C<sub>13</sub>H<sub>18</sub>ClNO (<sup>35</sup>Cl): 239.1077; found 239.1077.

**N-(2-(1,3-Dioxolan-2-yl)propan-2-yl)-4-methylaniline (1h):** Purification by FCC (Hex:AcOEt 7:3) afforded a yellow oil (18% isolated yield). FTIR (liquid film) *v*<sub>max</sub> 3393, 2977, 2879, 1615, 1513, 1111, 810 cm<sup>-1</sup>; <sup>1</sup>H NMR CDCl<sub>3</sub> δ (ppm): 1.25 (s, 6H, 2CH<sub>3</sub>); 2.26 (s, 3H, CH<sub>3</sub>), 3.89-4.02 (m, 4H, 2CH<sub>2</sub>, Cyc), 4.75 (s, 1H, 1CH, Cyc), 6.79-6.81 (m, 2H, 2CH, Ar), 6.97-6.99 (m, 2H, 2CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 20.7, 22.9, 57.1, 65.7, 108.0, 113.3, 121.4, 129.4, 130.1, 143.4; GC/MS: 148 (100), 221 (2.8), 106 (5.7). HMRS calcd for C<sub>13</sub>H<sub>19</sub>NO<sub>2</sub>: 221.1416; found 221.1413

**N-(2-(1,4-Dioxan-2-yl)propan-2-yl)-4-methylaniline (1i):** Purification by FCC (Hex:AcOEt 75:25) afforded a yellow oil (30% isolated yield). FTIR (liquid film) *v*<sub>max</sub> 3379, 2972, 2855, 1513, 1121, 908 cm<sup>-1</sup>; <sup>1</sup>H NMR CDCl<sub>3</sub> δ (ppm): 1.20-1.21 (m, 6H, 2CH<sub>3</sub>), 2.27 (s, 3H, 1CH<sub>3</sub>), 3.46-3.60 (m, 3H, 1CH<sub>2</sub>, 1CH, Cyc), 3.66-3.75 (m, 2H, 1CH<sub>2</sub>, Cyc), 3.84-3.87 (m, 2H, 1CH<sub>2</sub>, Cyc), 6.76-6.78 (m, 2H, 2CH, Ar), 6.98-7.01 (m, 2H, 2CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 20.7, 24.0, 24.6, 55.9, 66.5, 67.4, 67.6, 80.6, 121.5, 129.4, 130.1, 143.3; GC/MS: 148 (100), 235 (2.3), 106 (6.7). HMRS calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>2</sub>: 235.1572; found 235.1582.

**N-(3-Ethoxy-2-methylbutan-2-yl)-4-methylaniline (1j):** Purification by FCC (Hex:AcOEt 9:1) afforded a yellow oil (25% isolated yield). FTIR (liquid film) *v*<sub>max</sub> 3385, 2975, 2870, 1513, 1111, 816 cm<sup>-1</sup>; <sup>1</sup>H NMR CDCl<sub>3</sub> δ (ppm): 1.13-1.14 (d, 3H, 1CH<sub>3</sub>, J=6.2 Hz); 1.19 (s, 3H, 1CH<sub>3</sub>), 1.22 (t, 3H, CH<sub>3</sub>, J=6.9 Hz), 1.23 (s, 3H, 1CH<sub>3</sub>), 2.26 (s, 3H, 1CH<sub>3</sub>), 3.31 (dd, 1H, 2CH, J=6.2 Hz), 3.35 (tt, 1H, 1CH<sub>2</sub>, J=6.9 Hz), 3.64 (tt, 1H,

1CH<sub>2</sub>, J=6.9 Hz), 6.74-6.76 (m, 2H, 2CH, Ar), 6.96-6.99 (m, 2H, 2CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 14.0, 15.8, 20.6, 23.0, 25.0, 57.9, 64.9, 80.8, 120.5, 129.1, 129.4, 144.3; GC/MS: 148 (100), 221 (0.9), 106 (4.5). HMRS calcd for C<sub>14</sub>H<sub>23</sub>NO: 221.1780; found 221.1792.

**2-Methyl-2-(*p*-tolylamino)propa-1-ol (1k):** characterization is reported in literature [27]

**3-Methyl-3-(*p*-tolylamino)butan-2-ol (1l):** Purification by FCC (Hex:AcOEt 7:3) afforded a pail liquid (64% isolated yield). FTIR (liquid film) v<sub>max</sub> 1903, 1611, 1436, 1041, 831, 540 cm<sup>-1</sup>; <sup>1</sup>H NMR CDCl<sub>3</sub> δ (ppm): 1.13 (s, 3H, CH<sub>3</sub>); 1.16 (s, 3H, CH<sub>3</sub>); 1.19 (d, 3H, 1CH<sub>3</sub>, J=6.5Hz), 2.27 (s, 3H, 1CH<sub>3</sub>), 3.80-3.85 (q, 1H, 1CH, J= 6.5Hz), 6.76-6.78 (m, 2H, 2CH, Ar), 6.99-7.01 (m, 2H, 2CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 17.0, 20.5, 22.0, 23.7, 58.9, 72.1, 121.5, 129.4, 130.8, 142.4; GC/MS: 148 (100), 193 (3), 106 (6); HMRS calcd for C<sub>12</sub>H<sub>19</sub>NO 193.1467; found 193.1468.

**1-(1-(*p*-Tolylamino)cyclohexyl)ethanol (1m):** Purification by FCC (Hex:AcOEt 9:1) afforded a pale liquid (75% isolated yield). FTIR (liquid film) v<sub>max</sub> 3407, 2931, 2858, 1615, 1514, 1247, 809 cm<sup>-1</sup>; <sup>1</sup>H NMR DMSO δ (ppm): 1.01 (d, 3H, 1CH<sub>3</sub>, J=6.4Hz), 1.13-1.18 (m, 1H, CH Cyc), 1.41-1.55 (m, 7H, 5CH Cyc); 1.70-1.73 (m, 1H, CH Cyc); 1.86-1.89 (m, 1H, CH Cyc); 2.13 (s, 3H, 1CH<sub>3</sub>), 3.82 (q, 1H, 1CH, J= 6.4Hz), 4.28 (sbr, 1H, NH), 4.33 (sbr, 1H, OH); 6.68-6.70 (m, 2H, 2CH, Ar), 6.82-6.84 (m, 2H, 2CH, Ar); <sup>13</sup>C DMSO δ (ppm): 17.2, 19.8, 20.8, 20.9, 25.6, 28.9, 30.3, 58.6, 69.7, 116.3, 124.5, 128.7, 144.8; GC/MS: 188 (100), 233 (2), 106 (8); HMRS calcd for C<sub>15</sub>H<sub>23</sub>NO: 233.1780; found 233.1780.

**3-Methyl-3-(*p*-tolylamino)hexan-2-ol (1n):** two isomers mixture 50/50; purification by FCC (Hex:AcOEt 8:2) afforded an oil (41% isolated yield). FTIR (liquid film) v<sub>max</sub> 3378, 2958, 2871, 1615, 1514, 1455, 1247, 1111, 812 cm<sup>-1</sup>; <sup>1</sup>H NMR CDCl<sub>3</sub> δ (ppm): 0.83 (t, 3H, CH<sub>3</sub>); 0.96 (t, 3H, CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>), 1.11 (s, 3H, CH<sub>3</sub>), 1.19 (d, 3H, CH<sub>3</sub>), 1.20 (d, 3H, CH<sub>3</sub>), 1.26-1.70 (m, 8H, 4CH<sub>2</sub>), 2.26 (s, 6H, 2 CH<sub>3</sub>), 3.90-3.95 (m, 2H, 2CH), 6.70-6.75 (m, 4H, 4CH, Ar), 6.97-7.00 (m, 4H, 4CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 14.5, 14.8, 16.4, 16.7, 16.9, 17.0, 20.1, 20.4, 20.4, 21.3, 3.75, 3.80, 60.4, 61.2, 70.8, 72.2, 119.3, 120.2, 129.3, 129.5, 129.5, 129.8, 143.2, 143.3; GC/MS: 221 (3), 176 (100), 160 (4), 146 (8), 134 (2), 106 (8). HMRS calcd for C<sub>14</sub>H<sub>23</sub>NO: 221.17797; found 221.17811.

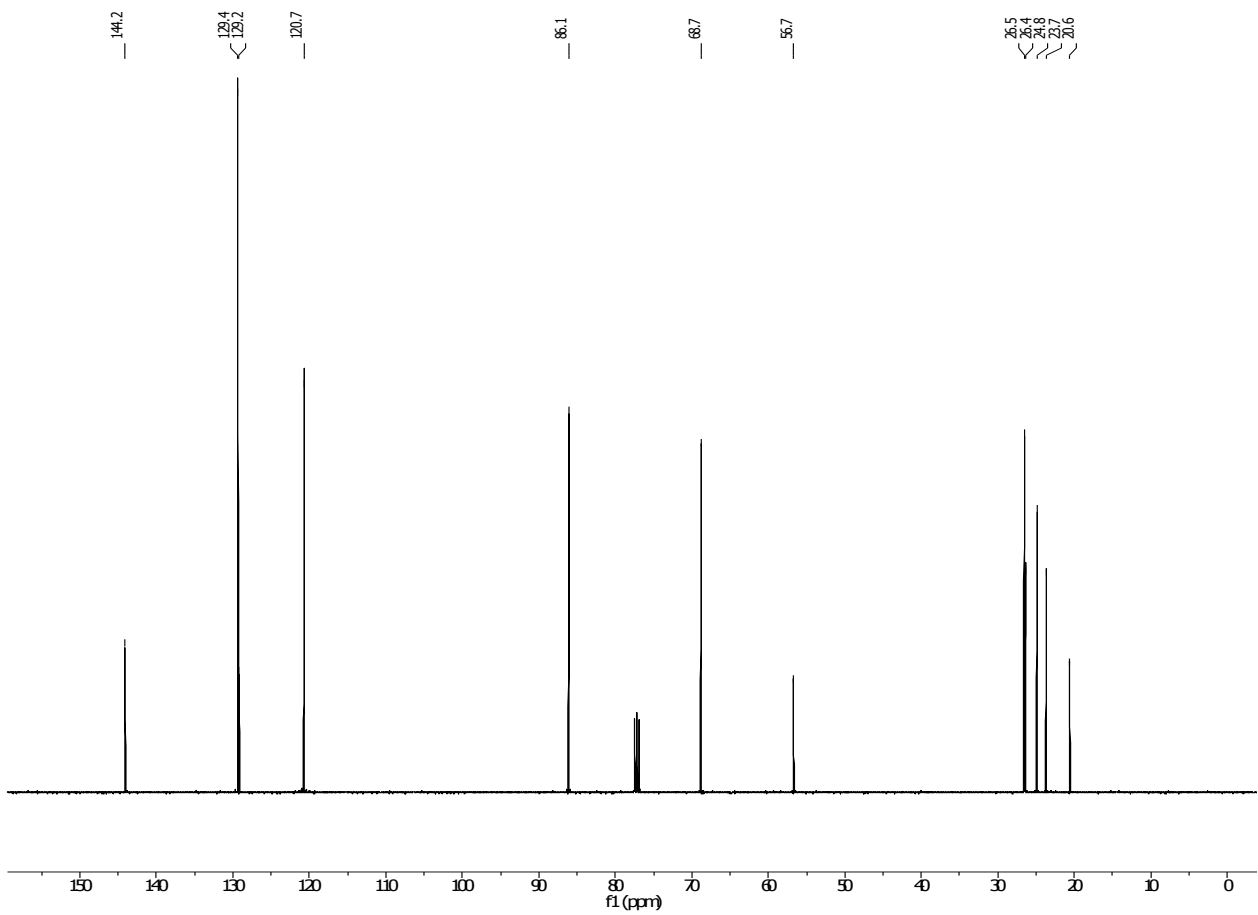
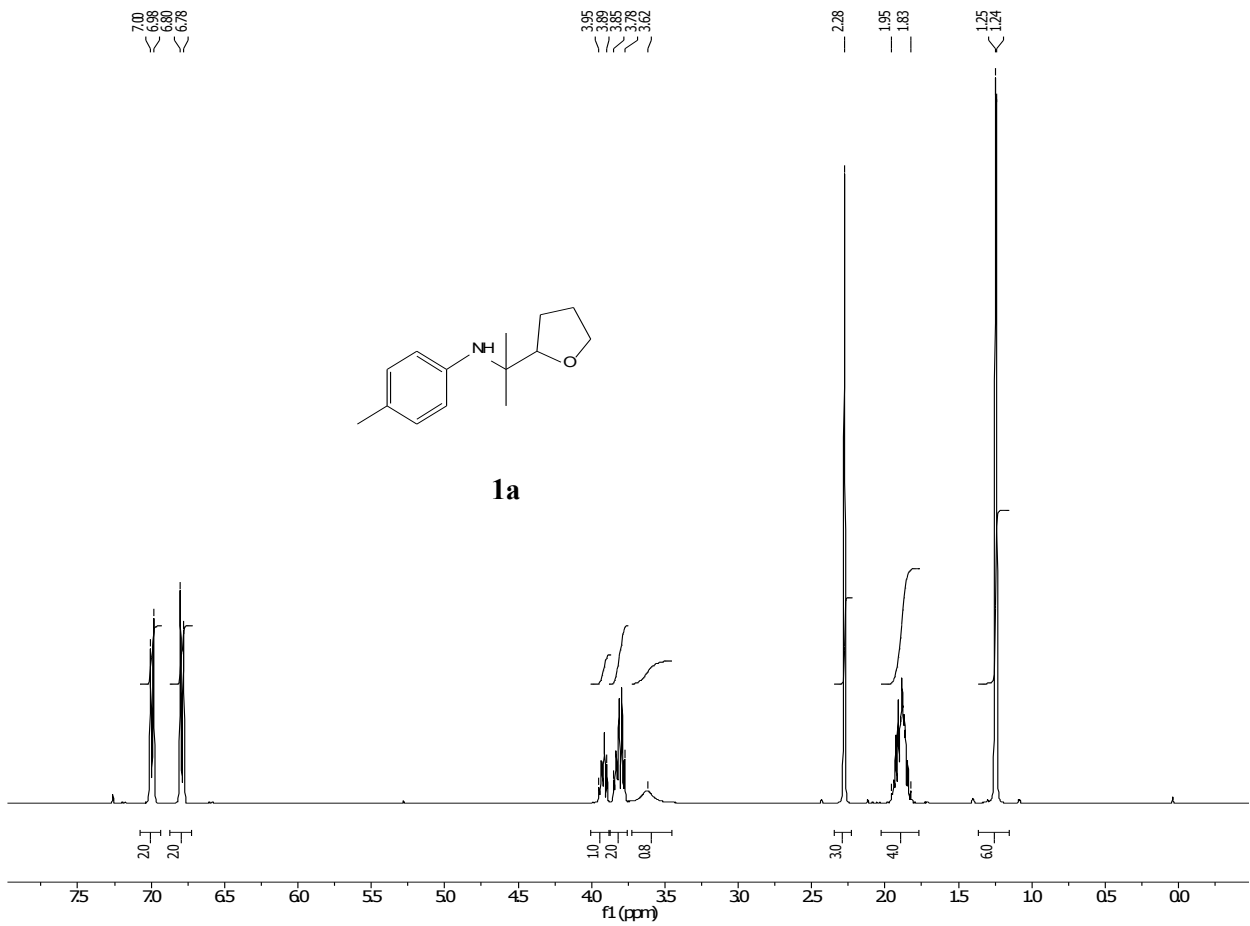
**2-Methyl-2-(*p*-tolylamino)pentan-3-ol (1o):** Purification by FCC (Hex:AcOEt 9:1) afforded white crystals (61% isolated yield). FTIR (liquid film) v<sub>max</sub> 3296, 2963, 2929, 2359, 1513, 1192, 830 cm<sup>-1</sup>; <sup>1</sup>H NMR CDCl<sub>3</sub> δ (ppm): 1.08 (t, 3H, 1CH<sub>3</sub>), 1.13 (s, 3H, 1CH<sub>3</sub>), 1.14 (s, 3H, 1CH<sub>3</sub>), 1.39 (m, 1H, CH), 1.60 (m, 1H, CH); 3.50 (dd, 1H, CH); 6.76-6.78 (m, 2H, 2CH, Ar), 7.00-7.02 (m, 2H, 2CH, Ar); <sup>13</sup>C CDCl<sub>3</sub> δ (ppm): 11.9, 20.6, 22.8, 23.9, 24.3, 58.7, 78.1, 121.4, 129.5, 130.7, 142.6; GC/MS: 148 (100), 207 (1.3), 106 (6.7); HMRS calcd for C<sub>13</sub>H<sub>21</sub>NO: 207.1623; found 207.1645.

