

## Supplementary Information

# Reductive Cross-Coupling of *N*-Acyl Pyrazole and Nitroarene using tetrahydroxydiboron: Synthesis of Secondary Amides

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## **1. General Information**

All reagents were purchased and used without further purification.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  or  $(\text{CD}_3)_2\text{SO}$  on 500 MHz NMR spectrometers and data are reported as follows: chemical shift, multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), heptet (hept), doublet of doublets (dd), triplet of triplet (tt) and multiplet (m)], coupling constants (Hz) and integration.  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  or  $(\text{CD}_3)_2\text{SO}$  on 126 MHz NMR spectrometers and resonances ( $\delta$ ) are given in ppm. Starting materials of amides were synthesized according to corresponding literature.<sup>1</sup>

## **2. General procedure for the synthesis of products**

*N*-Acyl pyrazole (1 mmol, 1.0 equiv), nitroarene (1.0 mmol, 1.0 equiv),  $\text{B}_2(\text{OH})_4$  (269 mg, 3.0 mmol, 3.0 equiv) were dissolved in DMF (5 mL, 0.2M). The resulting solution was stirred at 100 °C for 24 h. The reaction was diluted with ethyl acetate, then washed with brine. The organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated under vacuum. The crude product was purified by silica gel column chromatography with ethyl acetate/hexane (1:9).

### 3. Characterization Data for the Products



#### **N-Phenylbenzamide (3aa)<sup>2</sup>**

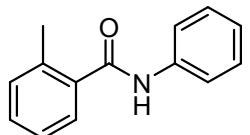
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3aa** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (171 mg, 0.87 mmol, 87%).

m.p. 162–163 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.27 (s, 1H), 7.99 – 7.97 (m, 2H), 7.82 – 7.80 (m, 2H), 7.61 – 7.57 (m, 1H), 7.55 – 7.52 (m, 2H), 7.38 – 7.34 (m, 2H), 7.10 (tt, *J* = 7.4, 1.25 Hz, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.58, 139.20, 135.02, 131.52, 128.59, 128.36, 127.66, 123.65, 120.38;

MS (EI) m/z = 197.08 (M<sup>+</sup>).



#### **2-Methyl-N-phenylbenzamide (3ba)<sup>[2]</sup>**

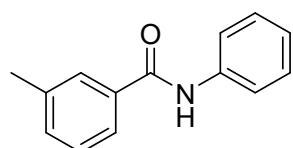
According to the general procedure using (1H-pyrazol-1-yl)(*o*-tolyl)methanone (186 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ba** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (160 mg, 0.76 mmol, 76%).

m.p. 126–127 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 7.95 (s, 1H), 7.68 (s, 1H), 7.66 – 7.62 (m, 3H), 7.38 – 7.33 (m, 4H), 7.16 – 7.13 (m, 1H), 2.41 (s, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 166.01, 138.69, 138.01, 134.99, 132.58, 129.08, 128.64, 127.82, 124.51, 123.98, 120.23, 21.39;

MS (EI) m/z = 211.10 (M<sup>+</sup>).



#### **3-Methyl-N-phenylbenzamide (3ca)<sup>[2]</sup>**

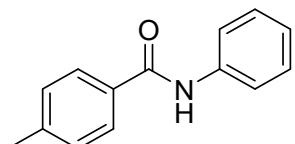
According to the general procedure using (1H-pyrazol-1-yl)(*m*-tolyl)methanone (186 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ca** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (116 mg, 0.55 mmol, 55%).

m.p. 125–126 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.21 (s, 1H), 7.81 (d, *J* = 3.3 Hz, 1H), 7.80 – 7.78 (m, 2H), 7.76 (d, *J* = 6.3 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.37 – 7.34 (m, 2H), 7.10 (tt, *J* = 7.4, 1.2 Hz, 1H), 2.40 (s, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.67, 139.24, 137.67, 135.02, 132.09, 128.57, 128.26, 128.13, 124.81, 123.58, 120.33, 20.96;

MS (EI) m/z = 211.10 (M<sup>+</sup>).



#### **4-Methyl-N-phenylbenzamide (3da)<sup>[2]</sup>**

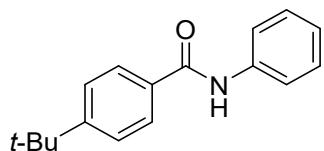
According to the general procedure using (1H-pyrazol-1-yl)(*p*-tolyl)methanone (186 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3da** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (148 mg, 0.73 mmol, 73%).

m.p. 145–146 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.15 (s, 1H), 7.89 – 7.87 (m, 2H), 7.79 – 7.77 (m, 2H), 7.36 – 7.32 (m, 4H), 7.09 (tt, *J* = 7.4, 2.5 Hz, 1H), 2.39 (s, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.33, 141.53, 139.24, 132.08, 128.88, 128.56, 127.68, 123.52, 120.34, 21.00;

MS (EI) m/z = 211.10 (M<sup>+</sup>).



#### **4-(tert-Butyl)-N-phenylbenzamide (3ea)<sup>[2]</sup>**

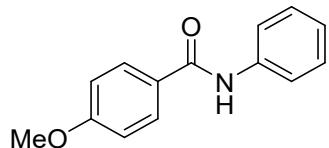
According to the general procedure using (4-(*tert*-butyl)phenyl)(1H-pyrazol-1-yl)methanone (228 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ea** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (197 mg, 0.78 mmol, 78%).

m.p. 123–125 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.17 (s, 1H), 7.90 – 7.88 (m, 2H), 7.79 – 7.77 (m, 2H), 7.55 – 7.53 (m, 2H), 7.36 – 7.33 (m, 2H), 7.09 (tt, *J* = 7.4, 1.2 Hz, 1H), 1.32 (s, 9H);

$^{13}\text{C}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  165.49, 154.36, 139.27, 132.30, 128.56, 127.51, 125.12, 123.50, 120.25, 34.66, 30.93;

MS (EI) m/z = 253.15 ( $\text{M}^+$ ).



**4-Methoxy-N-phenylbenzamide (3fa)<sup>[2]</sup>**

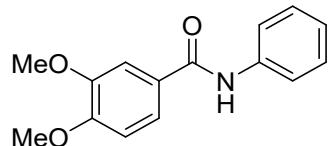
According to the general procedure using (4-methoxyphenyl)(1H-pyrazol-1-yl)methanone (202 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3fa** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (3:1) and obtained as a white solid (173 mg, 0.76 mmol, 76%).

m.p. 160-161 °C;

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (m, 3H), 7.63 (d,  $J = 8.0$  Hz, 2H), 7.35 (t,  $J = 7.8$  Hz, 2H), 7.13 (t,  $J = 7.4$  Hz, 1H), 6.93 (d,  $J = 8.3$  Hz, 2H), 3.86 (s, 3H);

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.42, 162.60, 138.25, 129.19, 129.07, 127.27, 124.48, 120.34, 114.10, 55.62;

MS (EI) m/z = 227.09 ( $\text{M}^+$ ).



**3,4-Dimethoxy-N-phenylbenzamide (3ga)<sup>[3]</sup>**

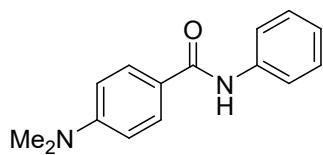
According to the general procedure using (3,4-dimethoxyphenyl)(1H-pyrazol-1-yl)methanone (232 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ga** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (3:1) and obtained as a white solid (184 mg, 0.72 mmol, 72%).

m.p. 174-175 °C;

$^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  10.06 (s, 1H), 7.77 – 7.75 (m, 2H), 7.63 (dd,  $J = 8.4, 2.1$  Hz, 1H), 7.54 (d,  $J = 2.2$  Hz, 1H), 7.35 (t,  $J = 7.9$  Hz, 2H), 7.10 – 7.07 (m, 2H), 3.85 (s, 3H), 3.84 (s, 3H);

$^{13}\text{C}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  164.88, 151.61, 148.29, 139.27, 128.53, 126.99, 123.46, 121.00, 120.46, 111.04, 110.88, 55.66, 55.62;

MS (EI) m/z = 257.11 ( $\text{M}^+$ ).



**4-(Dimethylamino)-N-phenylbenzamide (3ha)<sup>[4]</sup>**

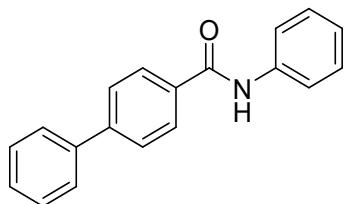
According to the general procedure using (4-(dimethylamino)phenyl)(1H-pyrazol-1-yl)methanone (215 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ha** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (154 mg, 0.64 mmol, 64%).

m.p. 181–182 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 9.85 (s, 1H), 7.89 – 7.86 (m, 2H), 7.78 – 7.76 (m, 2H), 7.33 – 7.29 (m, 2H), 7.05 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.77 – 6.74 (m, 2H), 3.00 (s, 6H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.19, 152.37, 139.71, 129.12, 128.45, 122.96, 121.08, 120.18, 110.75, 39.69;

MS (EI) m/z = 240.13 (M<sup>+</sup>).



**N-Phenyl-(1,1'-biphenyl)-4-carboxamide (3ia)<sup>[2]</sup>**

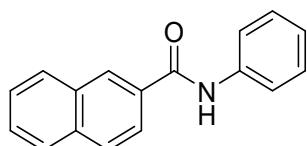
According to the general procedure using [1,1'-biphenyl]-4-yl(1H-pyrazol-1-yl)methanone (248 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ia** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (207 mg, 0.76 mmol, 76%).

m.p. 222–223 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.30 (s, 1H), 8.09 – 8.06 (m, 2H), 7.85 – 7.81 (m, 4H), 7.77 – 7.75 (m, 2H), 7.53 – 7.49 (m, 2H), 7.44 – 7.41 (m, 1H), 7.38 – 7.35 (m, 2H), 7.11 (tt, *J* = 7.4, 2.5 Hz, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.18, 143.10, 139.21, 139.12, 133.73, 129.07, 128.62, 128.38, 128.15, 126.92, 126.59, 123.67, 120.39;

MS (EI) m/z = 273.12 (M<sup>+</sup>).



**N-Phenyl-2-naphthamide (3ja)<sup>[2]</sup>**

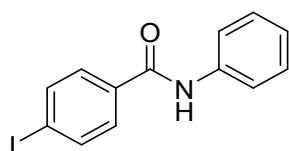
According to the general procedure using naphthalen-2-yl(1H-pyrazol-1-yl)methanone (222 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ja** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (217 mg, 0.88 mmol, 88%).

m.p. 168–169 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.43 (s, 1H), 8.59 (s, 1H), 8.10 – 8.01 (m, 4H), 7.85 – 7.83 (m, 2H), 7.67 – 7.61 (m, 2H), 7.40 – 7.36 (m, 2H), 7.12 (tt, *J* = 7.4, 1.2 Hz, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.59, 139.24, 134.26, 132.29, 132.08, 128.94, 128.64, 128.00, 127.95, 127.80, 127.67, 126.84, 124.46, 123.68, 120.37;

MS (EI) m/z = 247.10 (M<sup>+</sup>).



#### **4-Iodo-N-phenylbenzamide (3ka)<sup>[4]</sup>**

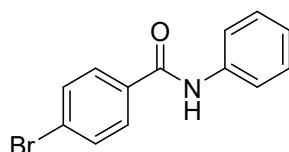
According to the general procedure using (4-iodophenyl)(1H-pyrazol-1-yl)methanone (298 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ka** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (239 mg, 0.74 mmol, 74%).

m.p. 205–207 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.28 (s, 1H), 7.93 – 7.91 (m, 2H), 7.77 – 7.74 (m, 4H), 7.37 – 7.33 (m, 2H), 7.11 (tt, *J* = 7.4, 2.5 Hz, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 164.79, 138.96, 137.24, 134.31, 129.61, 128.61, 123.79, 120.40, 99.24;

MS (EI) m/z = 322.98 (M<sup>+</sup>).



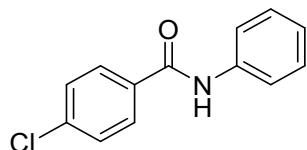
#### **4-Bromo-N-phenylbenzamide (3la)<sup>[4]</sup>**

According to the general procedure using (4-bromophenyl)(1H-pyrazol-1-yl)methanone (251 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3la** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (183 mg, 0.78 mmol, 78%). m.p. 202–203 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.31 (s, 1H), 7.92 – 7.91 (m, 2H), 7.77 – 7.74 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 164.53, 138.95, 134.01, 131.38, 129.79, 128.62, 125.30, 123.82, 120.41;

MS (EI) m/z = 274.99 (M<sup>+</sup>).



**4-Chloro-N-phenylbenzamide (3ma)<sup>[4]</sup>**

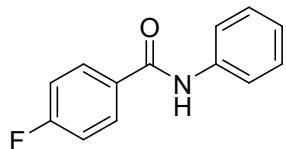
According to the general procedure using (4-chlorophenyl)(1H-pyrazol-1-yl)methanone (207 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ma** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (208 mg, 0.90 mmol, 90%).

m.p. 199–201 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.30 (s, 1H), 8.00 – 7.97 (m, 2H), 7.77 – 7.75 (m, 2H), 7.62 – 7.59 (m, 2H), 7.38 – 7.34 (m, 2H), 7.13 – 7.09 (m, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 164.42, 138.96, 136.37, 133.65, 129.62, 128.62, 128.45, 123.82, 120.41;

MS (EI) m/z = 231.05 (M<sup>+</sup>).



**4-Fluoro-N-phenylbenzamide (3na)<sup>[2]</sup>**

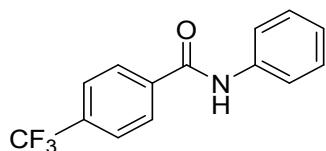
According to the general procedure using (4-fluorophenyl)(1H-pyrazol-1-yl)methanone (190 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3na** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (183 mg, 0.85 mmol, 85%).

m.p. 183–185 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.26 (s, 1H), 8.06 – 8.02 (m, 2H), 7.78 – 7.75 (m, 2H), 7.39 – 7.33 (m, 4H), 7.10 (tt, *J* = 7.4, 1.2 Hz, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 164.43, 164.06(d, *J* = 249.5 Hz), 139.07, 131.40 (d, *J* = 3.8 Hz), 130.39 (d, *J* = 8.8 Hz), 128.60, 123.72, 120.41, 115.31 (d, *J* = 21.4 Hz);

MS (EI) m/z = 215.07 (M<sup>+</sup>).



**N-Phenyl-4-(trifluoromethyl)benzamide (3oa)<sup>[2]</sup>**

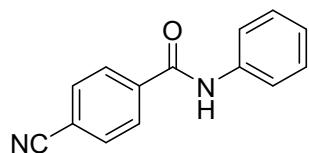
According to the general procedure using (1H-pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methanone (240 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3oa** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (215 mg, 0.81 mmol, 81%).

m.p. 197–199 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.46 (s, 1H), 8.16 – 8.14 (m, 2H), 7.92 – 7.90 (m, 2H), 7.80 – 7.77 (m, 2H), 7.39 – 7.33 (m, 2H), 7.15 – 7.11 (m, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 164.39, 138.83, 138.80, 131.36 (q, *J* = 31.5 Hz), 128.68, 128.59, 125.38 (q, *J* = 3.8 Hz), 124.02, 123.94 (q, *J* = 273.4 Hz), 120.46;

MS (EI) m/z = 265.07 (M<sup>+</sup>).



#### **4-Cyano-N-phenylbenzamide (3pa)<sup>[2]</sup>**

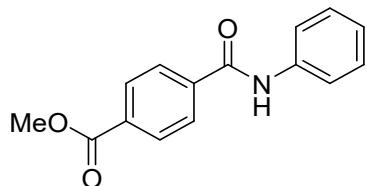
According to the general procedure using 4-(1H-pyrazole-1-carbonyl)benzonitrile (197 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3pa** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (195 mg, 0.88 mmol, 88%).

m.p. 175–177 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.47 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.35 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 164.13, 138.98, 138.75, 132.44, 128.68, 128.53, 124.09, 120.46, 118.32, 113.84;

MS (EI) m/z = 222.08 (M<sup>+</sup>).



#### **Methyl-4-(phenylcarbamoyl)benzoate (3qa)<sup>[5]</sup>**

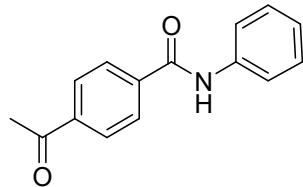
According to the general procedure using methyl 4-(1H-pyrazole-1-carbonyl)benzoate (230 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3qa** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (196 mg, 0.77 mmol, 77%).

m.p. 185–187 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.43 (s, 1H), 8.11 – 8.06 (m, 4H), 7.79 – 7.78 (m, 2H), 7.39 – 7.35 (m, 2H), 7.12 (tt, *J* = 7.3, 1.2 Hz, 1H), 3.90 (s, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.69, 164.69, 139.07, 138.89, 132.01, 129.17, 128.65, 128.07, 123.95, 120.44, 52.42;

MS (EI) m/z = 255.09 (M<sup>+</sup>).



**4-Acetyl-N-phenylbenzamide (3ra)<sup>[4]</sup>**

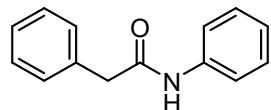
According to the general procedure using 4-(1H-pyrazole-1-carbonyl)benzonitrile (214 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ra** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (177 mg, 0.74 mmol, 74%).

m.p. 125-127 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.41 (s, 1H), 8.10 – 8.06 (m, 4H), 7.80 – 7.78 (m, 2H), 7.39 – 7.35 (m, 2H), 7.14 – 7.11 (m, 1H), 2.64 (s, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 197.70, 164.75, 138.92, 138.83, 138.76, 128.65, 128.17, 128.01, 123.93, 120.45, 26.99;

MS (EI) m/z = 239.09 (M<sup>+</sup>).



**N,2-Diphenylacetamide (3sa)<sup>[3]</sup>**

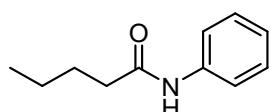
According to the general procedure using 2-phenyl-1-(1H-pyrazol-1-yl)ethan-1-one (186 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3sa** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (156 mg, 0.74 mmol, 74%).

m.p. 118-119 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.17 (s, 1H), 7.63 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.37 – 7.27 (m, 6H), 7.25 – 7.22 (m, 1H), 7.05 – 7.01 (m, 1H), 3.66 (s, 2H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 169.10, 139.25, 136.03, 129.10, 128.70, 128.29, 126.51, 123.20, 119.13, 43.37;

MS (EI) m/z = 211.10 (M<sup>+</sup>).



### **N-Phenylpentanamide (3ta)<sup>[6]</sup>**

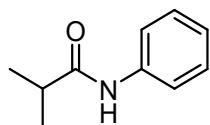
According to the general procedure using 1-(1H-pyrazol-1-yl)pentan-1-one (152 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ta** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (110 mg, 0.62 mmol, 62%).

m.p. 94-96 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 9.84 (s, 1H), 7.61 – 7.59 (m, 2H), 7.29 – 7.25 (m, 2H), 7.01 (tt, *J* = 7.4, 1.2 Hz, 1H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.36 – 1.29 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 171.23, 139.38, 128.58, 122.85, 119.01, 36.14, 27.27, 21.84, 13.72;

MS (EI) m/z = 177.12 (M<sup>+</sup>).



### **N-Phenyllisobutyramide (3ua)<sup>[4]</sup>**

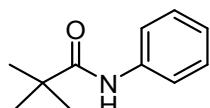
According to the general procedure using 2-methyl-1-(1H-pyrazol-1-yl)propan-1-one (138 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3ua** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (112 mg, 0.69 mmol, 69%).

m.p. 112-114 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 9.80 (s, 1H), 7.63 – 7.61 (m, 2H), 7.30 – 7.26 (m, 2H), 7.01 (tt, *J* = 7.5, 1.2 Hz, 1H), 2.59 (hept, *J* = 6.8 Hz, 1H), 1.10 (d, *J* = 6.7 Hz, 6H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 175.17, 139.46, 128.58, 122.87, 119.11, 34.91, 19.49;

MS (EI) m/z = 163.10 (M<sup>+</sup>).



### **N-Phenylpivalamide (3va)<sup>[4]</sup>**

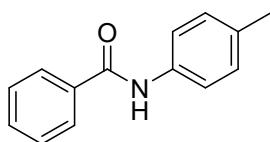
According to the general procedure using 2,2-dimethyl-1-(1H-pyrazol-1-yl)propan-1-one (152 mg, 1.0 mmol) and nitrobenzene (123 mg, 1.0 mmol), the product **3va** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (101 mg, 0.57 mmol, 57%).

m.p. 132-134 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 9.17 (s, 1H), 7.65 – 7.62 (m, 2H), 7.30 – 7.26 (m, 2H), 7.03 (tt, *J* = 7.3, 1.3 Hz, 1H), 1.23 (s, 9H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 176.38, 139.36, 128.35, 123.10, 120.23, 39.11, 27.20;

MS (EI) m/z = 177.12 (M<sup>+</sup>).



**N-(p-Tolyl)benzamide (3ab)<sup>[2]</sup>**

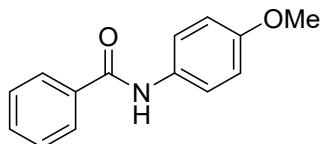
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-methyl-4-nitrobenzene (137 mg, 1.0 mmol), the product **3ab** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (146 mg, 0.69 mmol, 69%).

m.p. 154–156 °C;

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (s, 1H), 7.85 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.54 – 7.51 (m, 3H), 7.46 – 7.43 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H);

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 165.84, 135.50, 135.20, 134.34, 131.83, 129.68, 128.84, 127.14, 120.47, 21.03;

MS (EI) m/z = 211.10 (M<sup>+</sup>).



**N-(4-Methoxyphenyl)benzamide (3ac)<sup>[2]</sup>**

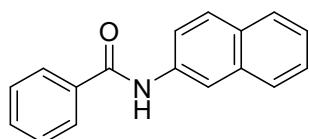
According to the general procedure, using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol), and 1-methoxy-4-nitrobenzene (153 mg, 1.0 mmol), the product **3ac** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (3:1) and obtained as a white solid (143 mg, 0.63 mmol, 63%).

m.p. 163–164 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.13 (s, 1H), 7.96 – 7.94 (m, 2H), 7.70 – 7.67 (m, 2H), 7.57 (m, 1H), 7.52 (m, 2H), 6.95 – 6.91 (m, 2H), 3.75 (s, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.09, 155.54, 135.05, 132.23, 131.36, 128.33, 127.54, 121.97, 113.72, 55.17;

MS (EI) m/z = 227.09 (M<sup>+</sup>).



**N-(Naphthalen-2-yl)benzamide (3ad)<sup>[7]</sup>**

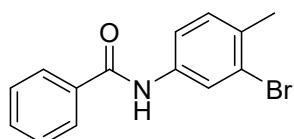
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 2-nitronaphthalene (173 mg, 1.0 mmol), the product **3ad** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (146 mg, 0.59 mmol, 59%).

m.p. 158–159 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.44 (s, 1H), 8.11 – 8.09 (m, 2H), 8.01 – 7.97 (m, 2H), 7.87 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.59 – 7.53 (m, 5H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 166.16, 134.45, 133.85, 133.76, 131.66, 129.23, 128.45, 128.07, 127.79, 126.28, 126.06, 125.97, 125.54, 123.92, 123.33;

MS (EI) m/z = 247.10 (M<sup>+</sup>).



#### **N-(3-Bromo-4-methylphenyl)benzamide (3ae)<sup>[8]</sup>**

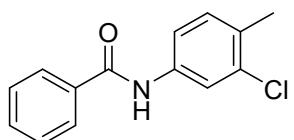
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 2-bromo-1-methyl-4-nitrobenzene (216 mg, 1.0 mmol), the product **3ae** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (237 mg, 0.82 mmol, 82%).

m.p. 135–137 °C;

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (s, 1H), 7.88 (d, *J* = 2.2 Hz, 1H), 7.84 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.48 – 7.44 (m, 3H), 7.18 (dd, *J* = 8.2, 0.9 Hz, 1H), 2.37 (s, 3H);

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 165.85, 136.83, 134.73, 134.13, 132.10, 130.95, 128.93, 127.16, 124.93, 124.13, 119.39, 22.43;

MS (EI) m/z = 289.01 (M<sup>+</sup>).



#### **N-(3-Chloro-4-methylphenyl)benzamide (3af)<sup>[9]</sup>**

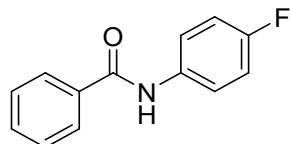
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 2-chloro-1-methyl-4-nitrobenzene (172 mg, 1.0 mmol), the product **3af** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (194 mg, 0.79 mmol, 79%).

m.p. 120–121 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.32 (s, 1H), 7.97 – 7.94 (m, 3H), 7.64 – 7.58 (m, 2H), 7.55 – 7.51 (m, 2H), 7.31 (dd, *J* = 8.3, 0.8 Hz, 1H), 2.90 (s, 3H);

$^{13}\text{C}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  165.57, 138.33, 134.63, 132.87, 131.70, 131.04, 130.24, 128.41, 127.64, 120.19, 118.86, 18.96;

MS (EI) m/z = 245.06 ( $\text{M}^+$ ).



**N-(4-Fluorophenyl)benzamide (3ag)<sup>[2]</sup>**

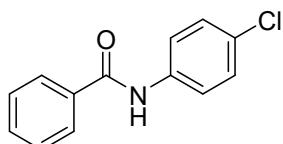
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-fluoro-4-nitrobenzene (141 mg, 1.0 mmol), the product **3ag** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (148 mg, 0.69 mmol, 69%).

m.p. 177–178 °C;

$^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  10.30 (s, 1H), 7.97 – 7.94 (m, 2H), 7.82 – 7.78 (m, 2H), 7.61 – 7.57 (m, 1H), 7.55 – 7.51 (m, 2H), 7.22 – 7.17 (m, 2H);

$^{13}\text{C}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  165.47, 158.29 (d,  $J$  = 240.7 Hz), 135.53 (d,  $J$  = 7.7 Hz), 134.81, 131.58, 128.39, 127.62, 122.17 (d,  $J$  = 10.1 Hz), 115.17 (d,  $J$  = 21.4 Hz);

MS (EI) m/z = 215.07 ( $\text{M}^+$ ).



**N-(4-Chlorophenyl)benzamide (3ah)<sup>[2]</sup>**

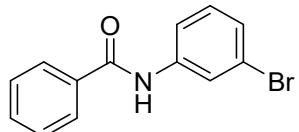
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-chloro-4-nitrobenzene (158 mg, 1.0 mmol), the product **3ah** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (136 mg, 0.59 mmol, 59%).

m.p. 191–192 °C;

$^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  10.37 (s, 1H), 7.97 – 7.94 (m, 2H), 7.85 – 7.82 (m, 2H), 7.61 – 7.58 (m, 1H), 7.55 – 7.51 (m, 2H), 7.42 – 7.39 (m, 2H);

$^{13}\text{C}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  165.66, 138.16, 134.72, 131.69, 128.51, 128.41, 127.68, 127.26, 121.84;

MS (EI) m/z = 231.05 ( $\text{M}^+$ ).



**N-(3-Bromophenyl)benzamide (3ai)<sup>[2]</sup>**

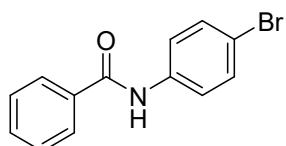
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-bromo-3-nitrobenzene (202 mg, 1.0 mmol), the product **3ai** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (170 mg, 0.62 mmol, 62%).

m.p. 132–133 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.40 (s, 1H), 8.14 (t, *J* = 1.9 Hz, 1H), 7.97 – 7.96 (m, 2H), 7.79 – 7.77 (m, 1H), 7.62 – 7.58 (m, 1H), 7.56 – 7.52 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.30 – 7.28 (m, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.78, 140.82, 134.56, 131.78, 130.58, 128.42, 127.71, 126.20, 122.56, 121.42, 118.99;

MS (EI) m/z = 274.99 (M<sup>+</sup>).