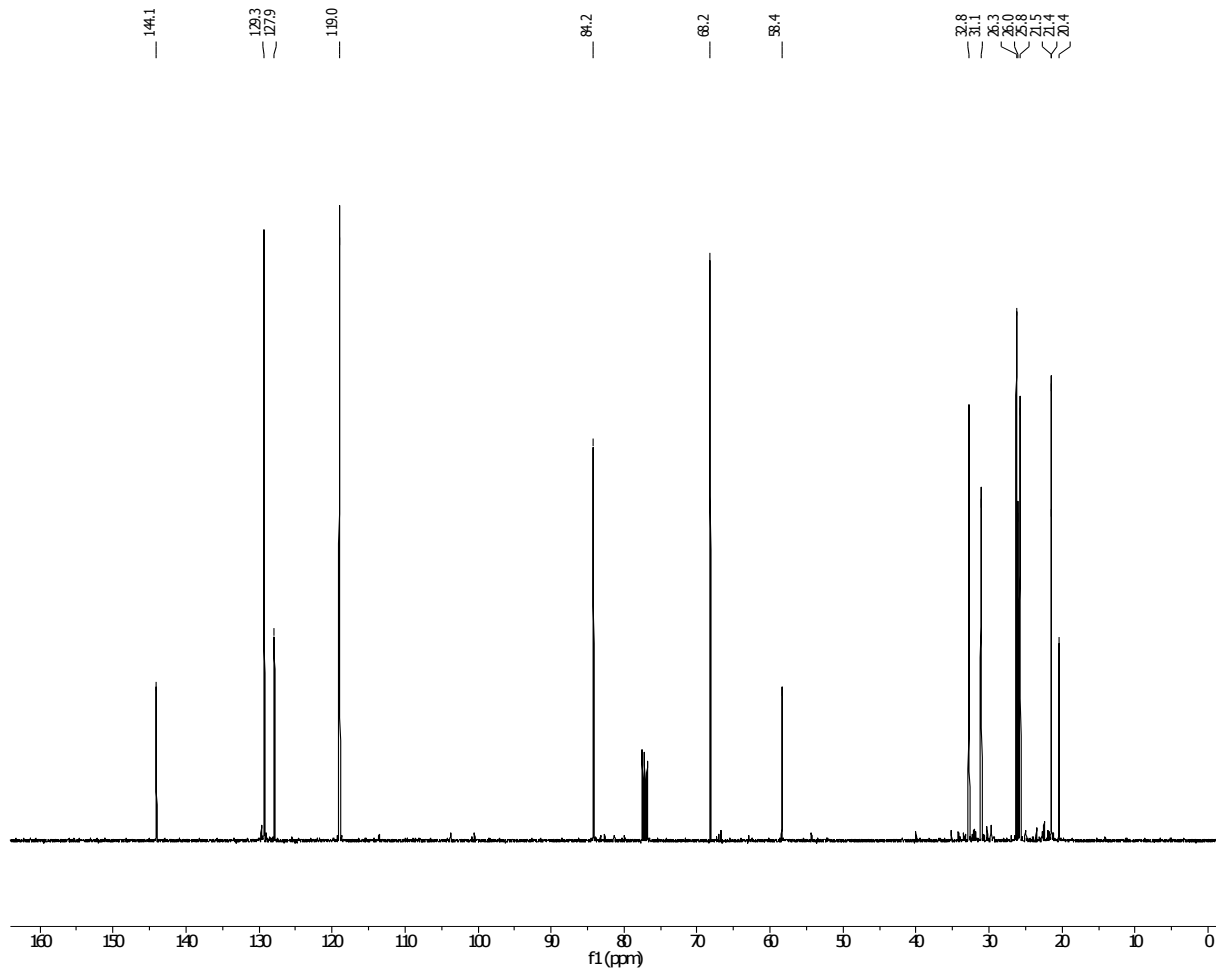
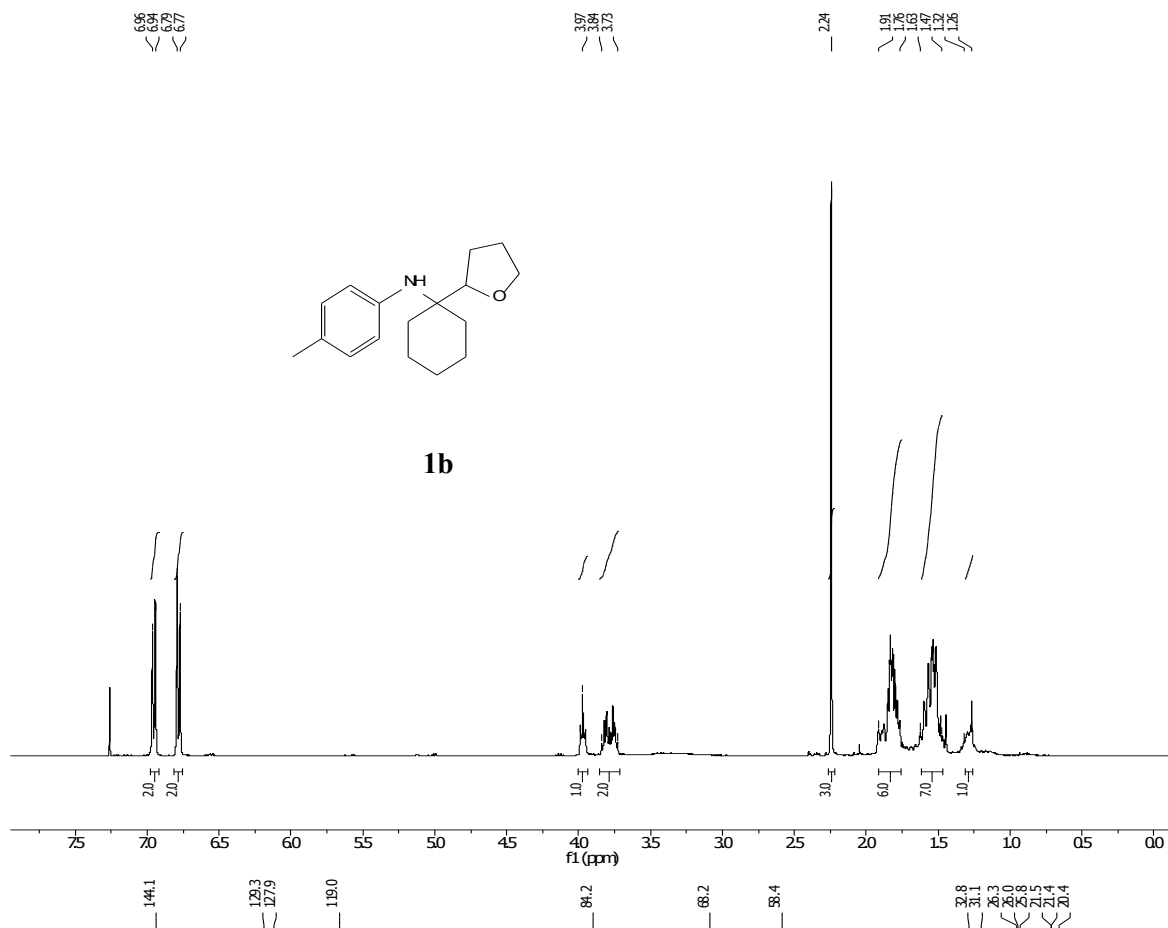
**1-(1-(*p*-Tolylamino)cyclohexyl)ethanol (1p):** Purification by FCC (Hex:AcOEt 9:1) afforded a pail liquid (60% isolated yield). FTIR (liquid film) v<sub>max</sub> 3407, 2931, 2858, 1615, 1514, 1247, 809 cm<sup>-1</sup>; <sup>1</sup>H NMR DMSO δ (ppm): 1.01 (d, 3H, 1CH<sub>3</sub>, J=6.4Hz), 1.13-1.18 (m, 1H, CH Cyc), 1.41-1.55 (m, 7H, 5CH Cyc);