**N-(4-Bromophenyl)benzamide (3aj)<sup>[2]</sup>**

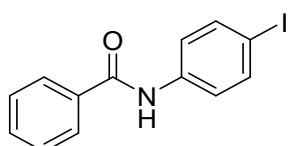
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-bromo-4-nitrobenzene (202 mg, 1.0 mmol), the product **3aj** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (181 mg, 0.66 mmol, 66%).

m.p. 201–203 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.37 (s, 1H), 7.96 – 7.94 (m, 2H), 7.79 – 7.76 (m, 2H), 7.62 – 7.58 (m, 1H), 7.55 – 7.52 (m, 4H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.65, 138.58, 134.70, 131.70, 131.42, 128.40, 127.67, 122.20, 115.31;

MS (EI) m/z = 274.99 (M<sup>+</sup>).



**N-(4-Iodophenyl)benzamide (3ak)<sup>[2]</sup>**

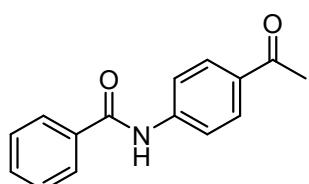
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol), the product **3ak** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (210 mg, 0.65 mmol, 65%).

m.p. 218–220 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.34 (s, 1H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.69 (d, *J* = 8.9 Hz, 2H), 7.64 (d, *J* = 8.9 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.54 – 7.52 (m, 2H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.64, 139.05, 137.26, 134.72, 131.69, 128.40, 127.67, 122.45, 87.30;

MS (EI) m/z = 322.98 (M<sup>+</sup>).



#### **N-(4-Acetylphenyl)benzamide (3al)<sup>[5]</sup>**

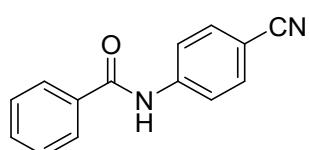
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-(4-nitrophenyl)ethan-1-one (165 mg, 1.0 mmol), the product **3al** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (125 mg, 0.52 mmol, 52%).

m.p. 197–198 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.56 (s, 1H), 7.99 – 7.94 (m, 6H), 7.63 – 7.60 (m, 1H), 7.57 – 7.53 (m, 2H), 2.55 (s, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 196.58, 165.99, 143.62, 134.58, 132.01, 131.88, 129.29, 128.44, 127.81, 119.43, 26.46;

MS (EI) m/z = 239.09 (M<sup>+</sup>).



#### **N-(4-Cyanophenyl)benzamide (3am)<sup>[2]</sup>**

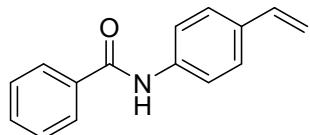
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 4-nitrobenzonitrile (148 mg, 1.0 mmol), the product **3am** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (162 mg, 0.73 mmol, 73%).

m.p. 168–170 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.64 (s, 1H), 8.01 – 7.99 (m, 2H), 7.97 – 7.95 (m, 2H), 7.83 – 7.81 (m, 2H), 7.64 – 7.61 (m, 1H), 7.57 – 7.54 (m, 2H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 166.19, 143.51, 134.39, 133.12, 132.04, 128.49, 127.84, 120.17, 119.08, 105.34;

MS (EI) m/z = 222.08 (M<sup>+</sup>).



**N-(4-Vinylphenyl)benzamide (3an)<sup>[5]</sup>**

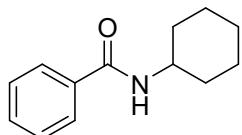
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-nitro-4-vinylbenzene (149 mg, 1.0 mmol), the product **3an** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (87 mg, 0.39 mmol, 39%).

m.p. 149–151 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 10.29 (s, 1H), 7.94 – 7.96 (m, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.52 – 7.55 (m, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.70 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.77 (dd, *J* = 17.7, 2.2 Hz, 1H), 5.20 (dd, *J* = 11.0, 1.0 Hz, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.50, 138.92, 136.19, 134.90, 132.53, 131.57, 128.38, 127.64, 126.44, 120.23, 112.94;

MS (EI) m/z = 223.10 (M<sup>+</sup>).



**N-Cyclohexylbenzamide (3ao)<sup>[2]</sup>**

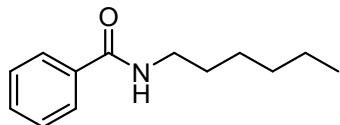
According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and nitrocyclohexane (129 mg, 1.0 mmol), the product **3ao** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a white solid (120 mg, 0.59 mmol, 59%).

m.p. 148–149 °C;

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.82 (m, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.45 – 7.42 (m, 2H), 3.79 – 3.72 (m, 1H), 1.83 – 1.80 (m, 2H), 1.74 – 1.72 (m, 2H), 1.60 (d, *J* = 12.3 Hz, 1H), 1.35 – 1.23 (m, 4H), 1.16 – 1.11 (m, 1H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 165.31, 134.90, 130.87, 128.09, 127.24, 48.30, 32.41, 25.26, 24.95;

MS (EI) m/z = 203.13 (M<sup>+</sup>).



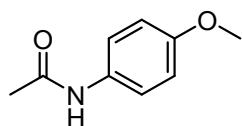
**N-Hexylbenzamide (3ap)<sup>[2]</sup>**

According to the general procedure using phenyl(1H-pyrazol-1-yl)methanone (172 mg, 1.0 mmol) and 1-nitrohexane (131 mg, 1.0 mmol), the product **3ap** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (9:1) and obtained as a yellow oil (141 mg, 0.69 mmol, 69%).

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 8.43 (t, *J* = 5.7 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.44 (t, 7.3 Hz, 2H), 3.29 – 3.22 (m, 2H), 1.51 (quin, *J* = 7.7 Hz, 2H), 1.34 – 1.23 (m, 6H), 0.89 – 0.82 (m, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 166.04, 134.75, 130.88, 128.14, 127.10, 39.20, 31.04, 29.11, 26.19, 22.07, 13.87;

MS (EI) m/z = 205.15(M<sup>+</sup>).



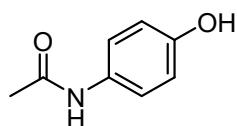
**N-(4-methoxyphenyl)acetamide (3xt)<sup>[10]</sup>**

According to the general procedure using 1-(1H-pyrazol-1-yl)ethan-1-one (110 mg, 1.0 mmol) and 1-methoxy-4-nitrobenzene (153 mg, 1.0 mmol), the product **3xt** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (3:1) and obtained as a brown solid (135 mg, 0.82 mmol, 82%).

<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 9.76 (s, 1H), 7.49 – 7.46 (m, 2H), 6.87 – 6.84 (m, 2H), 3.70 (s, 3H), 2.00 (s, 3H);

<sup>13</sup>C NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 167.72, 155.01, 132.54, 120.53, 113.77, 55.11, 23.79;

MS (EI) m/z = 165.08(M<sup>+</sup>).



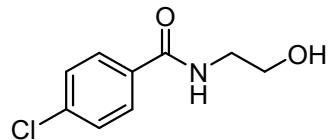
**N-(4-hydroxyphenyl)acetamide (3xu)<sup>[10]</sup>**

4-Nitrophenol (139 mg, 1.0 mmol) and  $B_2(OH)_4$  (269 mg, 3.0 mmol, 3.0 equiv) were dissolved in DMF (5 mL, 0.2M) and stirred at 100 °C for 6 h. 1-(1H-pyrazol-1-yl)ethan-1-one (110 mg, 1.0 mmol) was added to the reaction mixture and stirred at 70 °C for 18 h. The product **3xu** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (1:1) and obtained as a brown solid (109 mg, 0.72 mmol, 72%).

$^1H$  NMR (500 MHz,  $(CD_3)_2SO$ )  $\delta$  9.63 (s, 1H), 9.12 (s, 1H), 7.35 – 7.32 (m, 2H), 6.69 – 6.65 (m, 2H), 1.97 (s, 3H);

$^{13}C$  NMR (126 MHz,  $(CD_3)_2SO$ )  $\delta$  167.50, 153.11, 131.04, 120.81, 114.99, 23.74;

MS (EI) m/z = 151.06( $M^+$ ).



#### **4-chloro-N-(2-hydroxyethyl)cyclohexa-2,4-diene-1-carboxamide (3mv)<sup>[11]</sup>**

2-Nitroethan-1-ol (91 mg, 1.0 mmol) and  $B_2(OH)_4$  (269 mg, 3.0 mmol, 3.0 equiv) were dissolved in DMF (5 mL, 0.2M) and stirred at 100 °C for 6 h. (4-chlorophenyl)(1H-pyrazol-1-yl)methanone (207 mg, 1.0 mmol) was added to the reaction mixture and stirred at 70 °C for 18 h. The product **3mv** was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (1:4) and obtained as a white solid (124 mg, 0.62 mmol, 62%).

$^1H$  NMR (500 MHz,  $(CD_3)_2SO$ )  $\delta$  8.55 (t,  $J$  = 5.8 Hz, 1H), 7.93 – 7.90 (m, 2H), 7.58 – 7.55 (m, 2H), 4.77 (t, 5.6 Hz, 1H), 3.56 (q,  $J$  = 6.0 Hz, 2H), 3.37 (q,  $J$  = 6.0 Hz, 2H);

$^{13}C$  NMR (126 MHz,  $(CD_3)_2SO$ )  $\delta$  165.28, 135.90, 133.31, 129.15, 128.30, 59.69, 42.26;

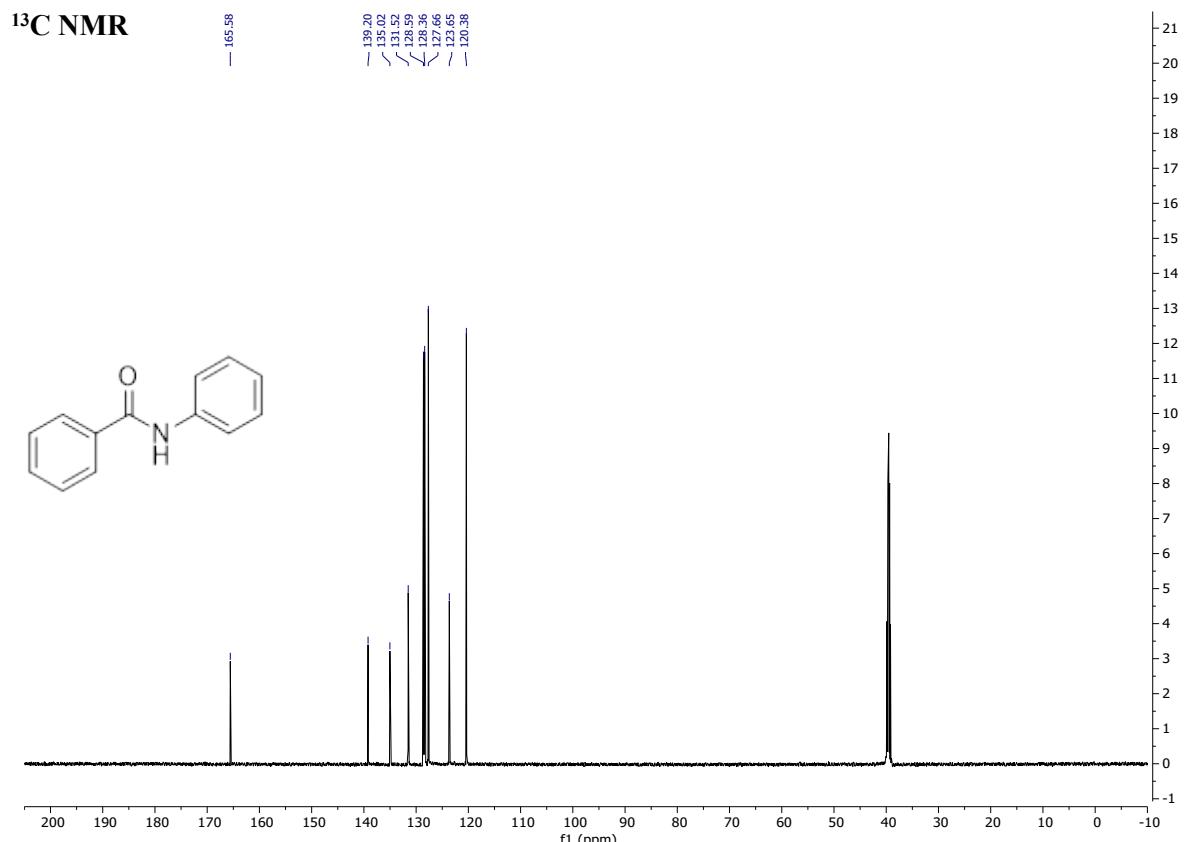
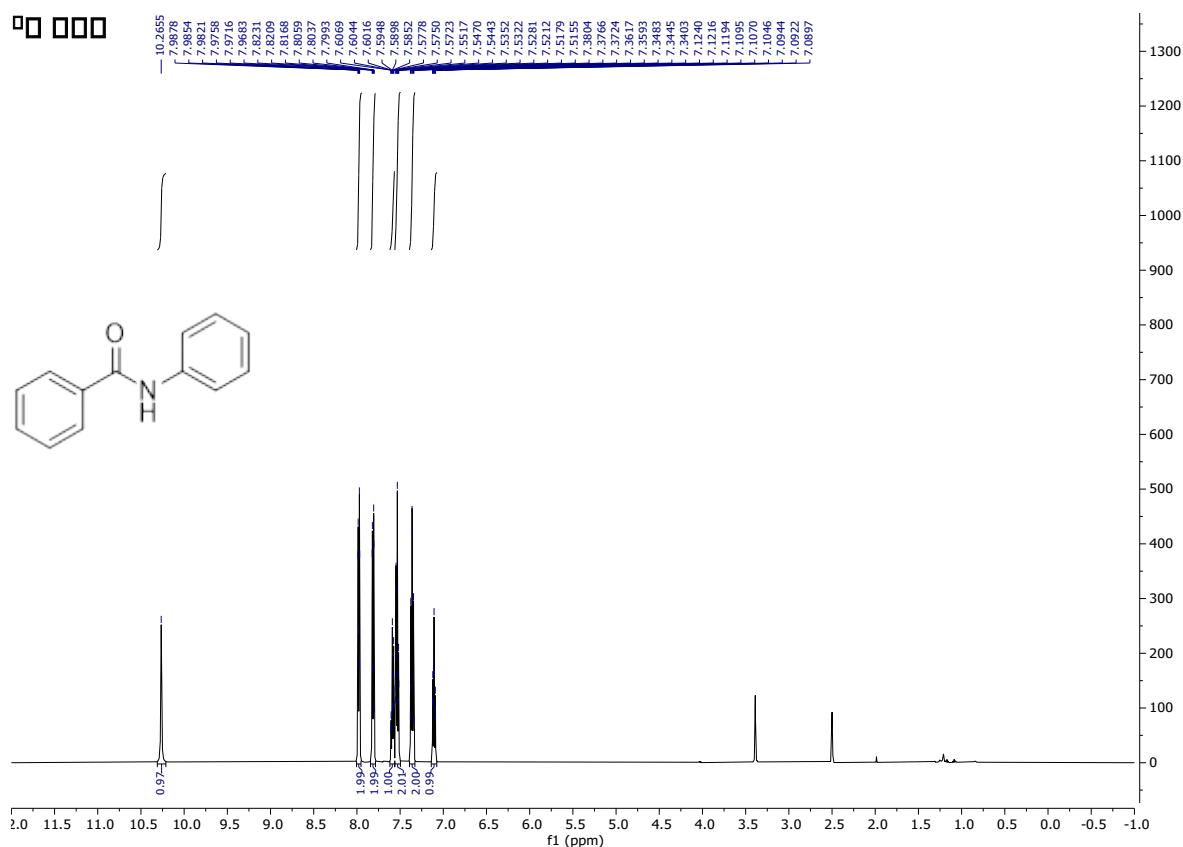
MS (EI) m/z = 201.06 ( $M^+$ ).