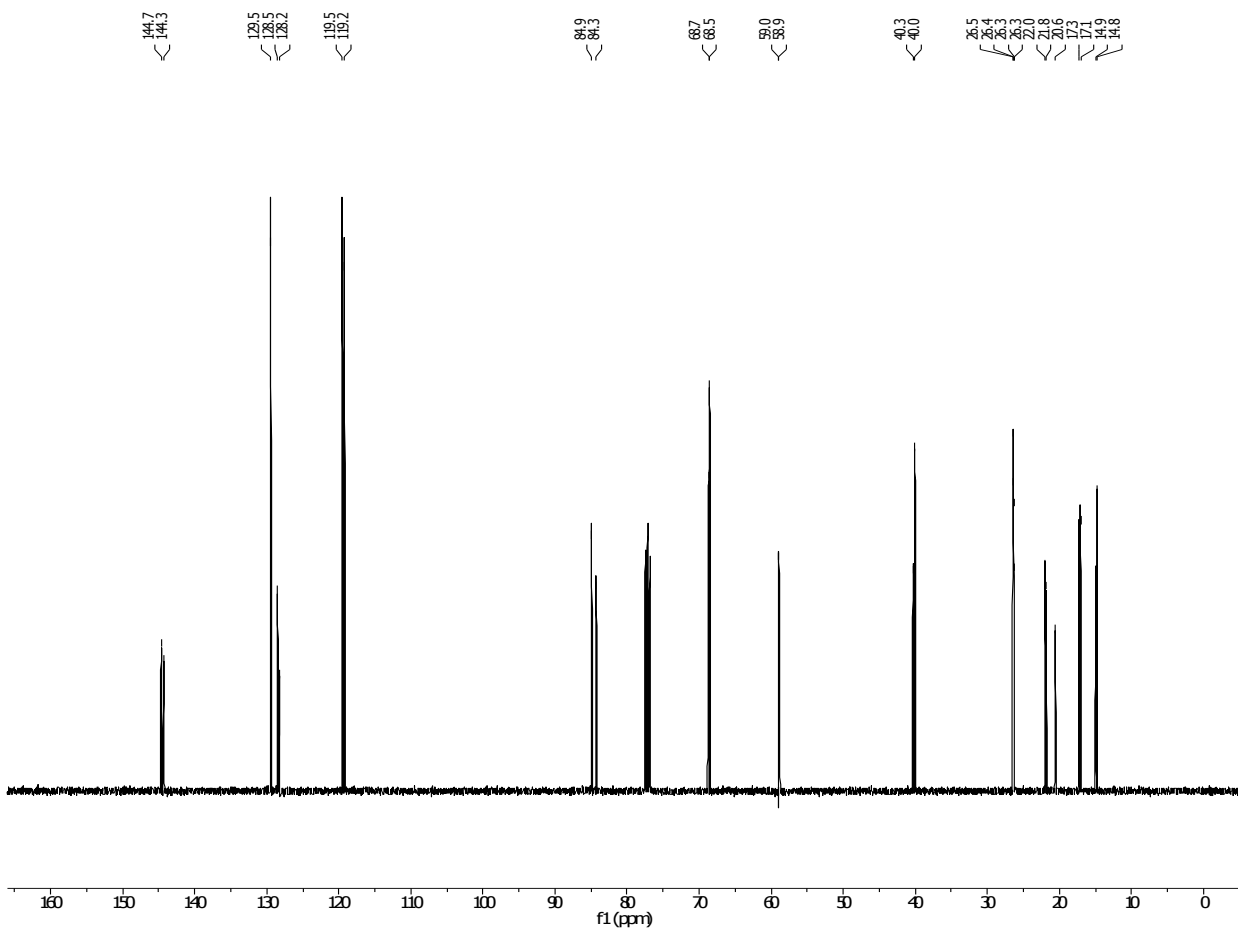
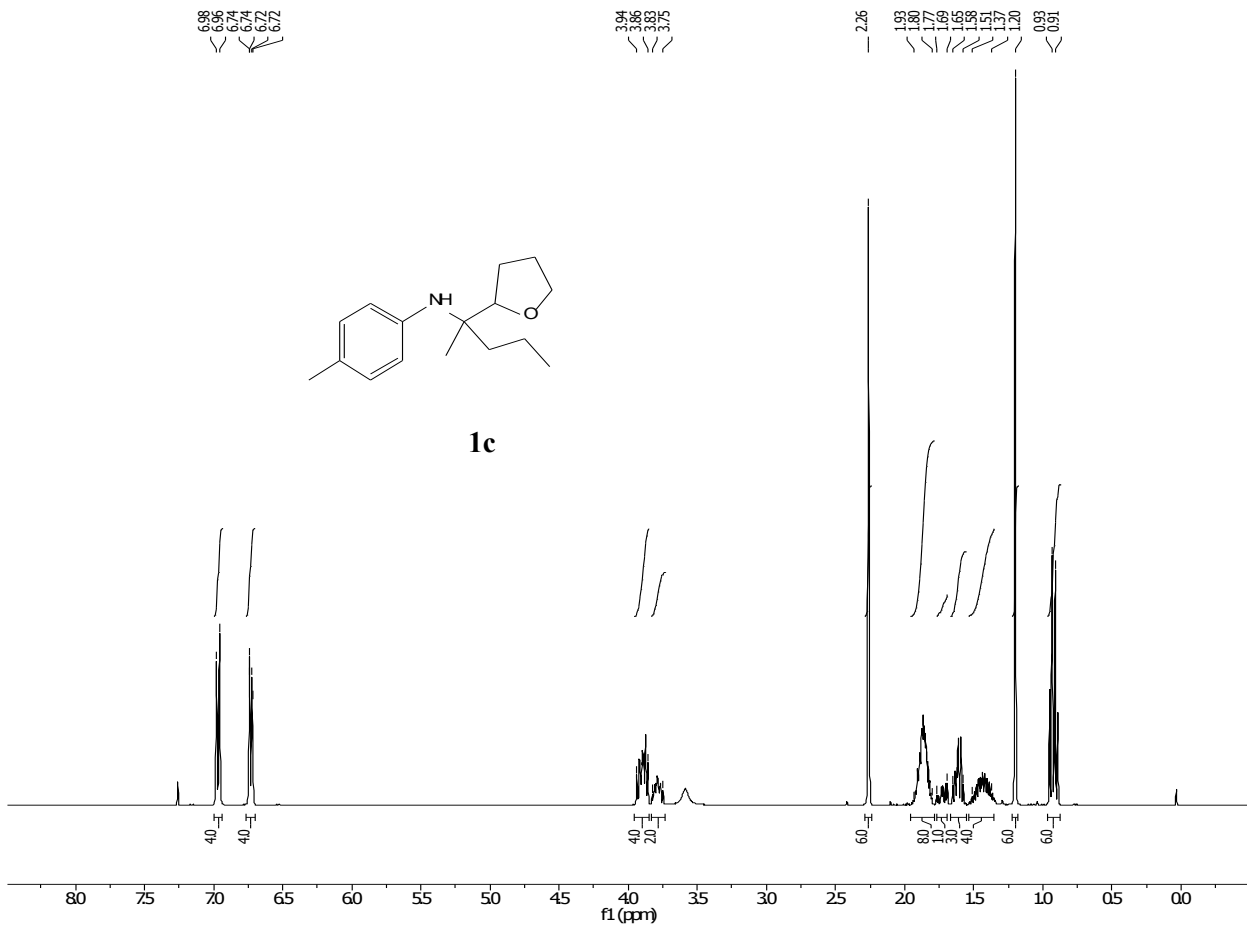
1.70-1.73 (m, 1H, CH Cyc); 1.86-1.89 (m, 1H, CH Cyc); 2.13 (s, 3H, 1CH<sub>3</sub>), 3.82 (q, 1H, 1CH, J= 6.4Hz), 4.28 (sbr, 1H, NH), 4.33 (sbr, 1H, OH); 6.68-6.70 (m, 2H, 2CH, Ar), 6.82-6.84 (m, 2H, 2CH, Ar); <sup>13</sup>C DMSO δ (ppm): 17.2, 19.8, 20.8, 20.9, 25.6, 28.9, 30.3, 58.6, 69.7, 116.3, 124.5, 128.7, 144.8; GC/MS: 188 (100), 233 (2), 106 (8); HMRS calcd for C<sub>15</sub>H<sub>23</sub>NO: 233.1780; found 233.1780.

**4-(Tetrahydrofuran-2-yl)-4-(*p*-tolylamino)butan-1-ol (2a):** characterization is reported in literature [30].

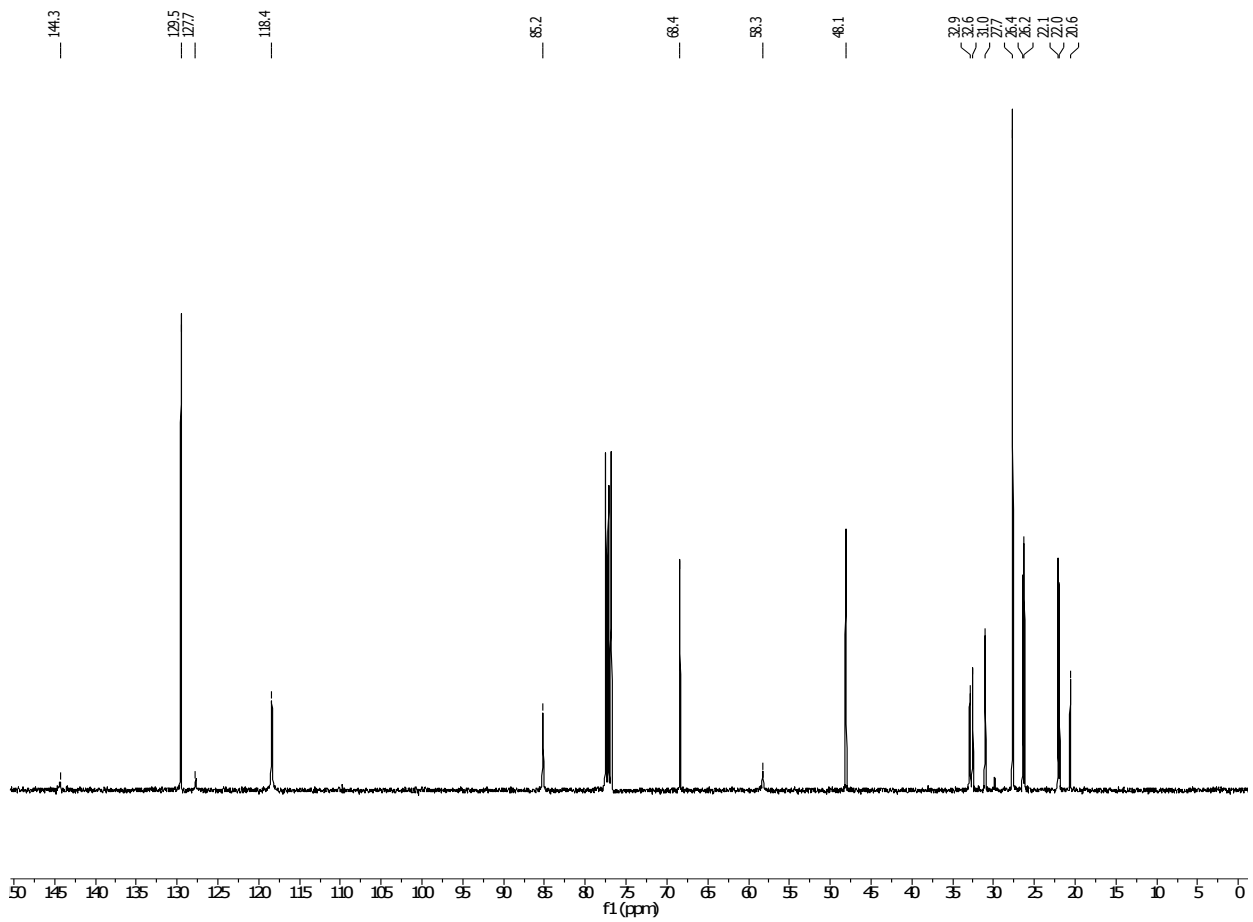
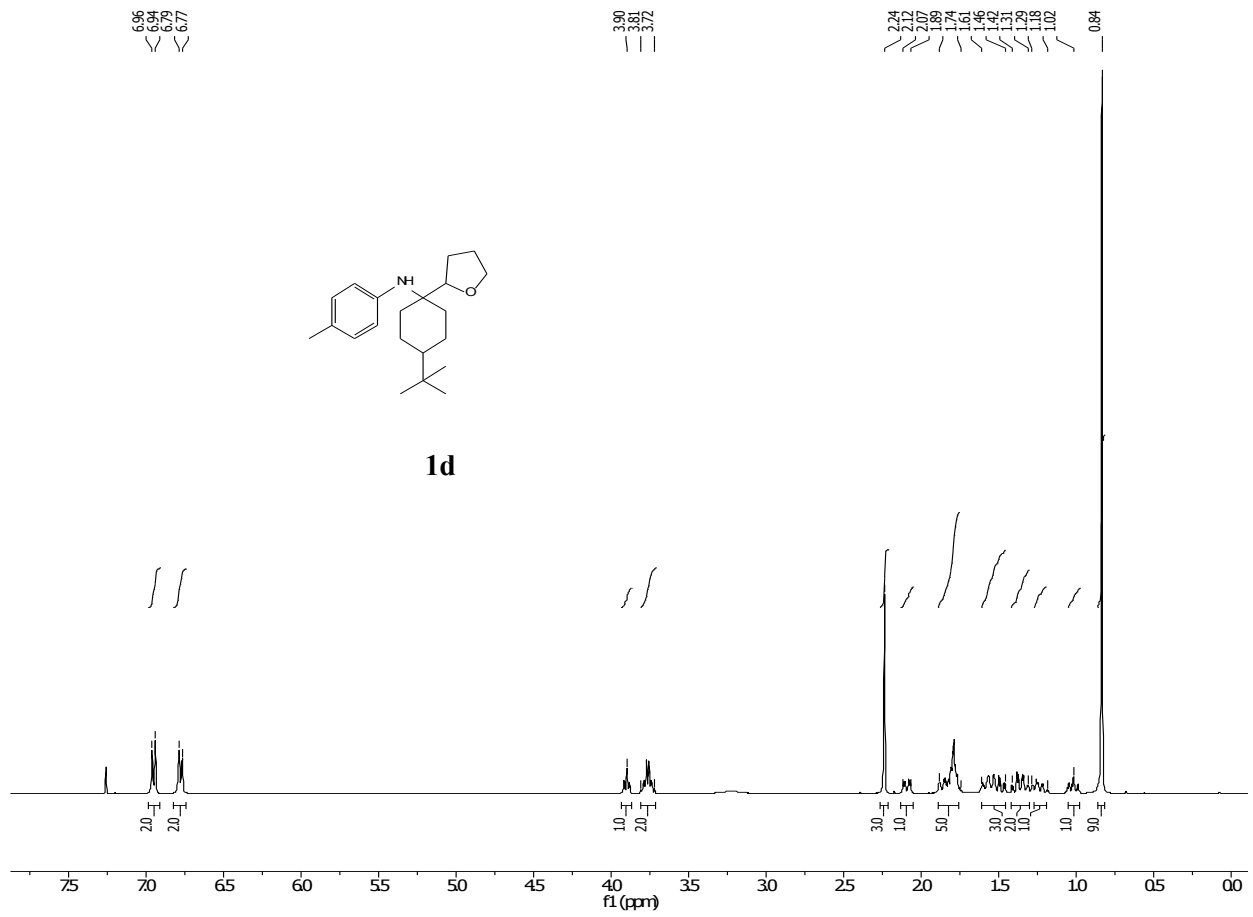
**3-(*p*-Tolylamino)butan-2-ol (2b):** characterization is reported in literature [29].

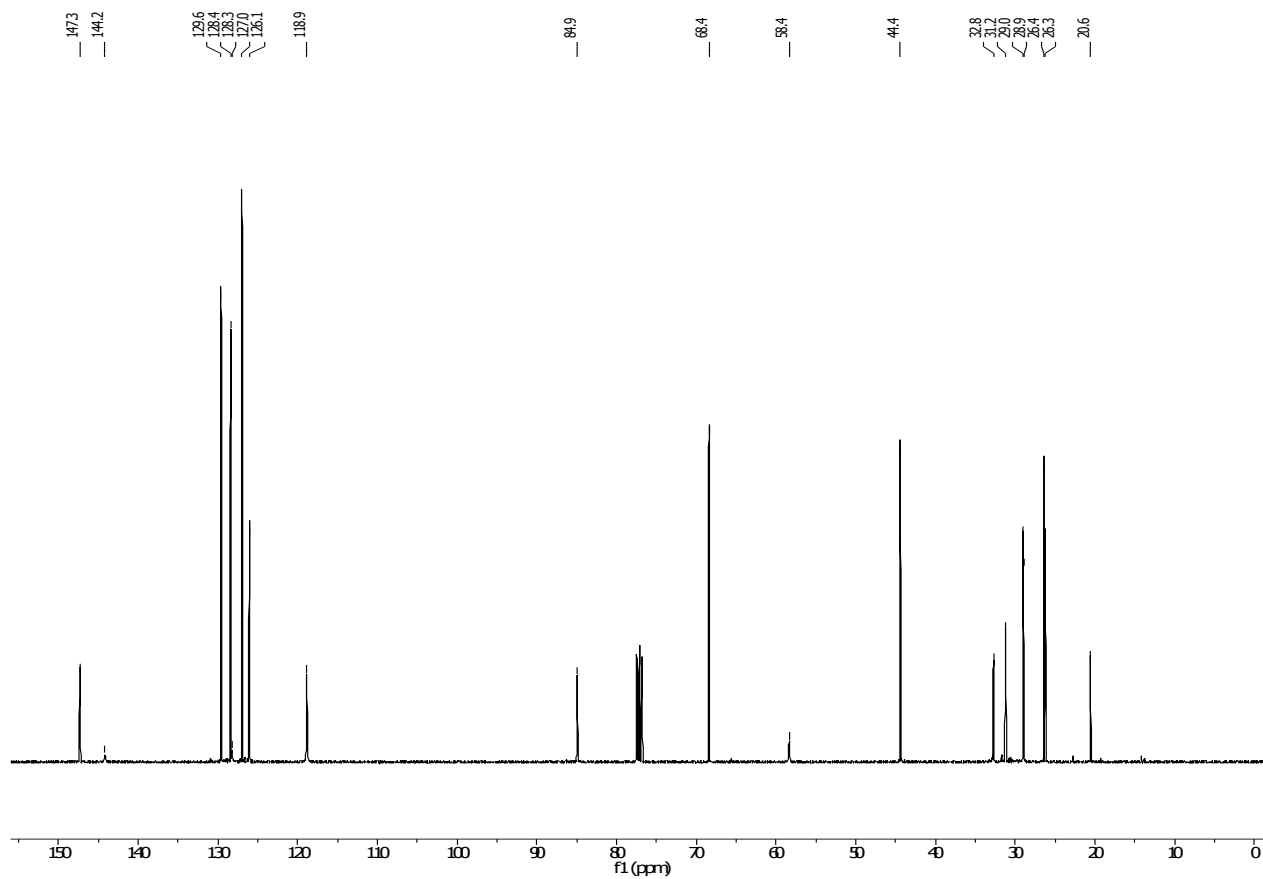
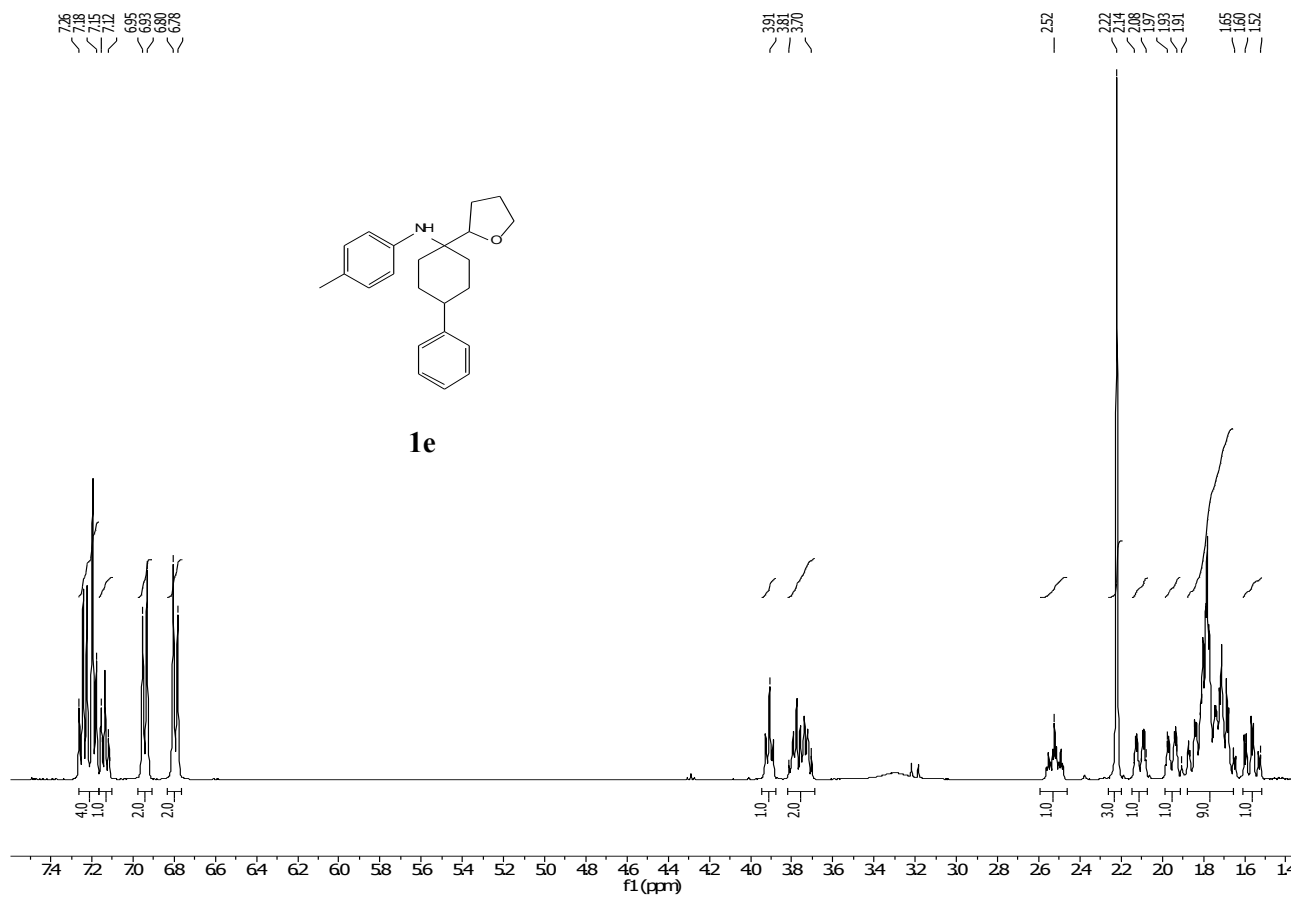


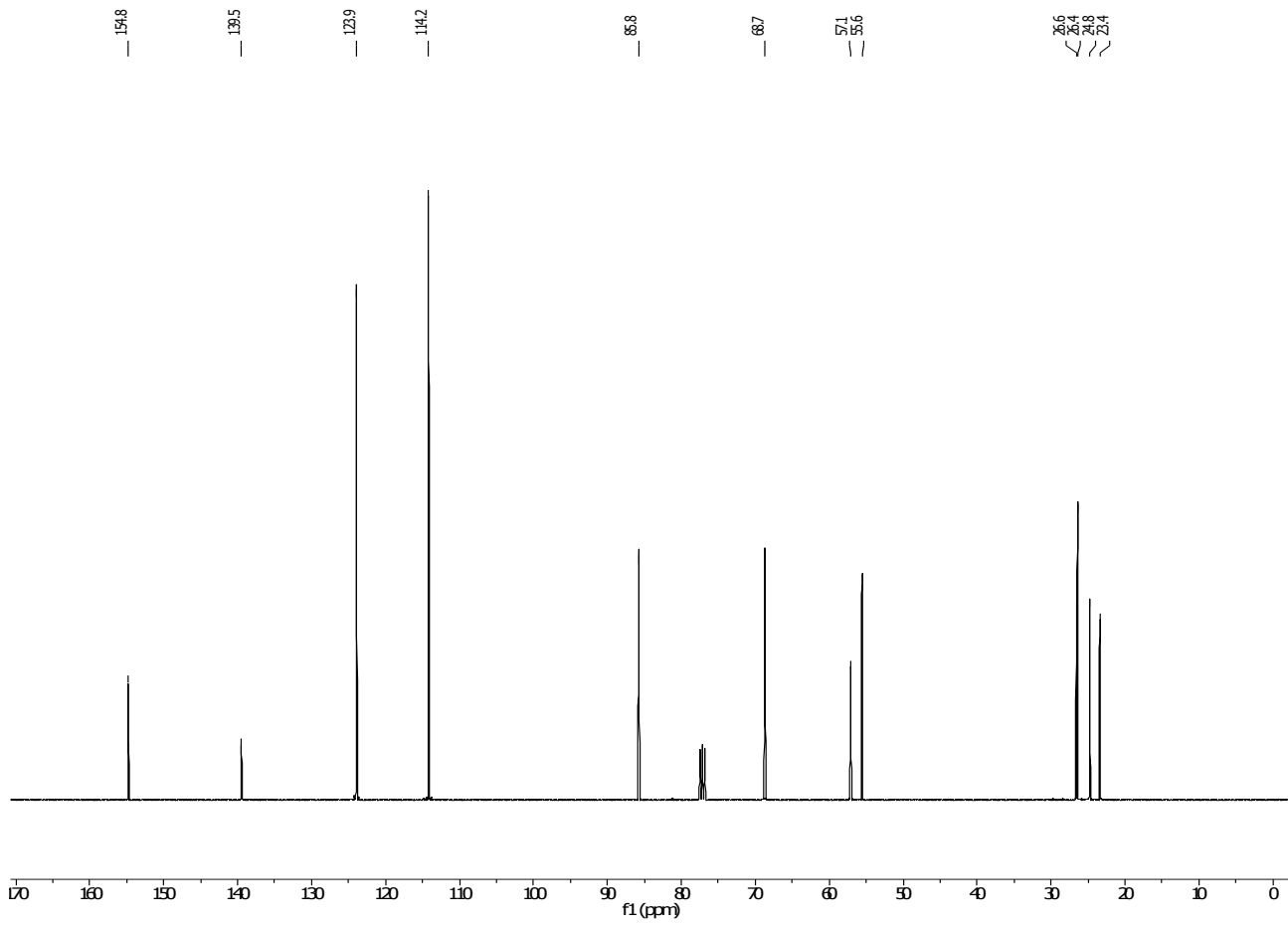
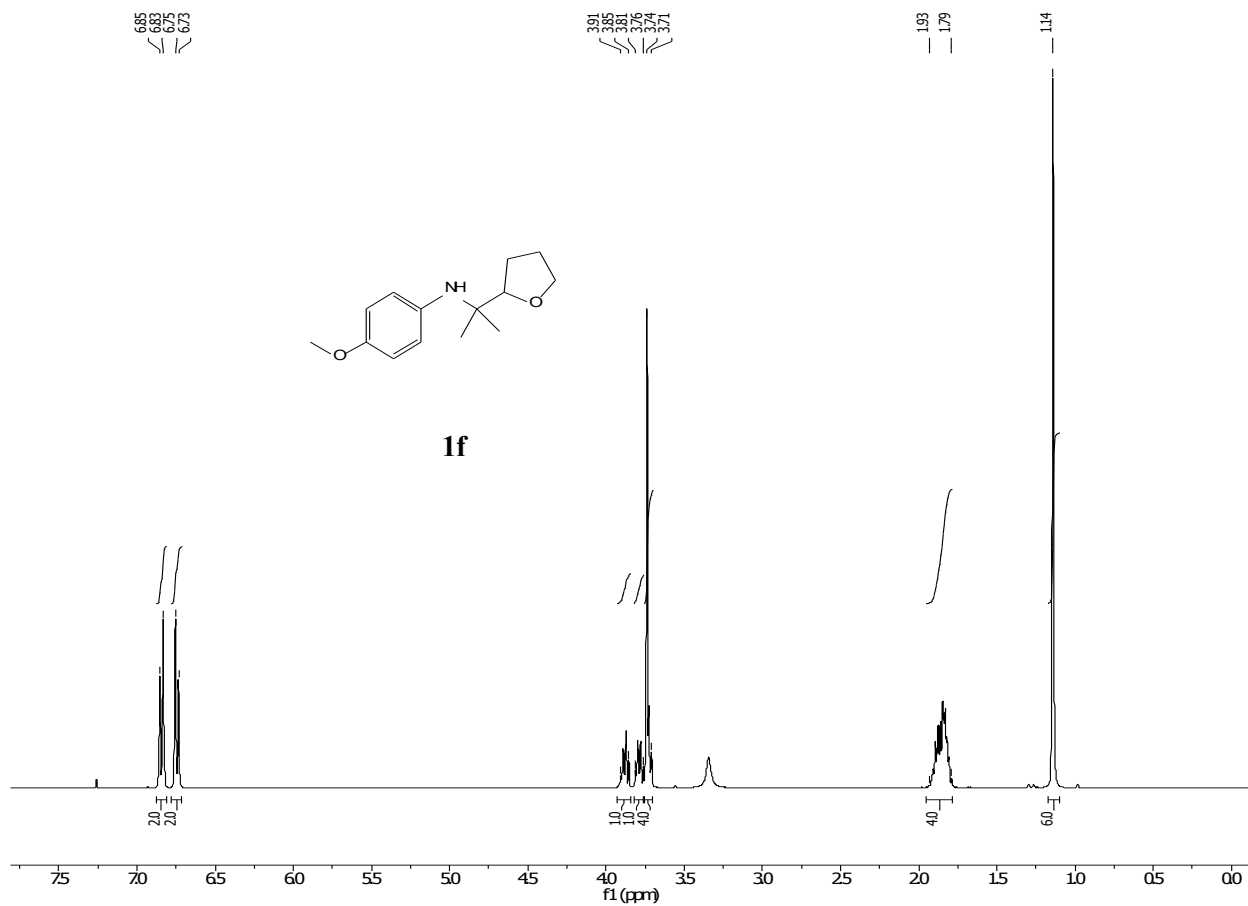