## 5. References

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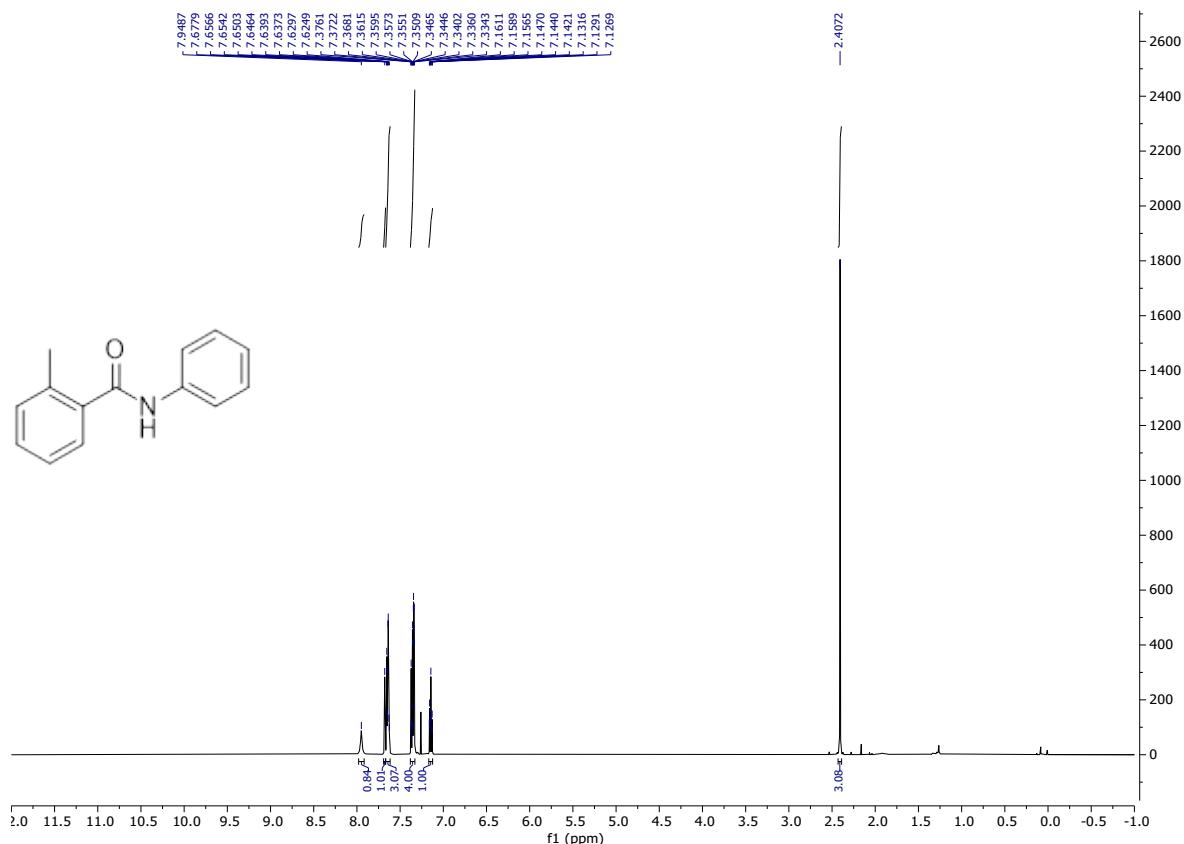
## 6. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products