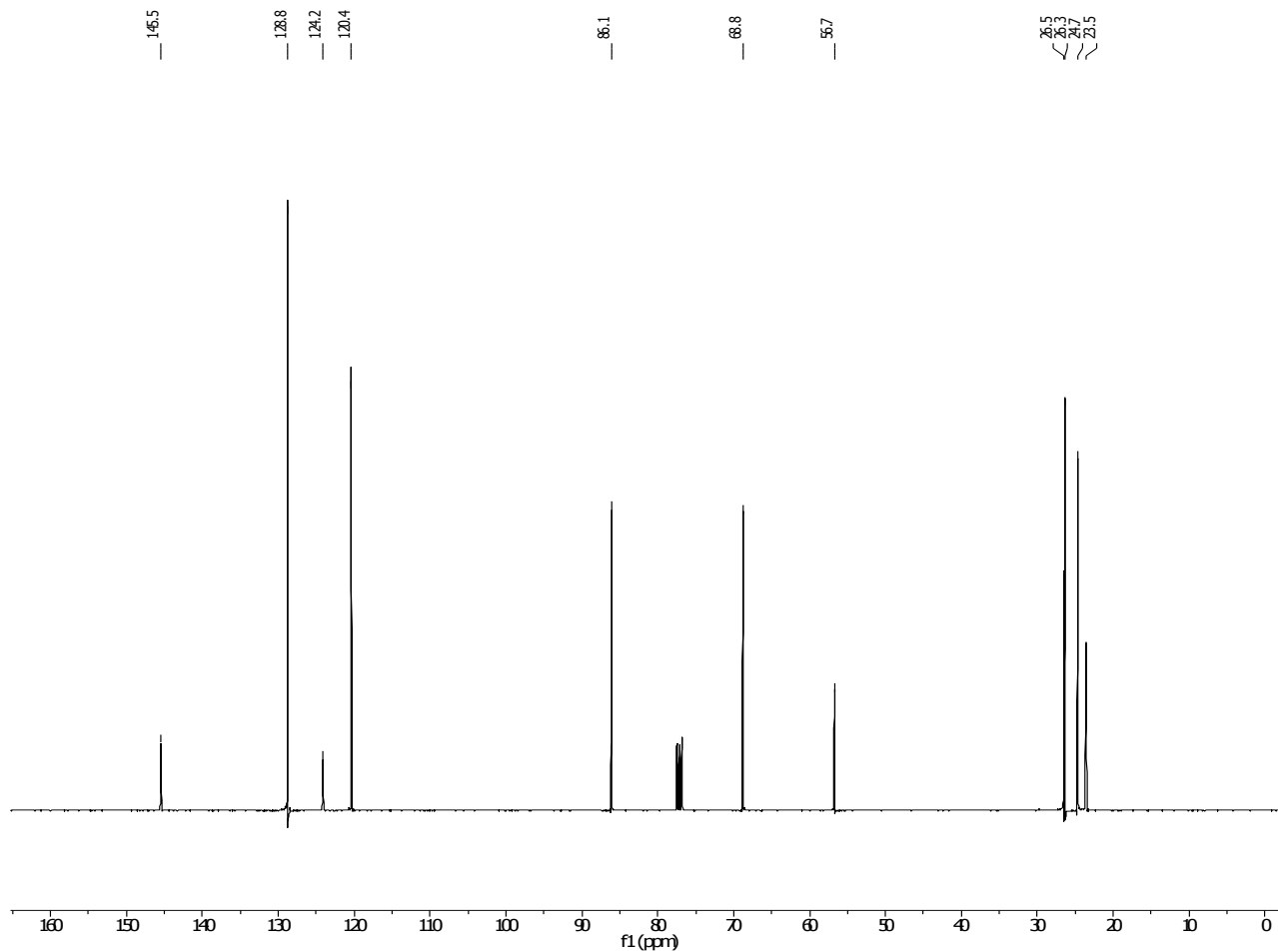
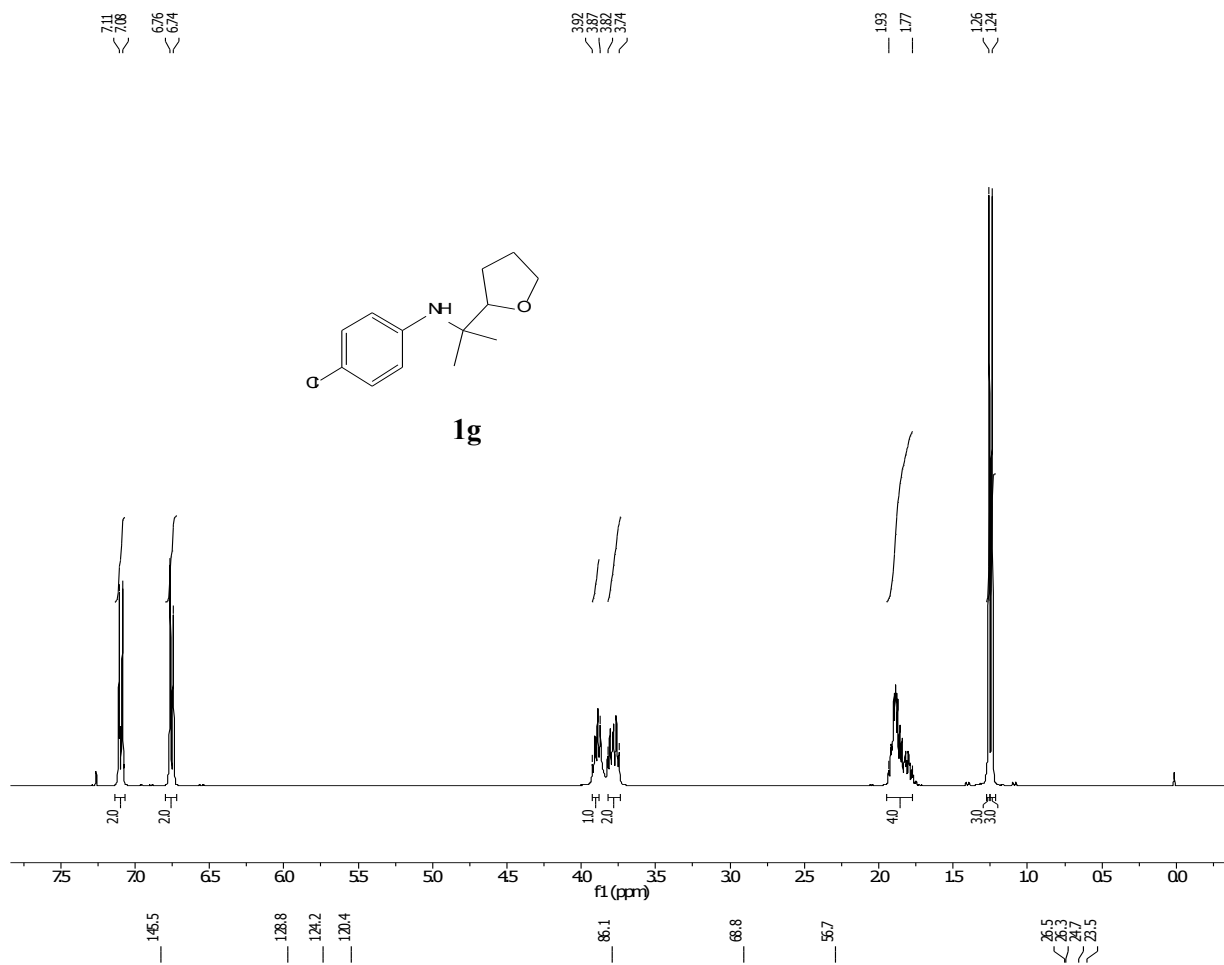


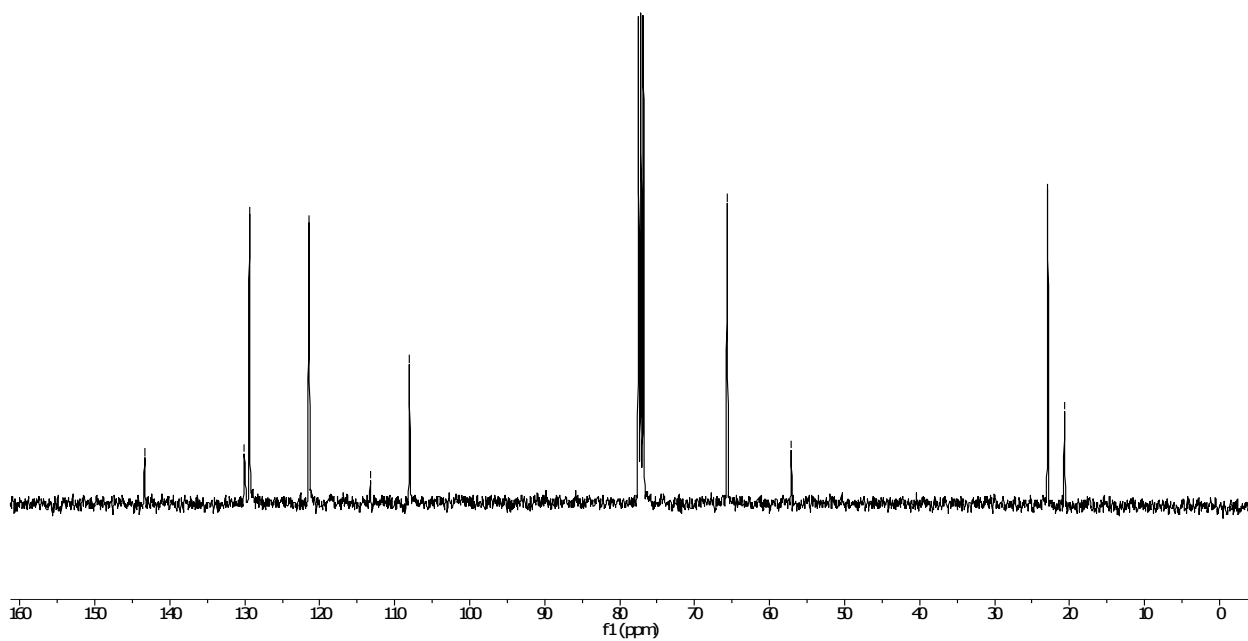
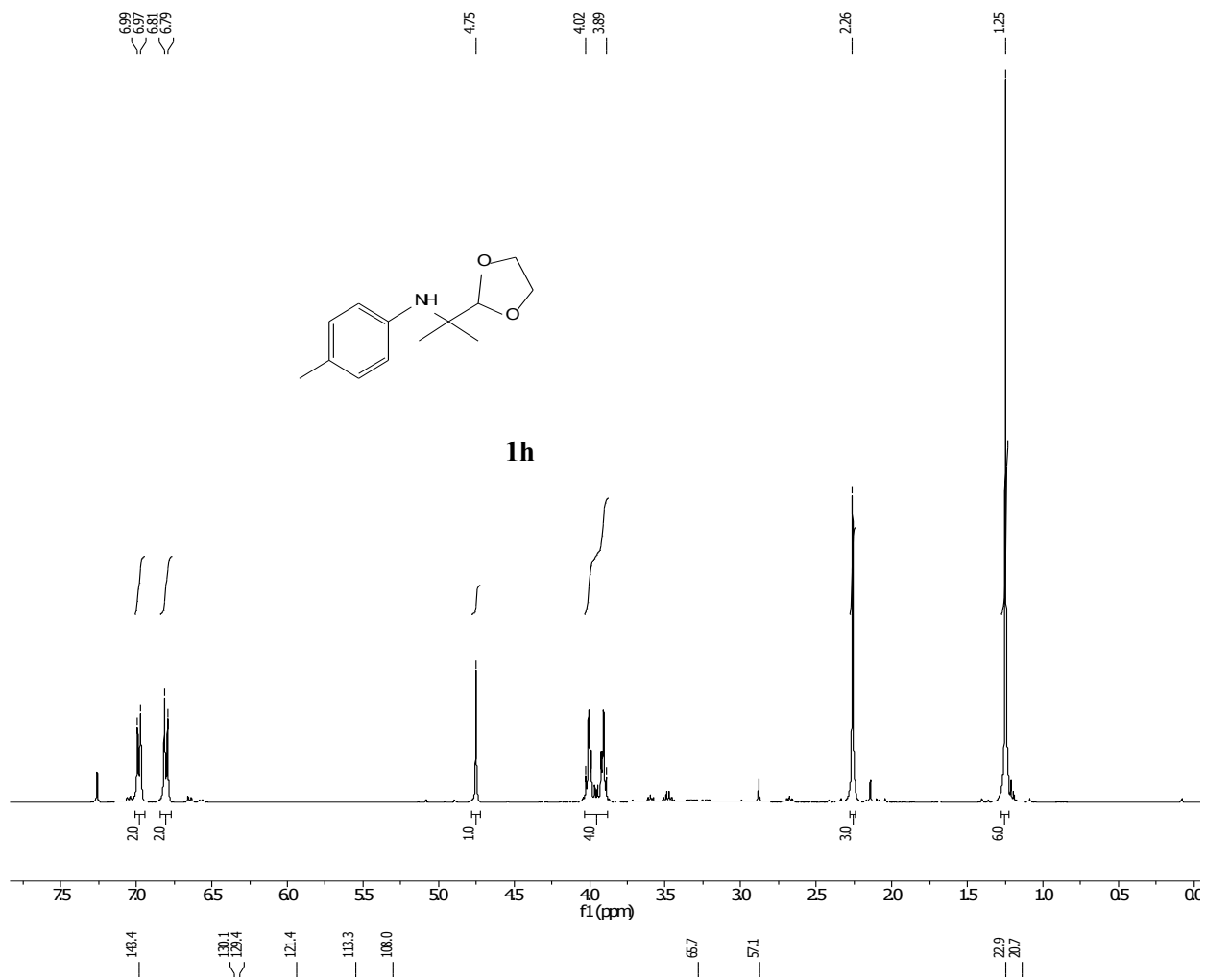


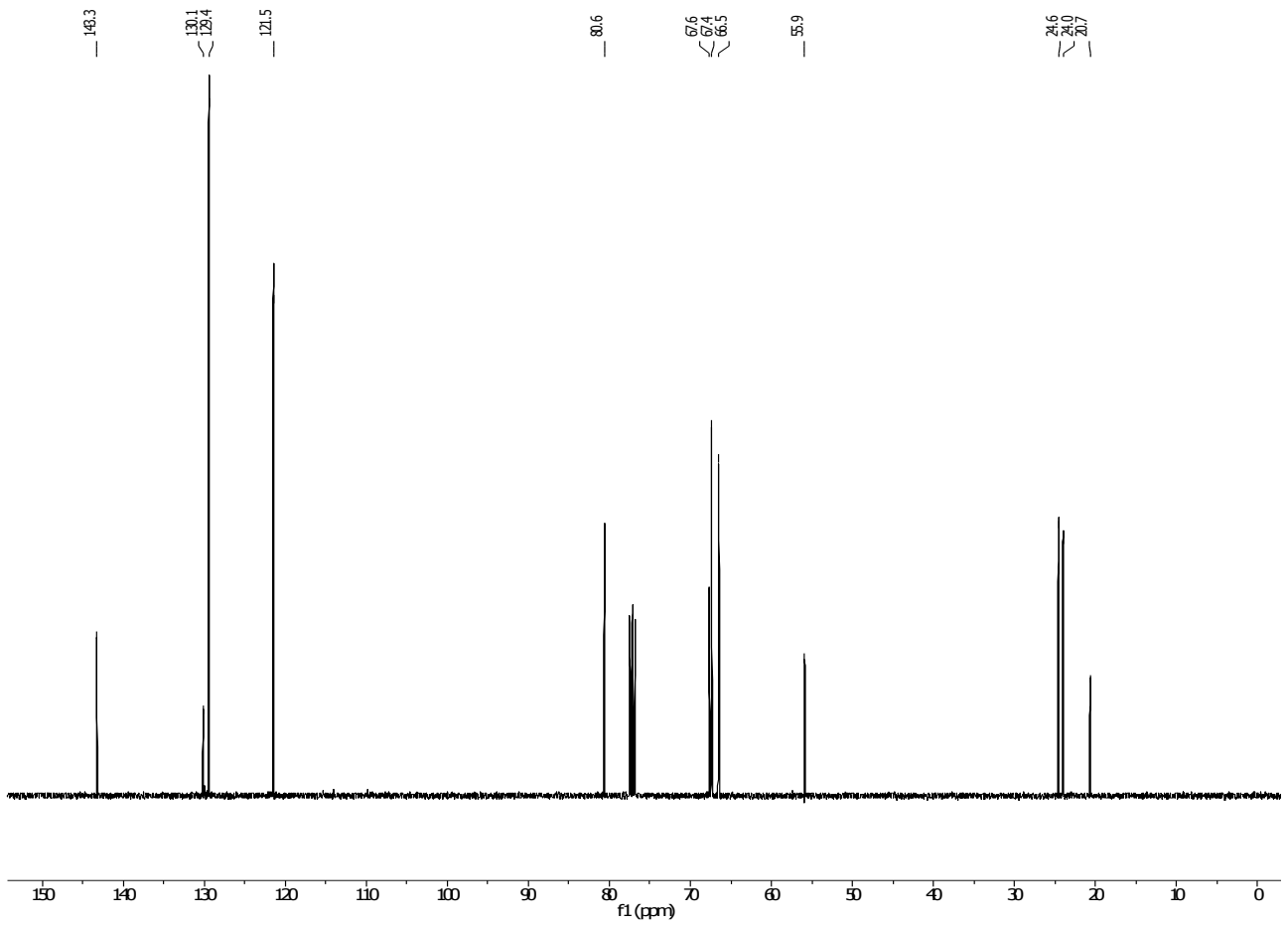
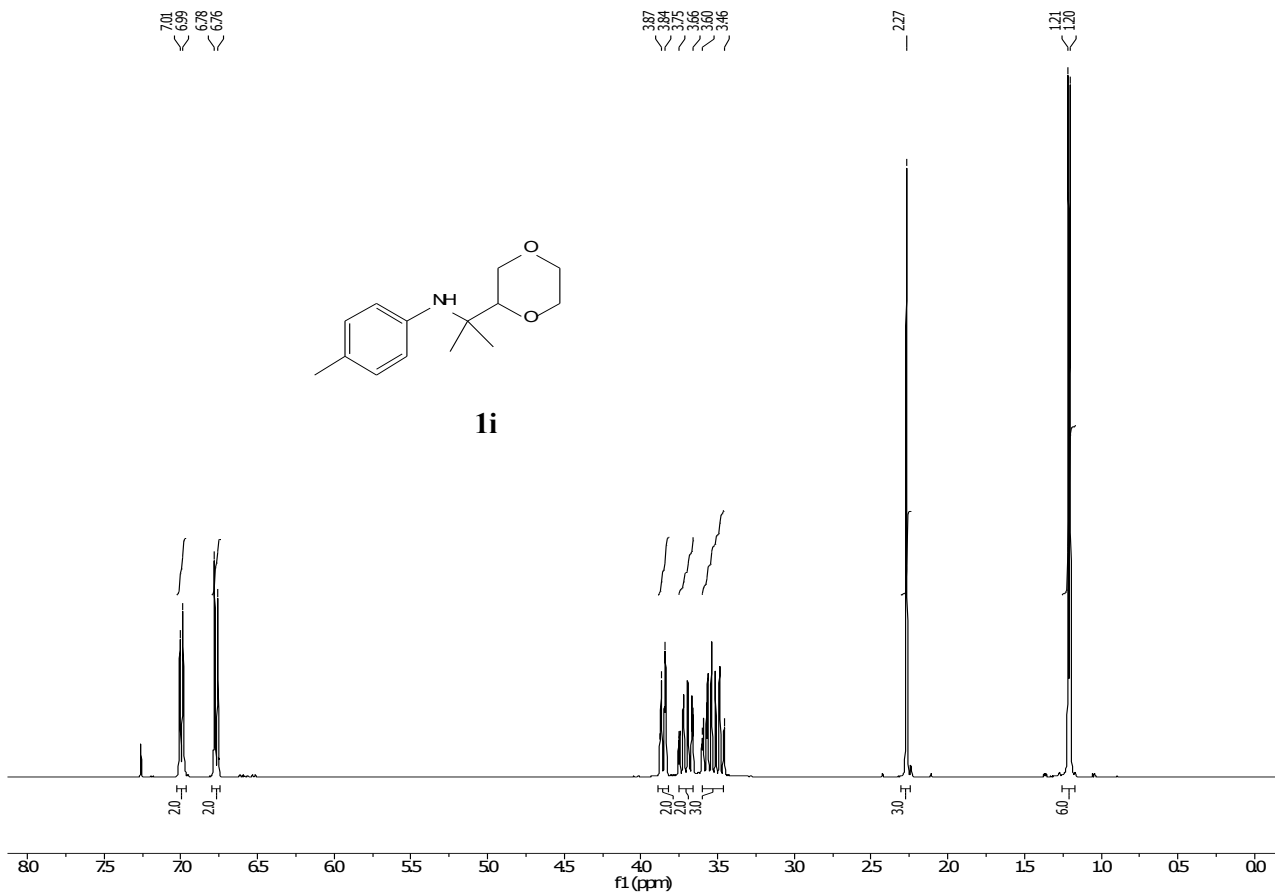


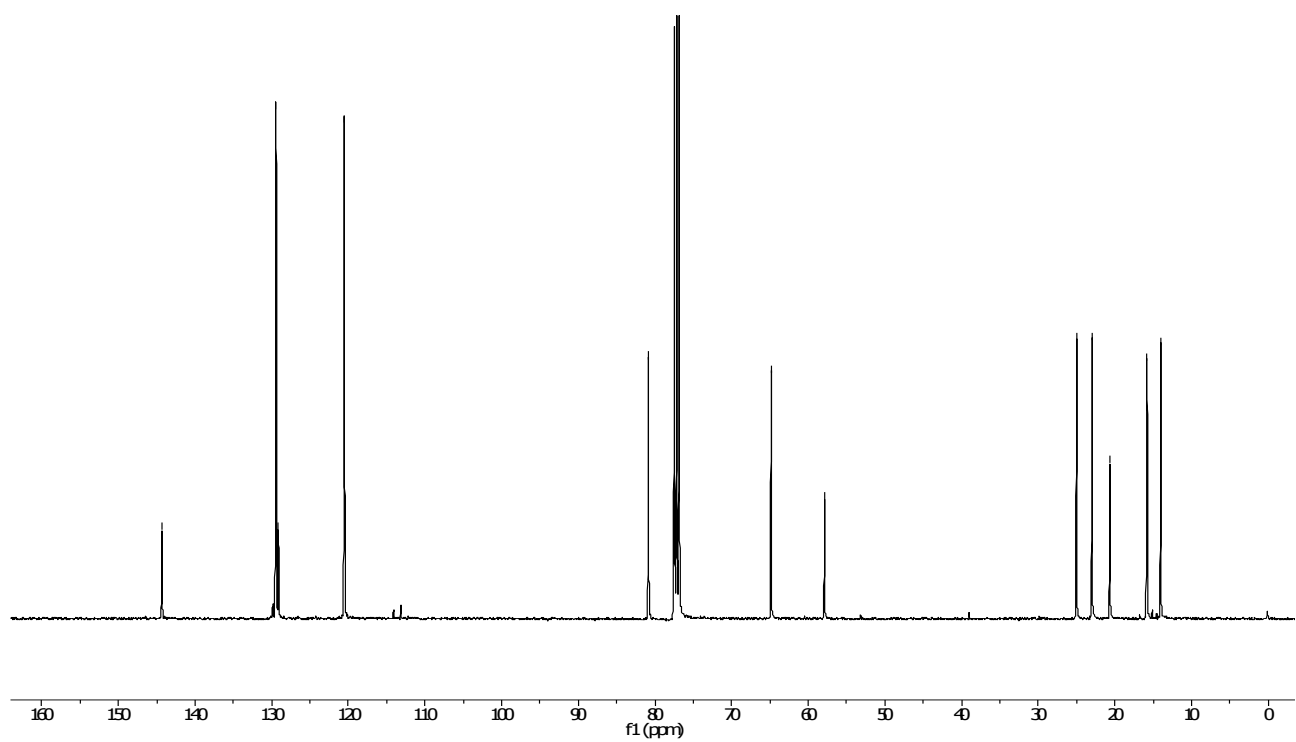
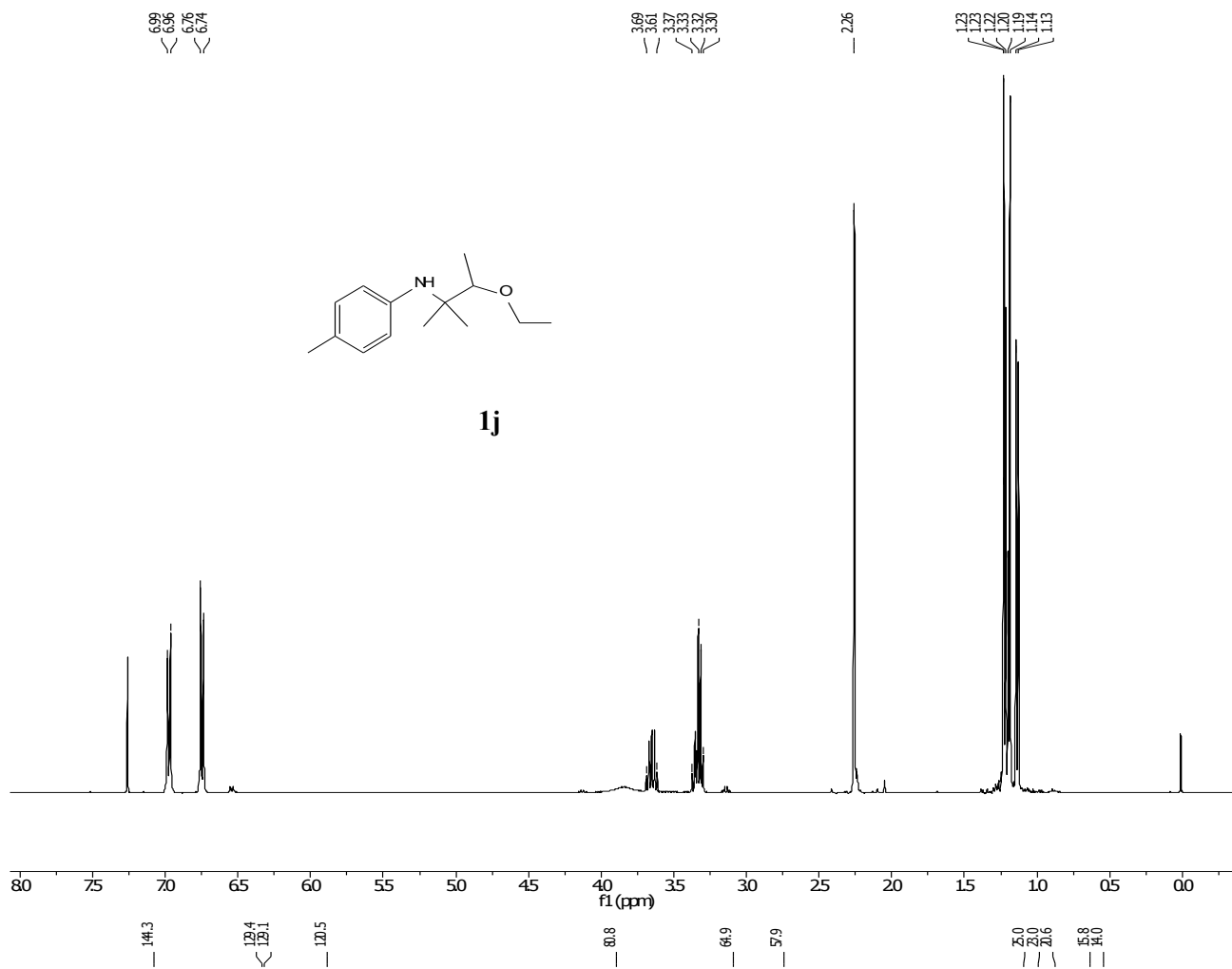