### *N*-Phenylbenzamide (3aa)

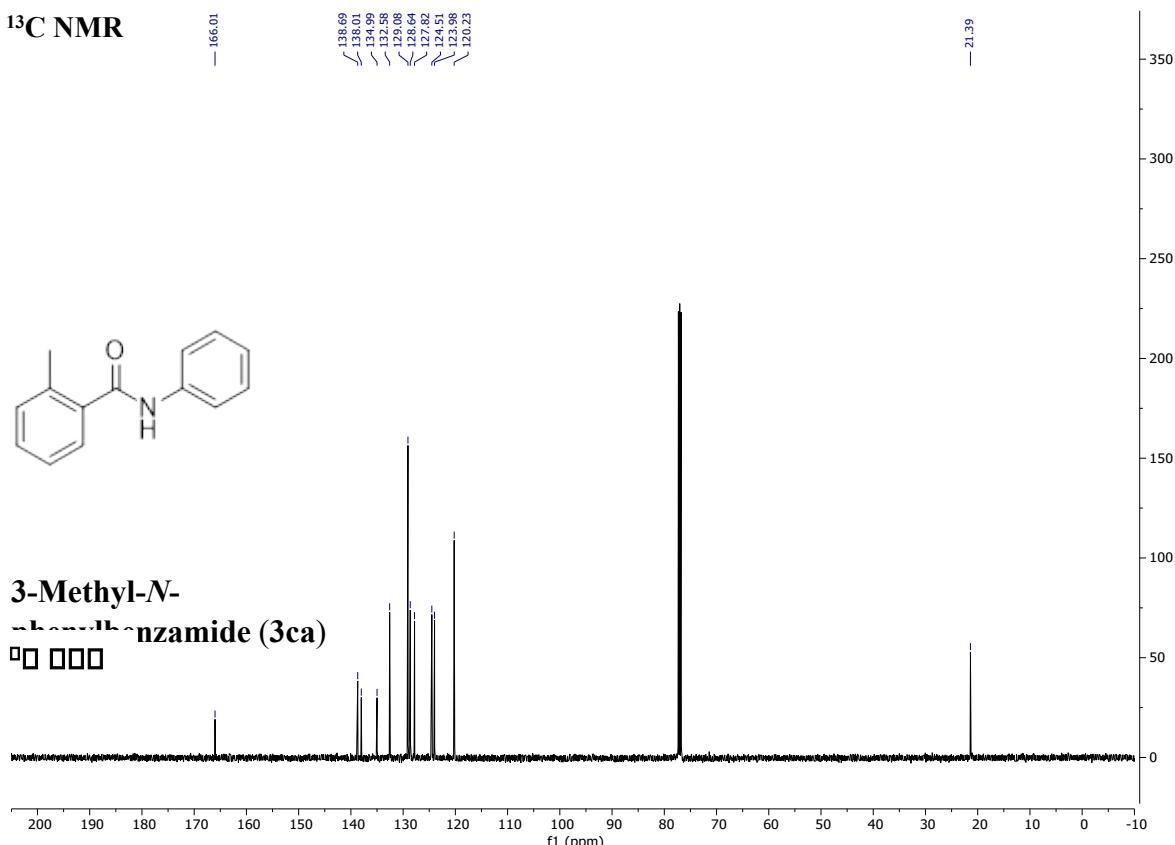


**2-Methyl-N-phenylbenzamide (3ba)**

■■■■■

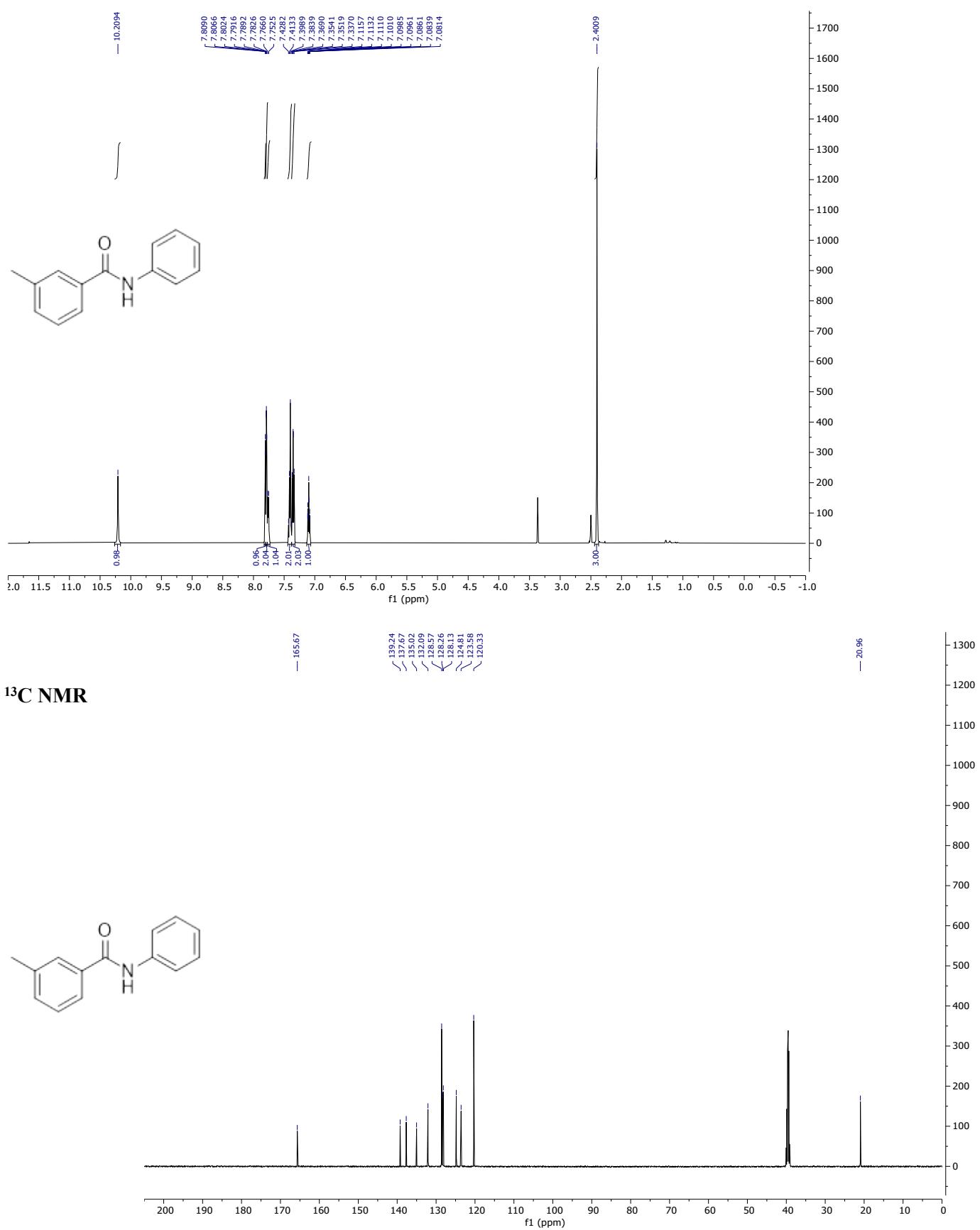


**<sup>13</sup>C NMR**

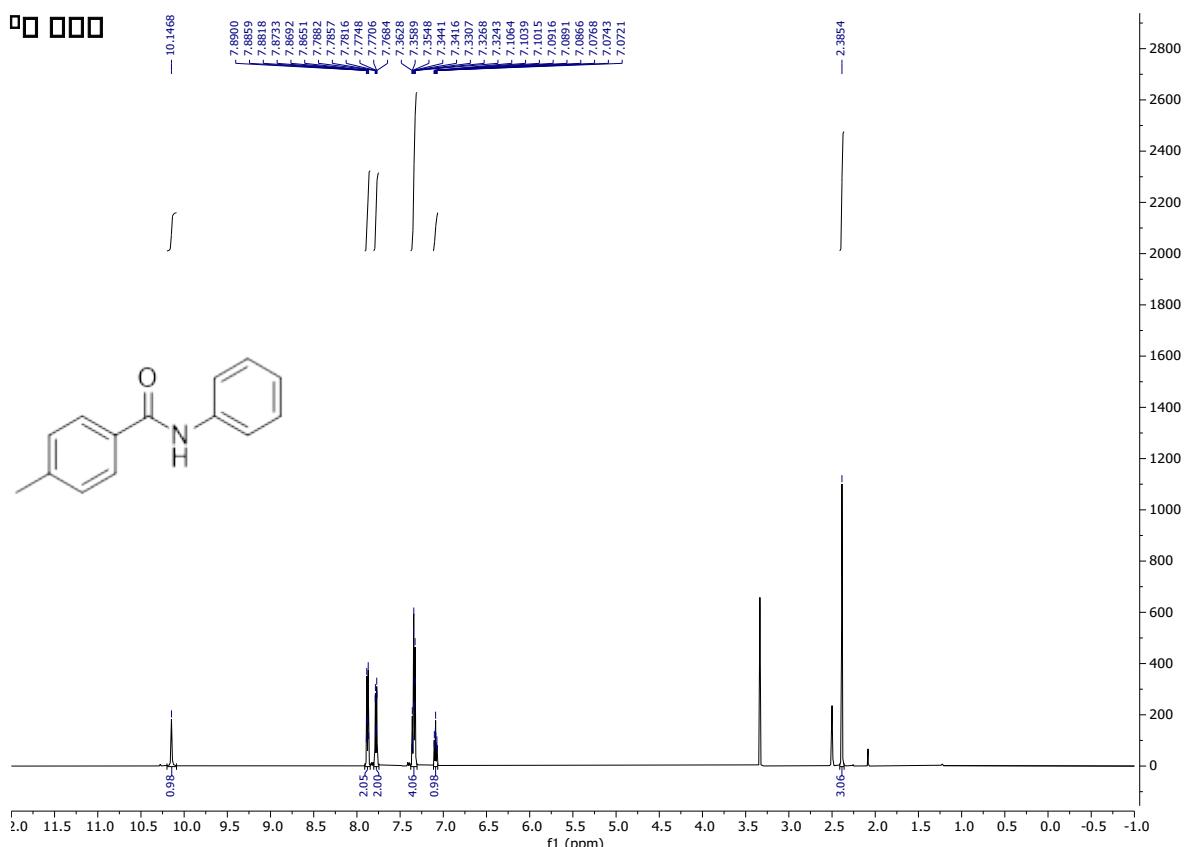


**3-Methyl-N-phenylbenzamide (3ca)**

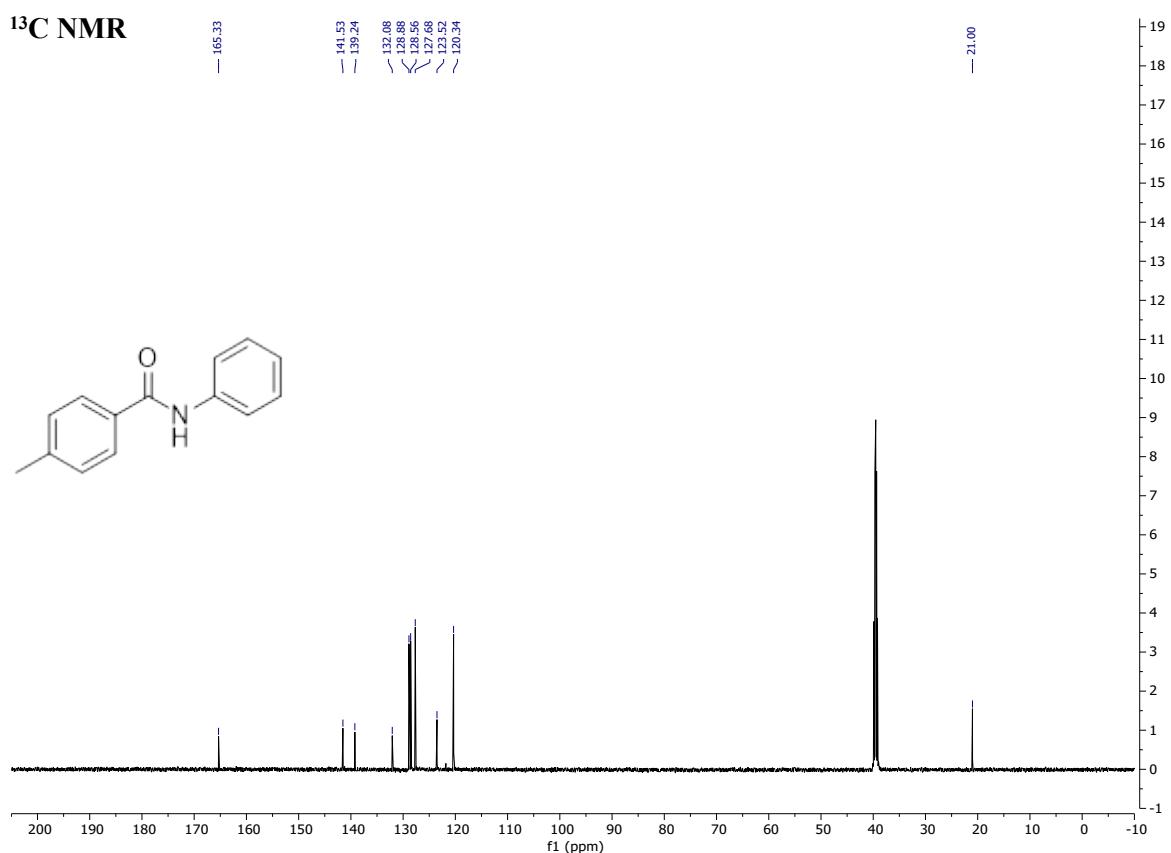
■■■■■



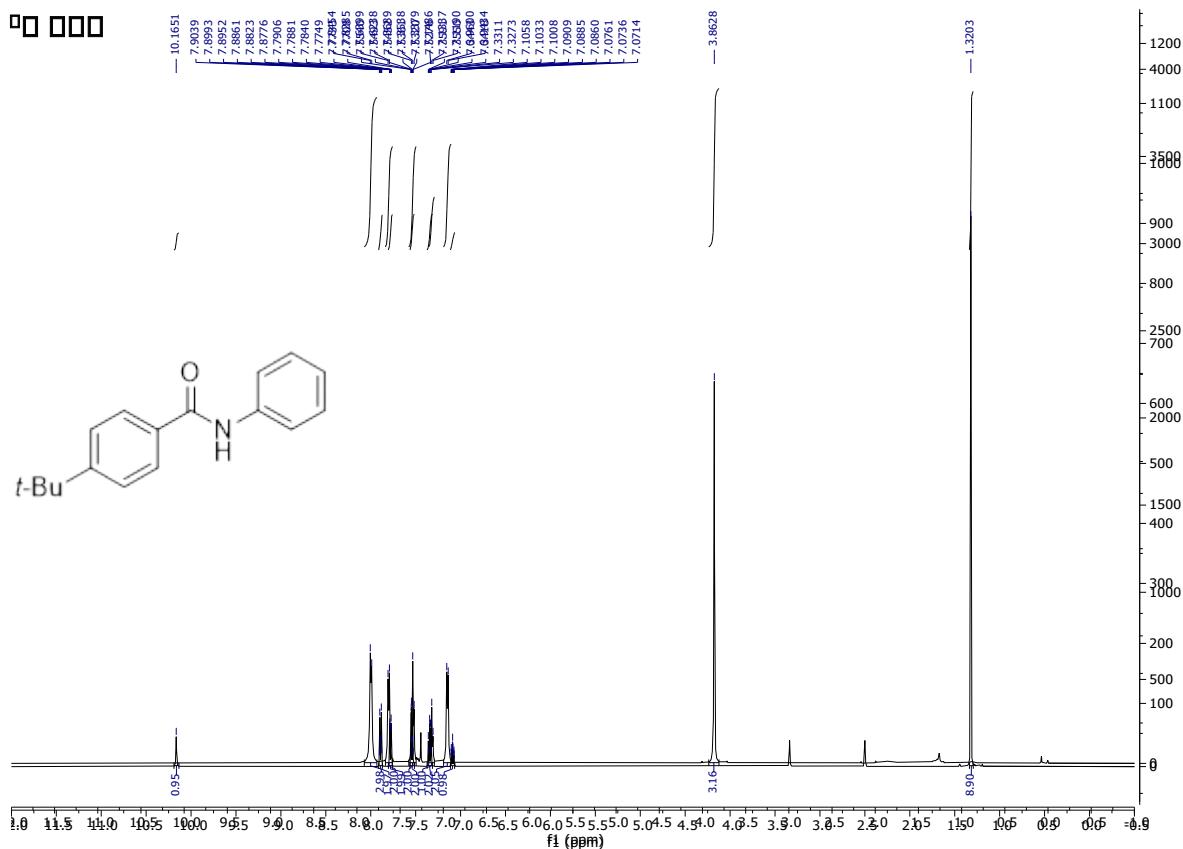
**4-Methyl-N-phenylbenzamide (3da)**



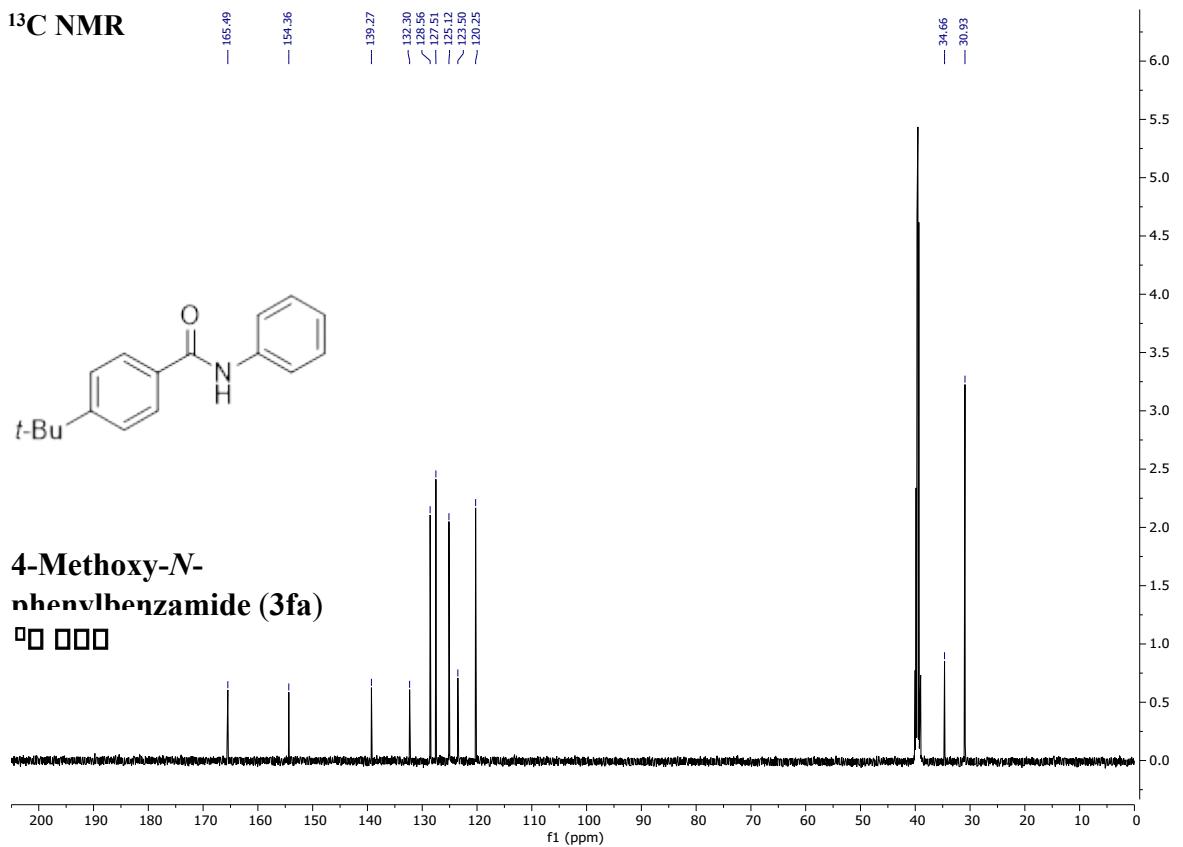
**$^{13}\text{C}$  NMR**

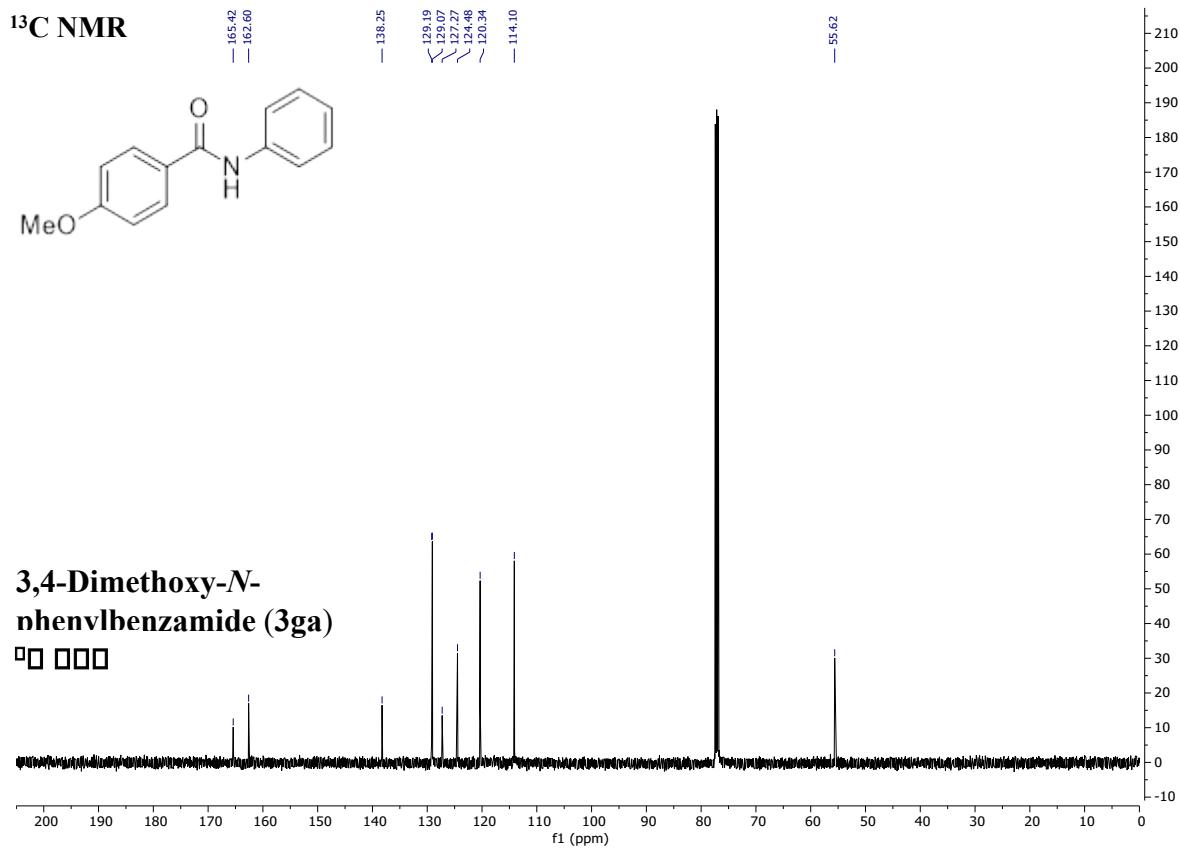
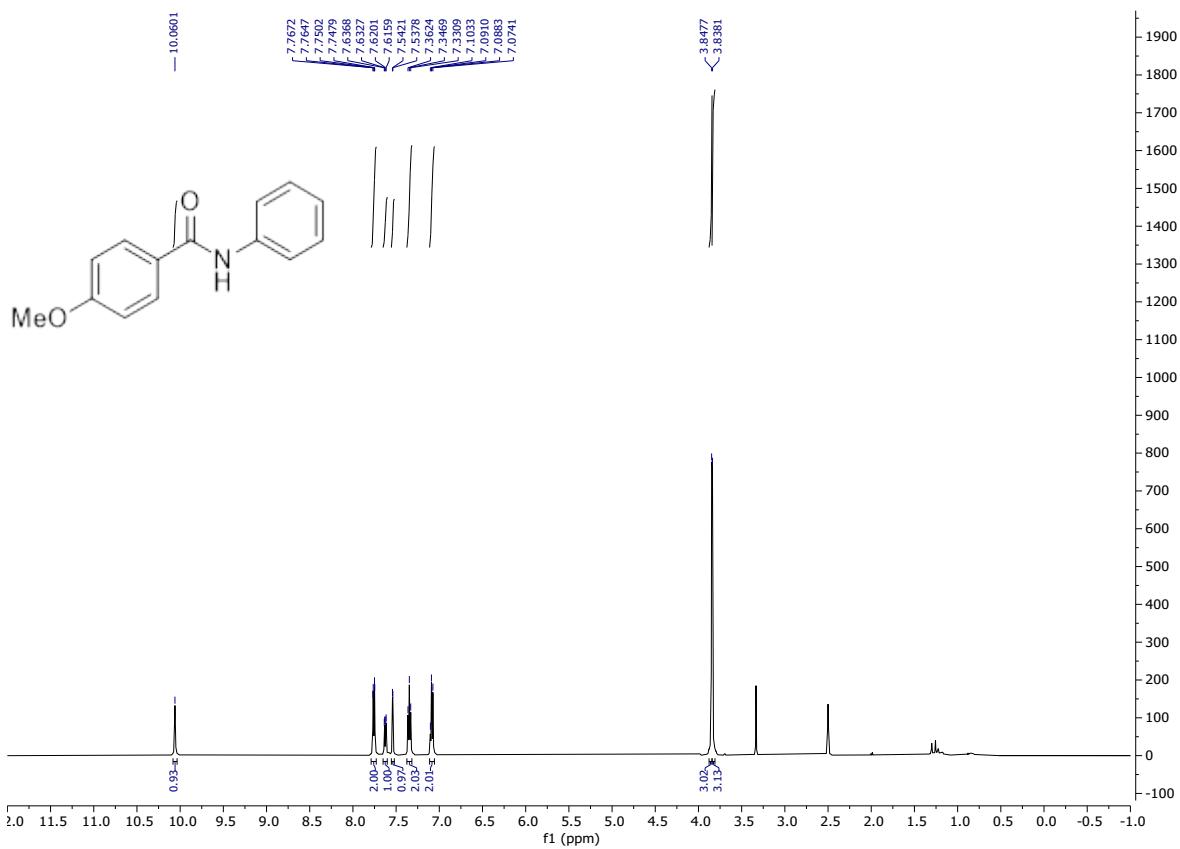


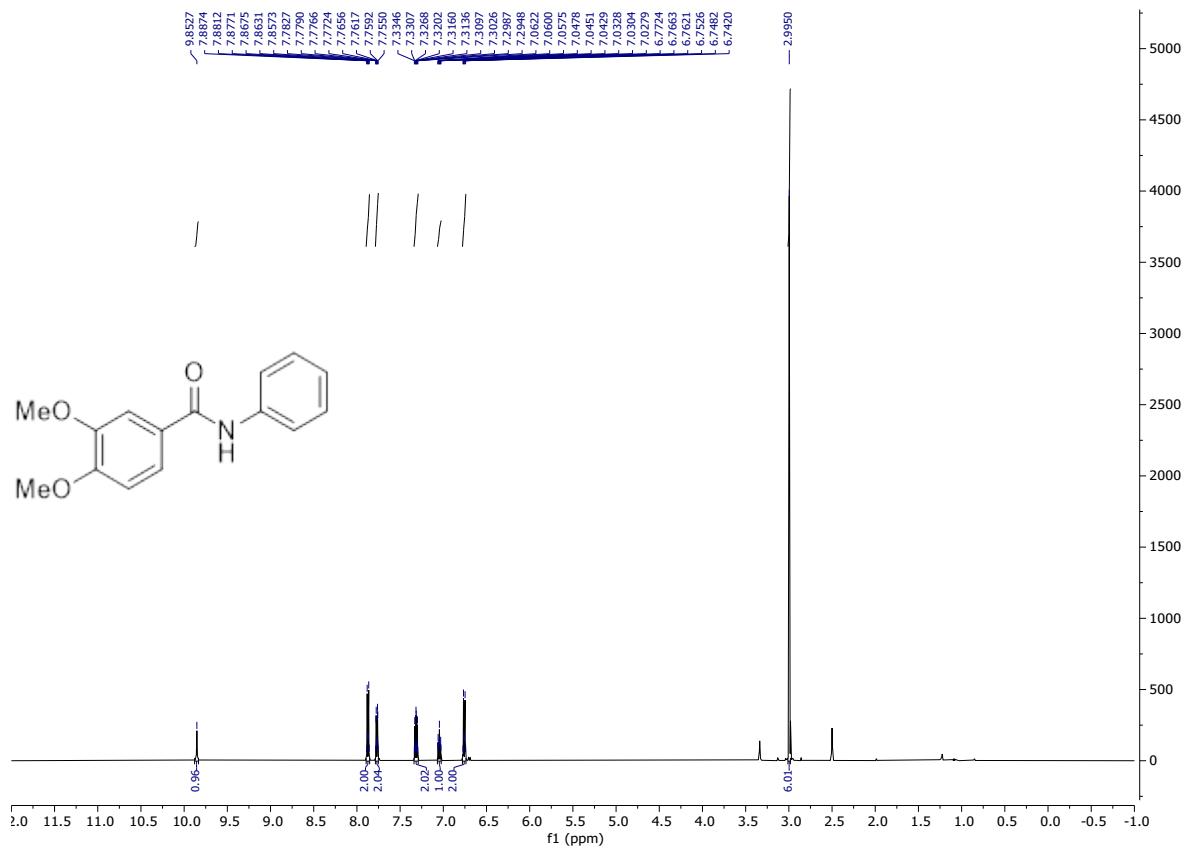
#### **4-(Tert-butyl)-*N*-phenylbenzamide (3ea)**



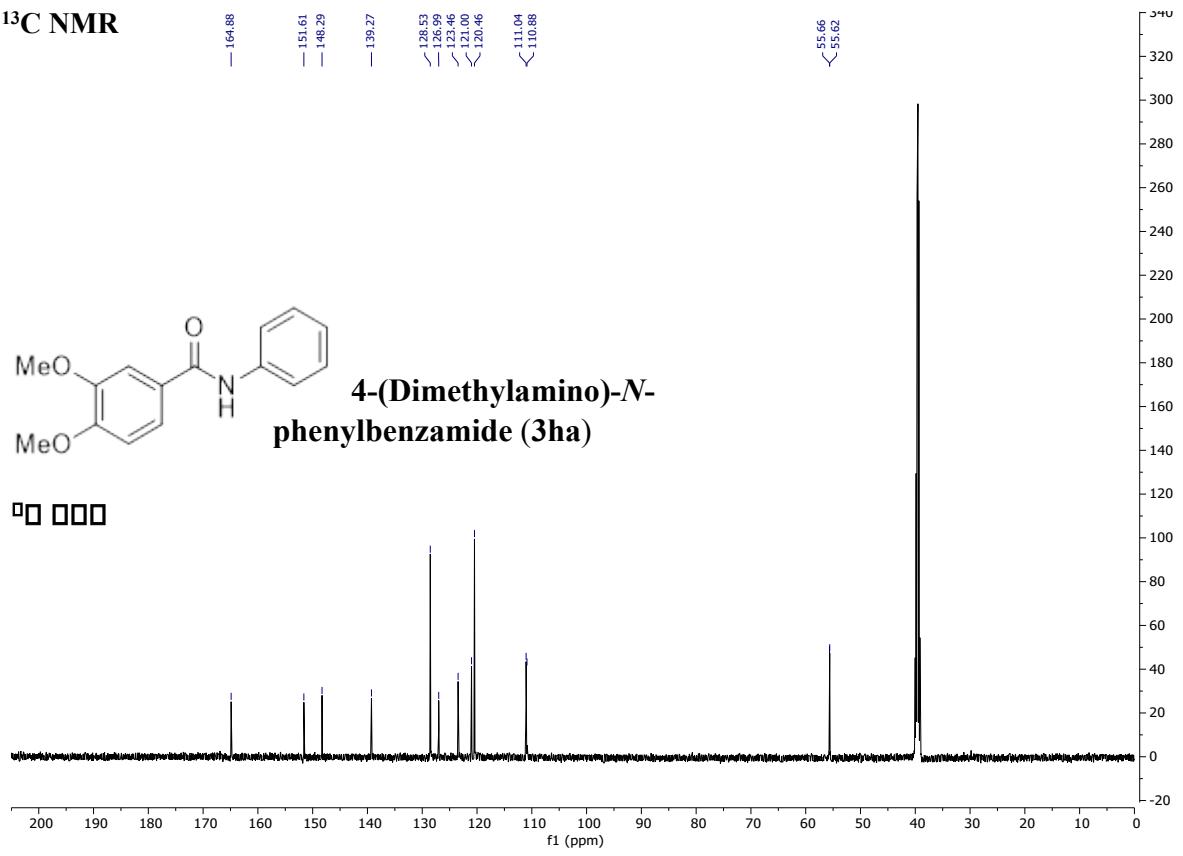
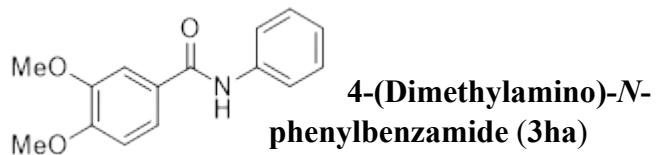
**<sup>13</sup>C NMR**