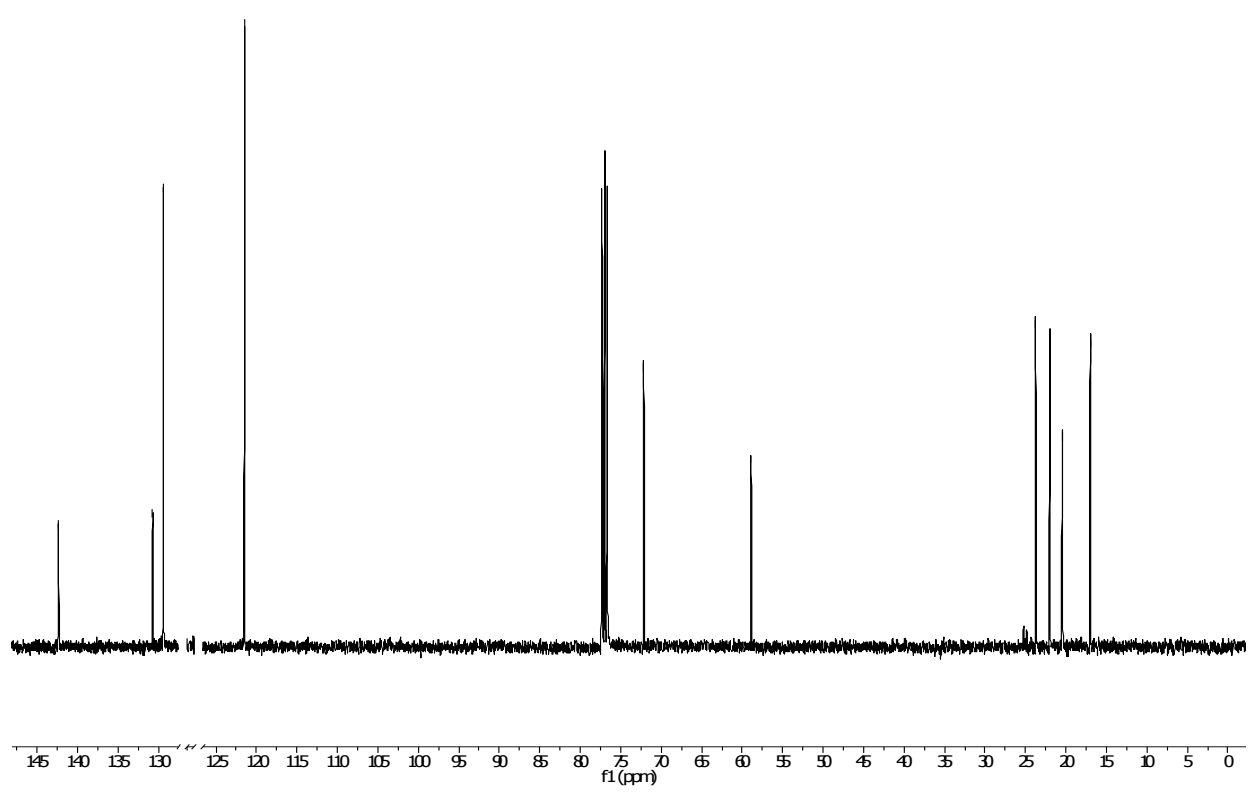
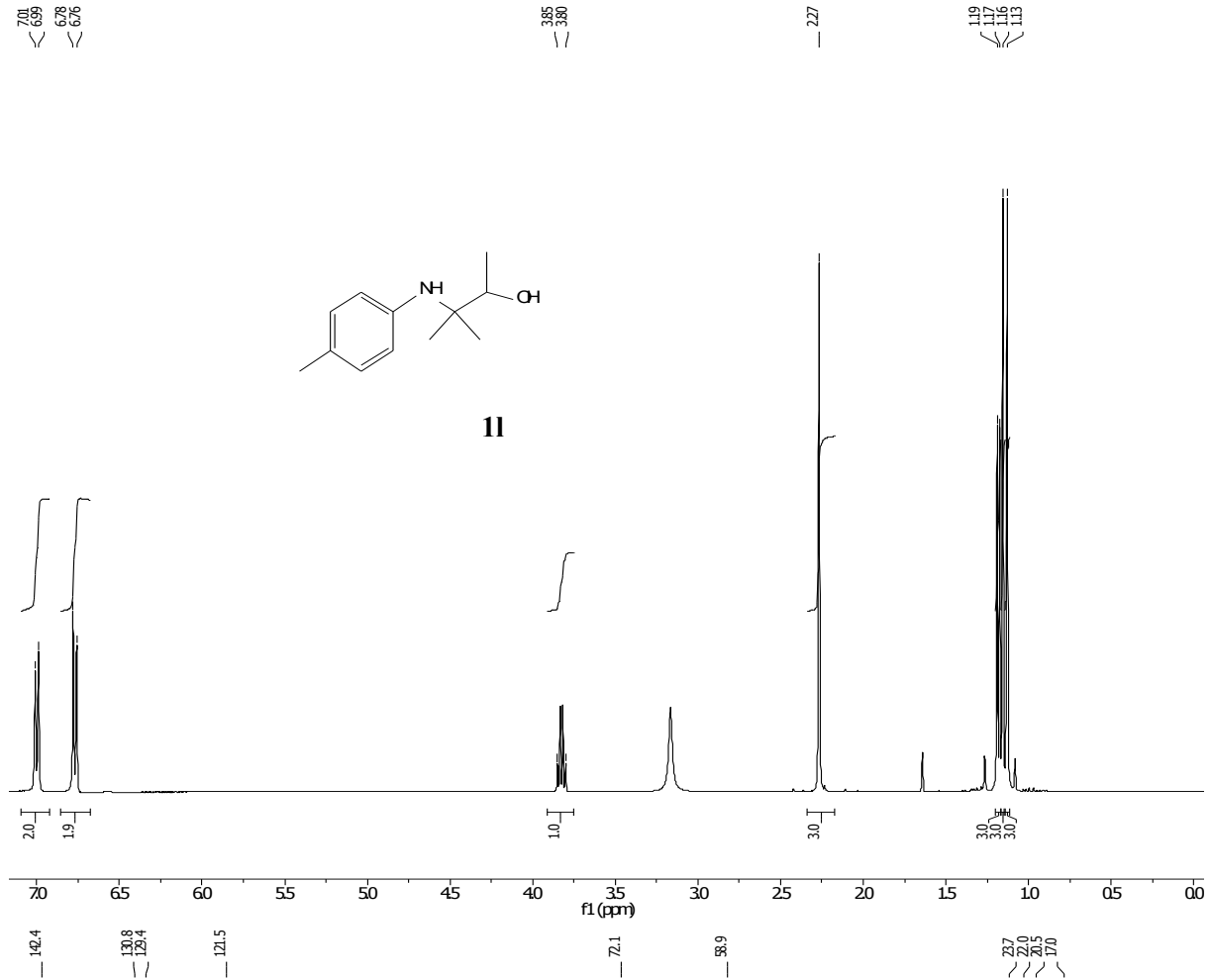




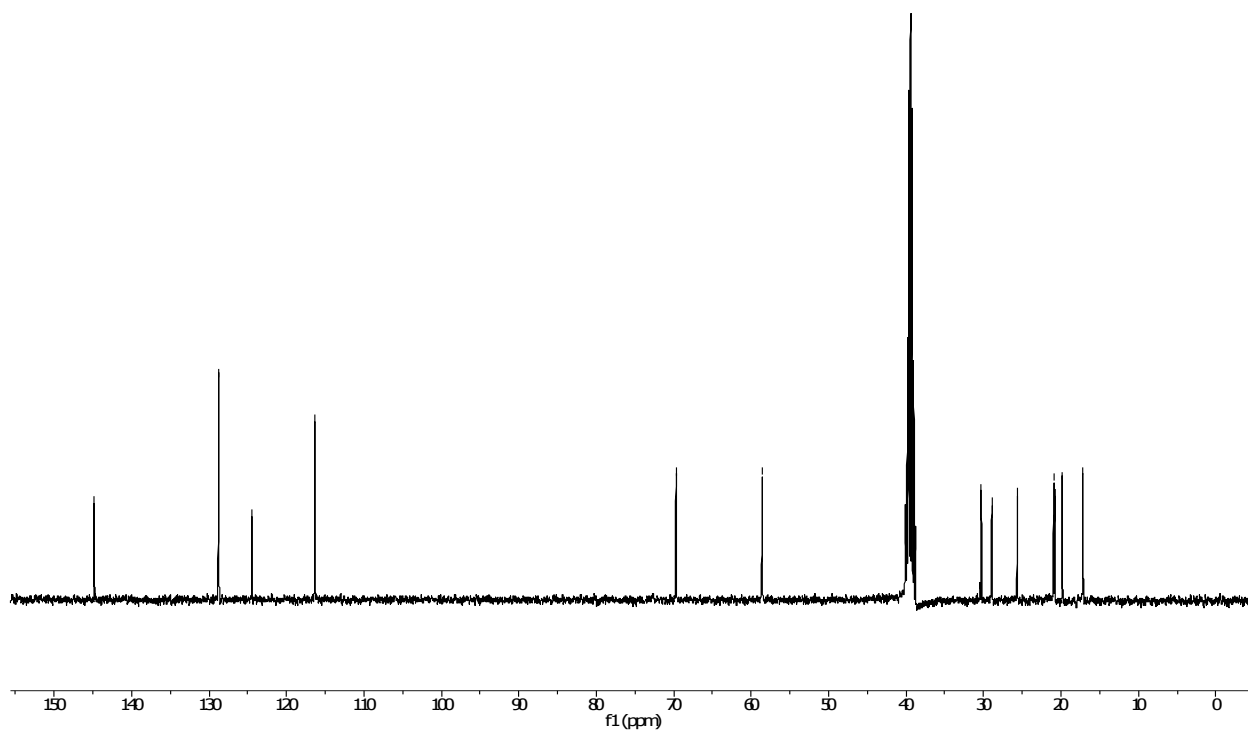
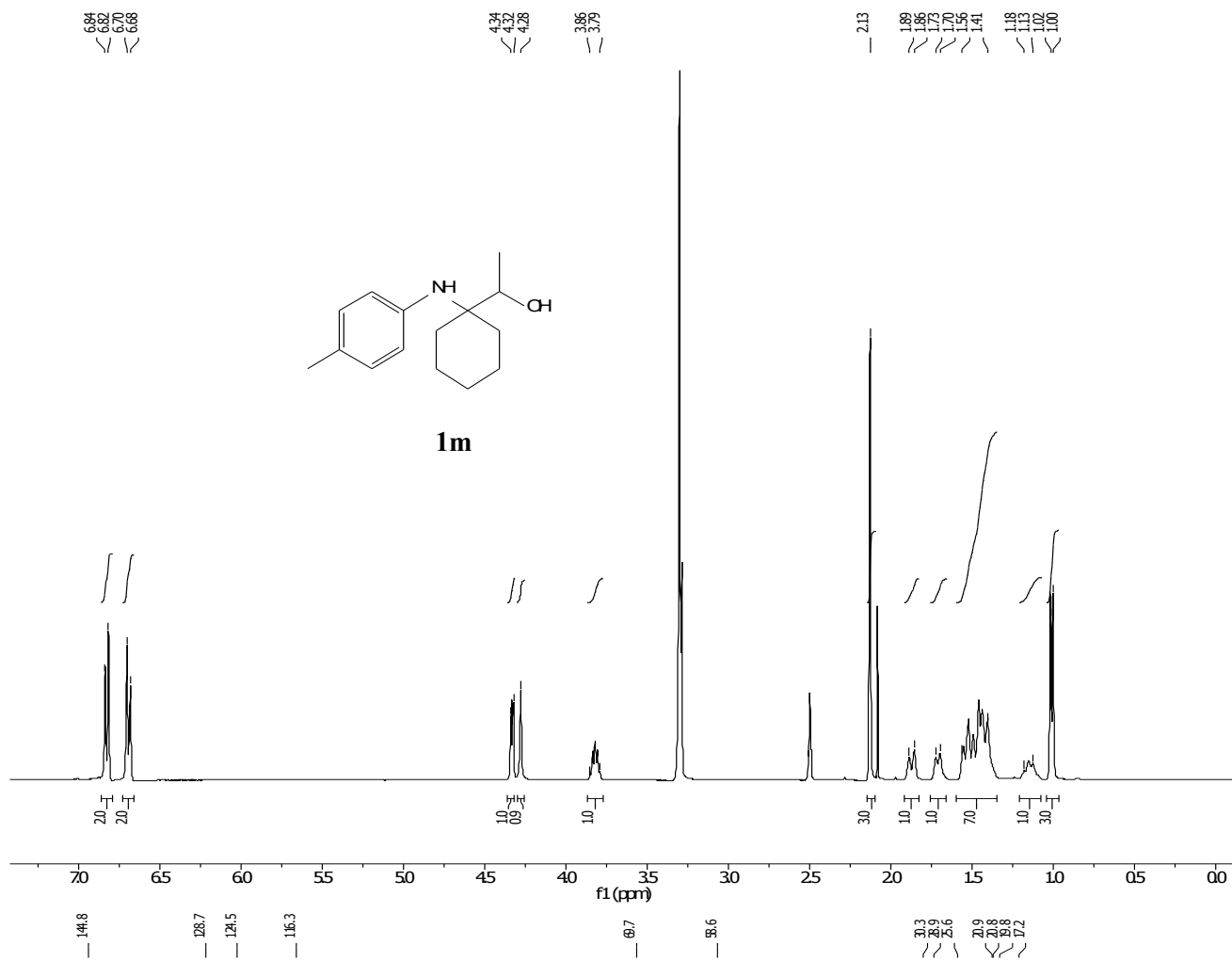