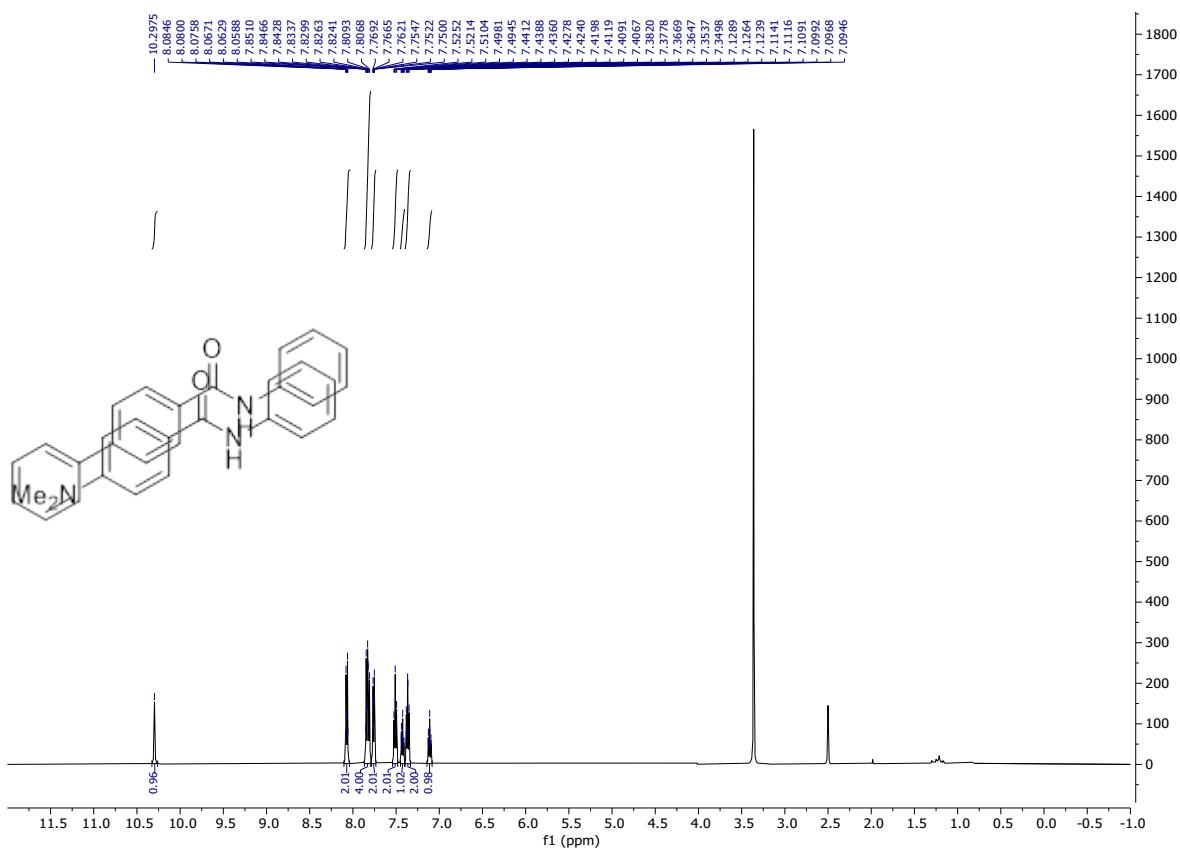




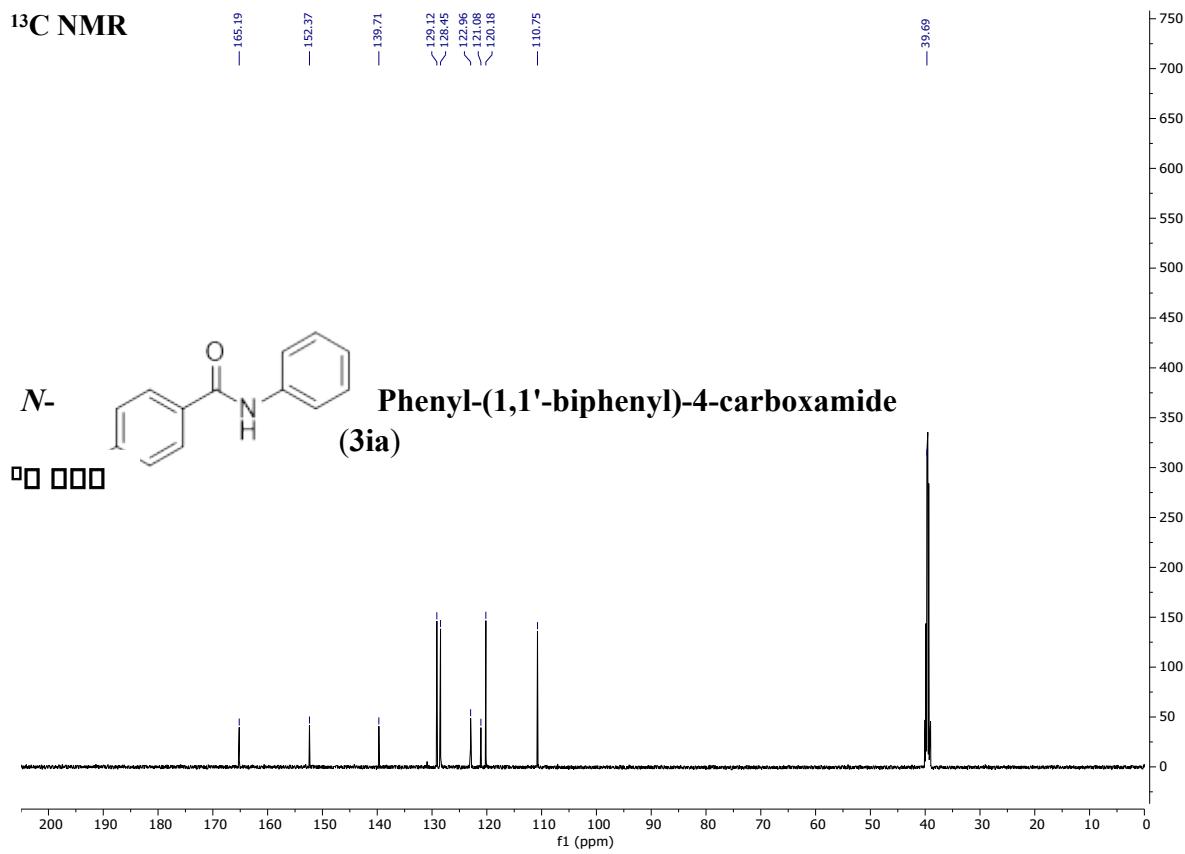


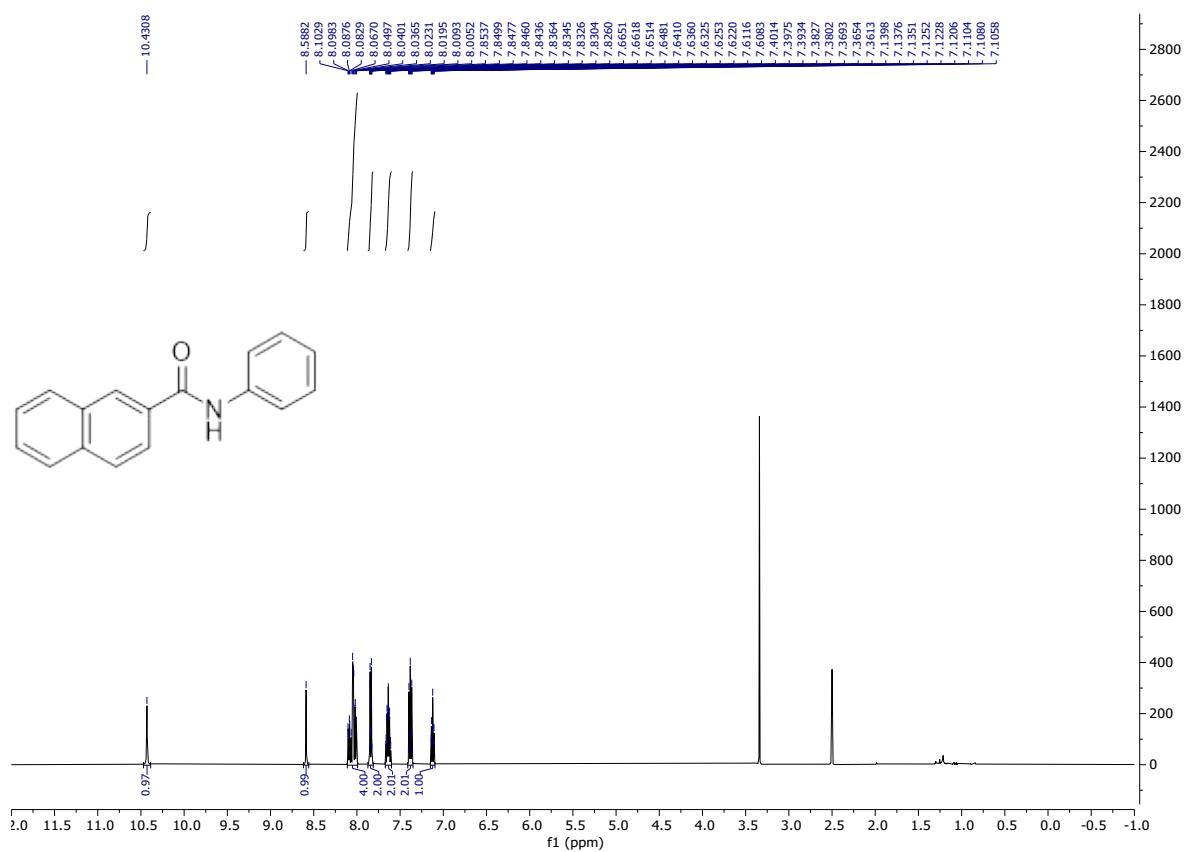
## **<sup>13</sup>C NMR**



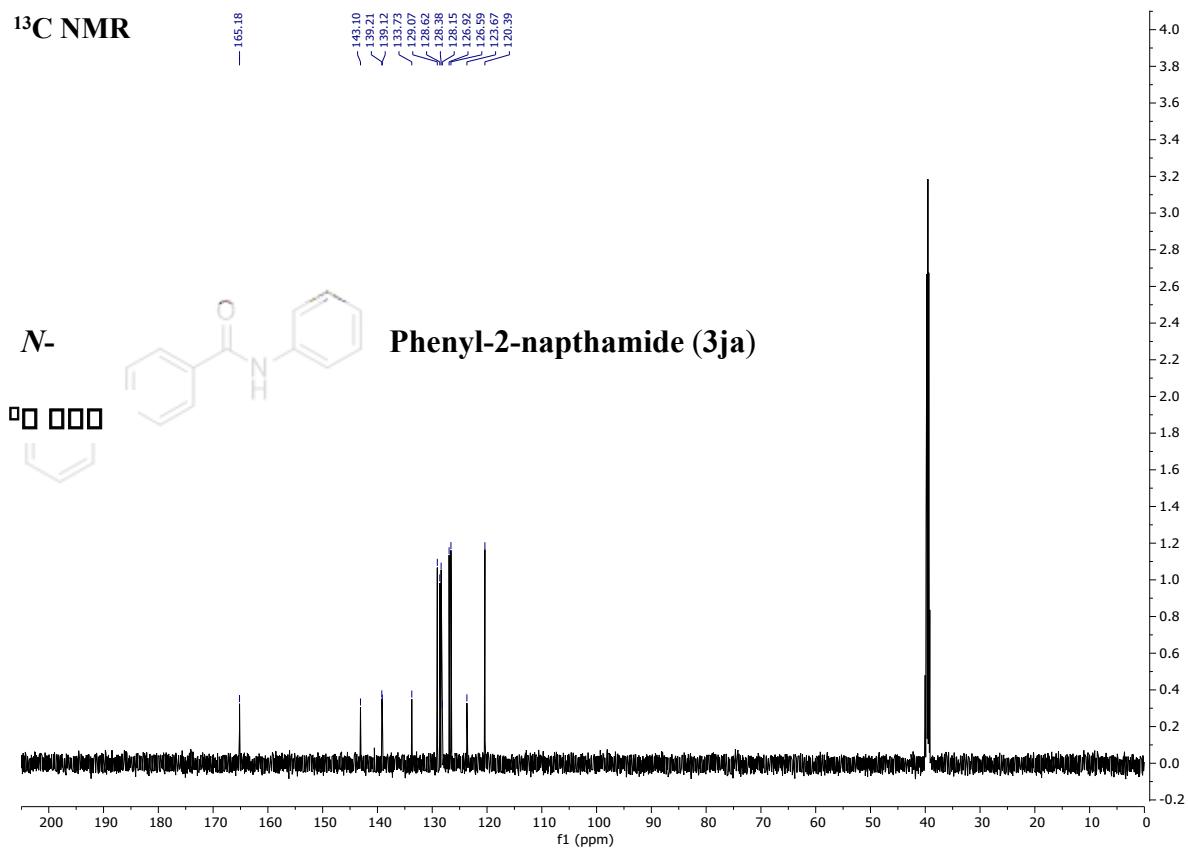


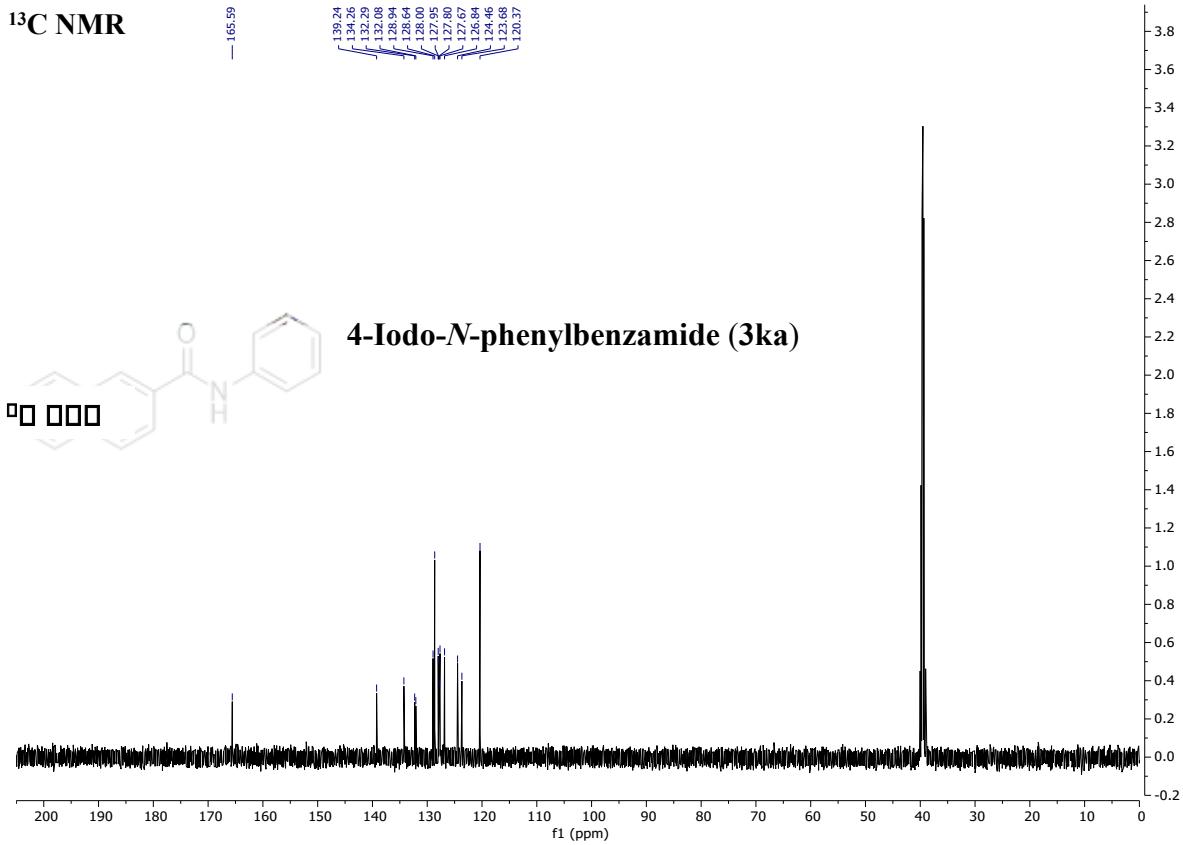
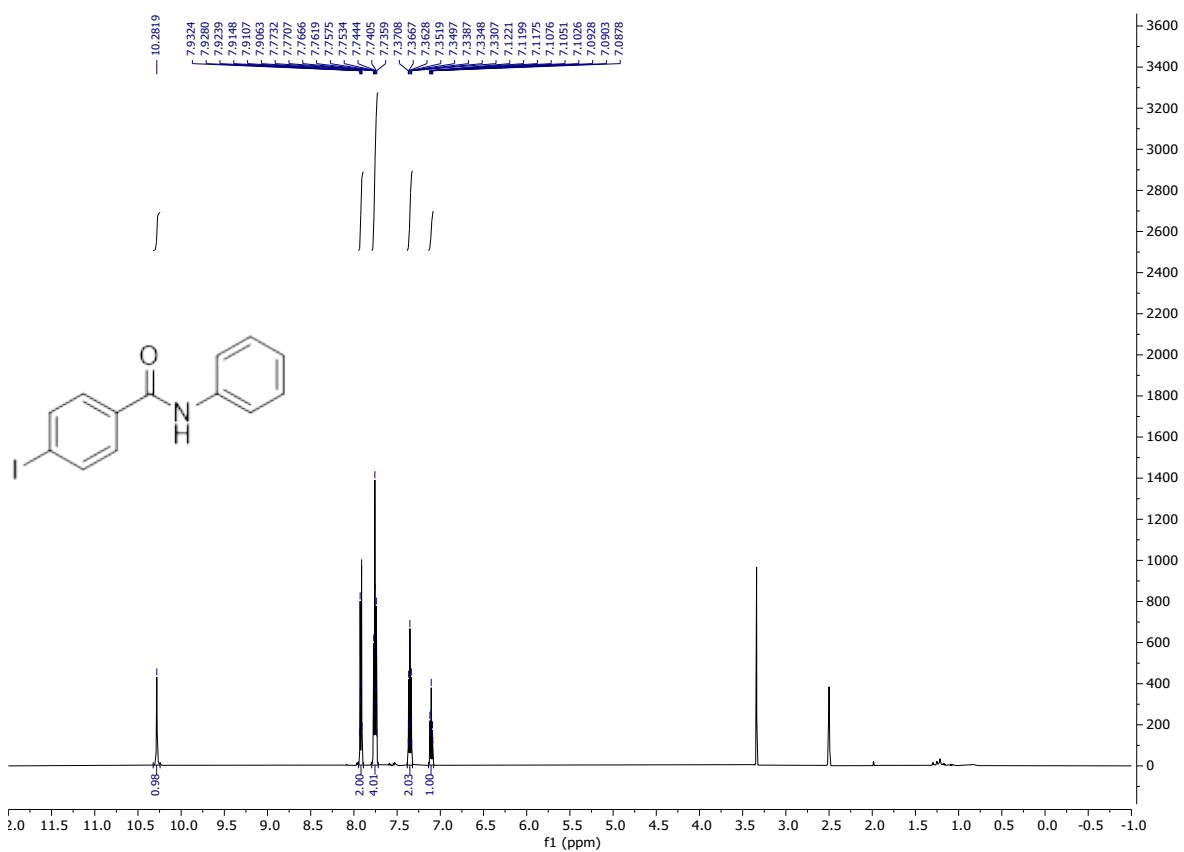
### <sup>13</sup>C NMR