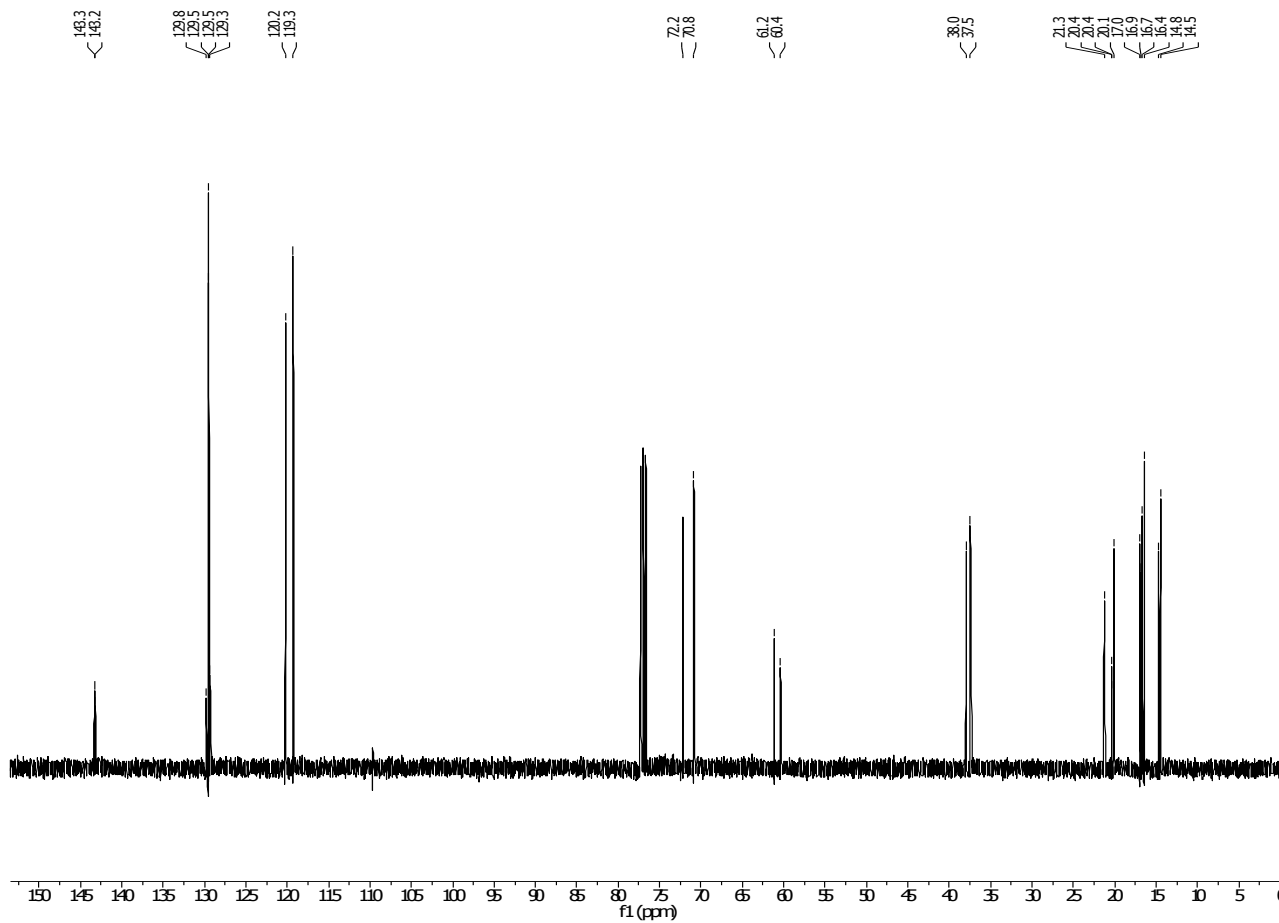
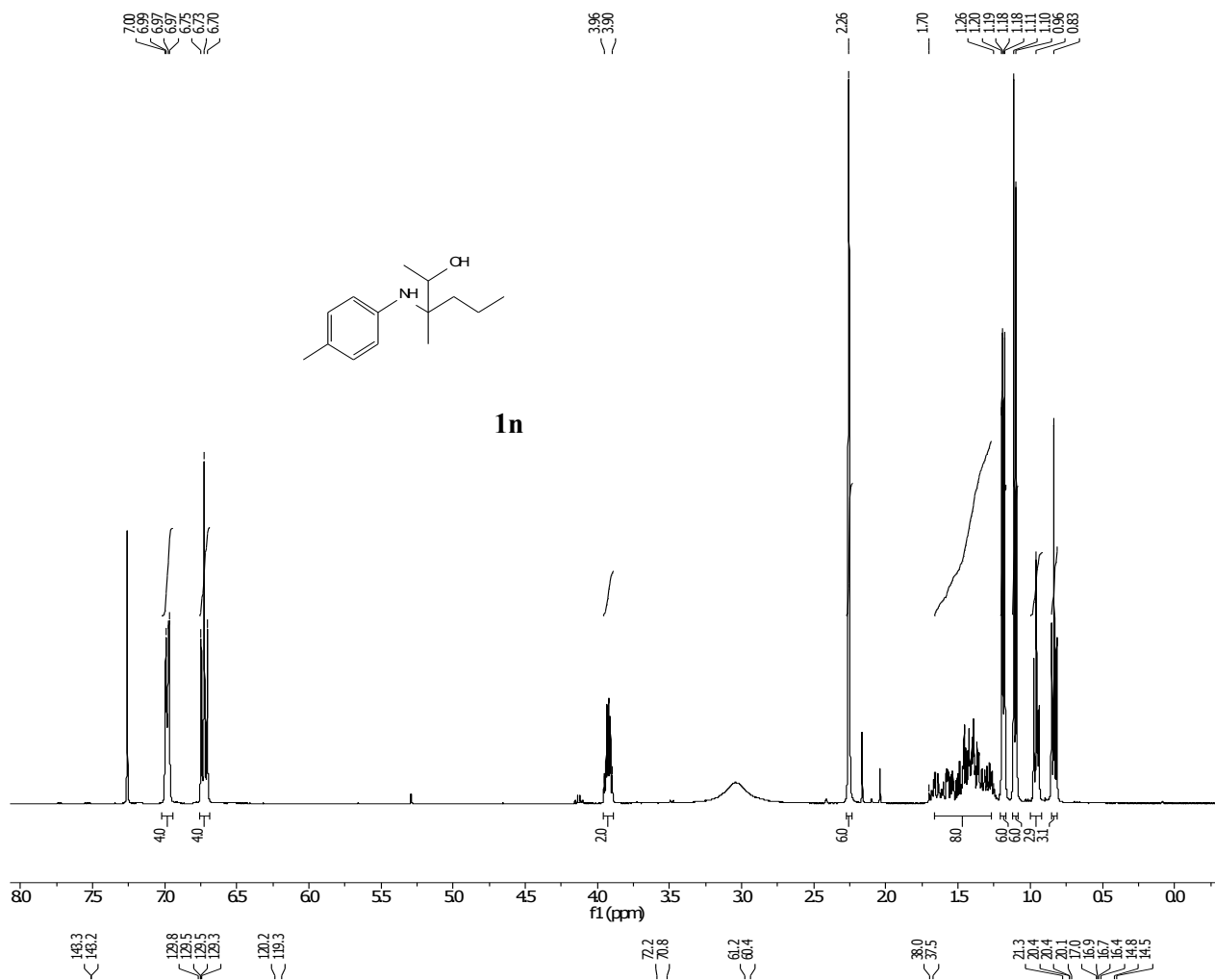










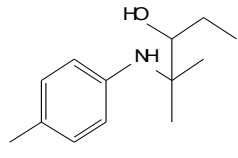


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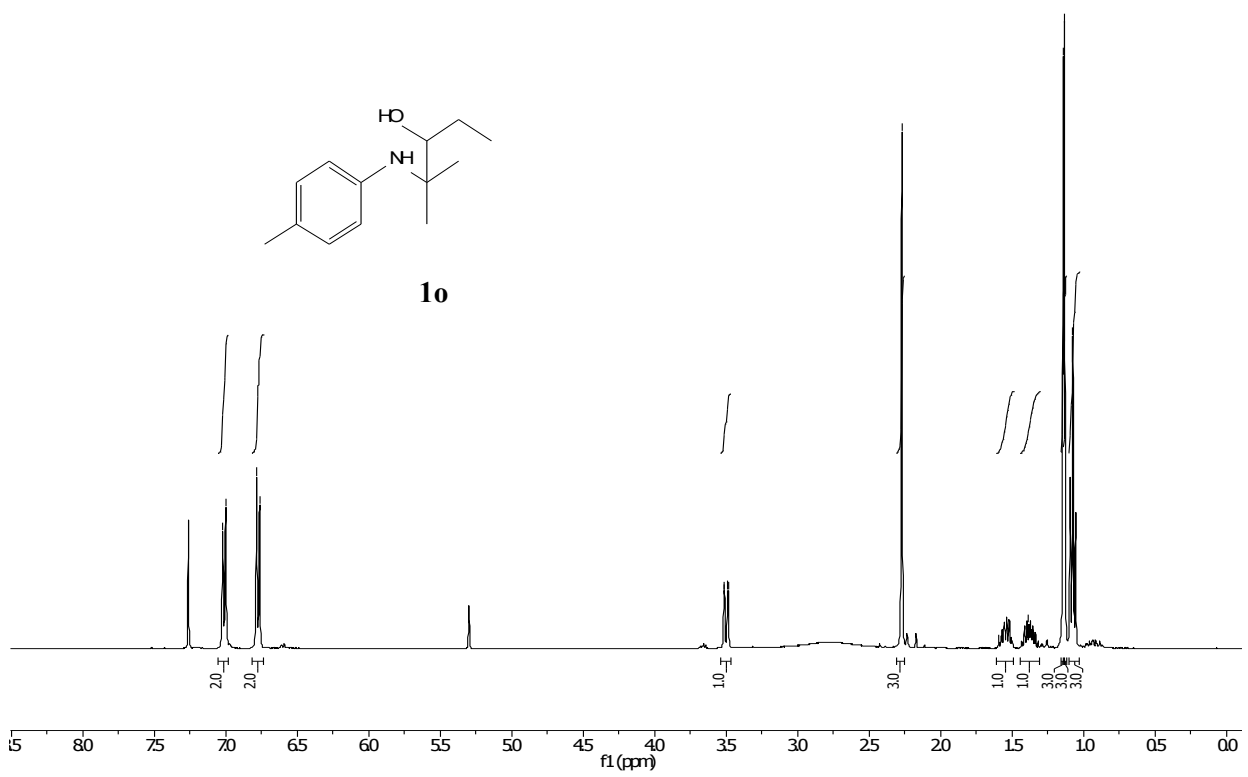
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2.27

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1o



142.6

130.7  
123.5

121.4

78.1

58.7

24.3  
23.9  
22.8  
20.6

11.9