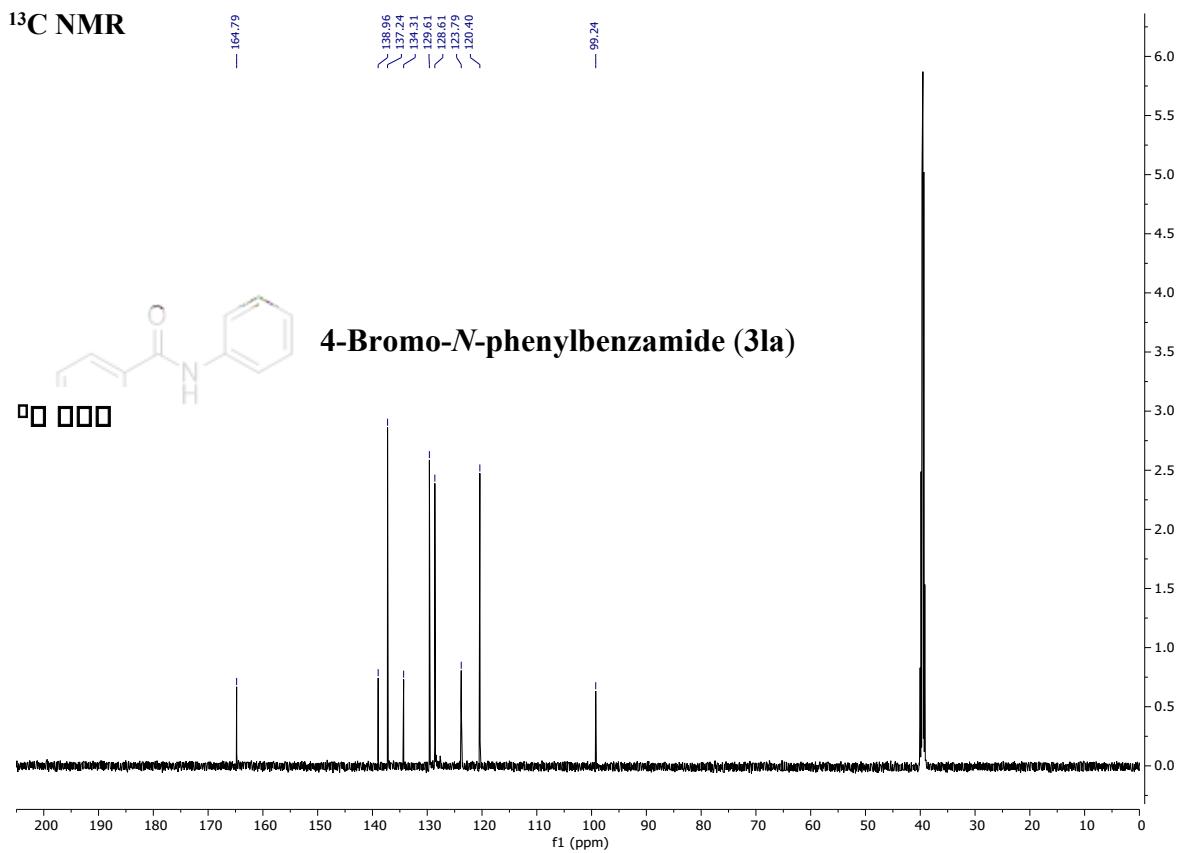
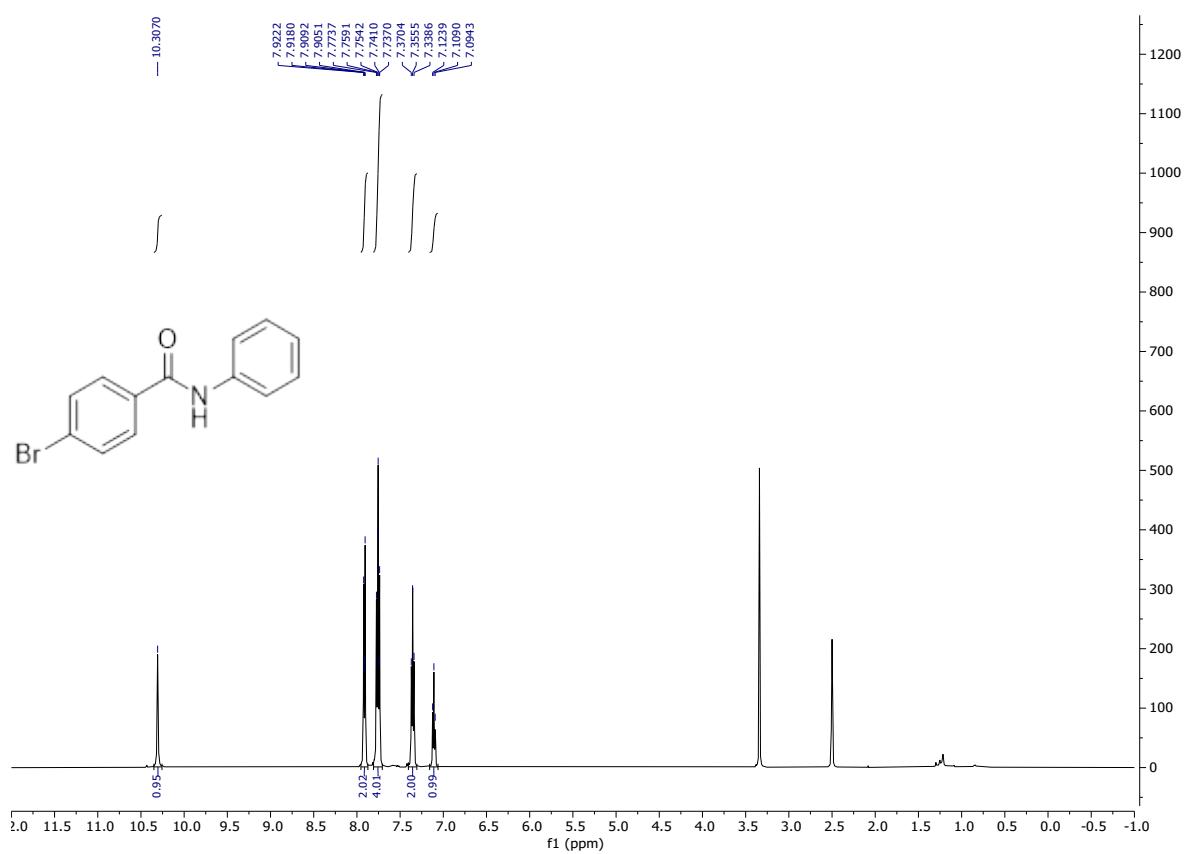




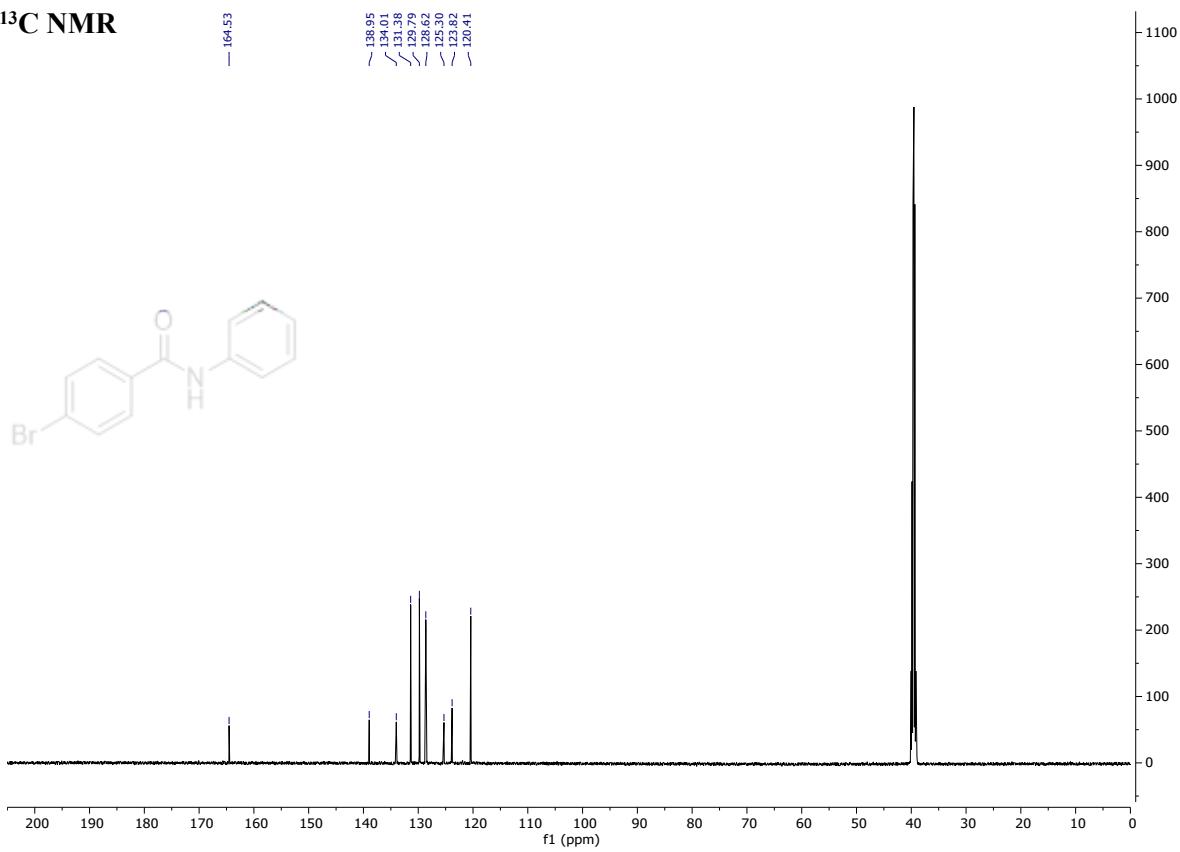
### <sup>13</sup>C NMR



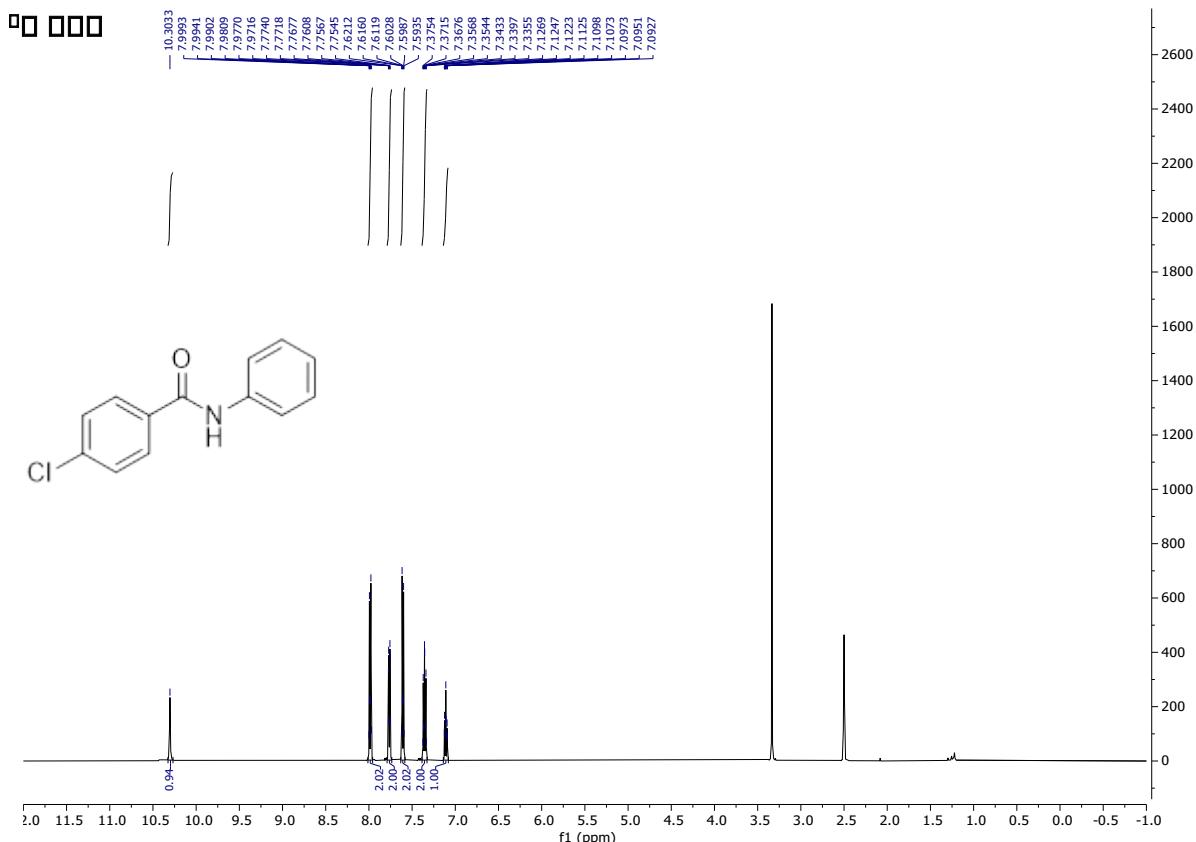




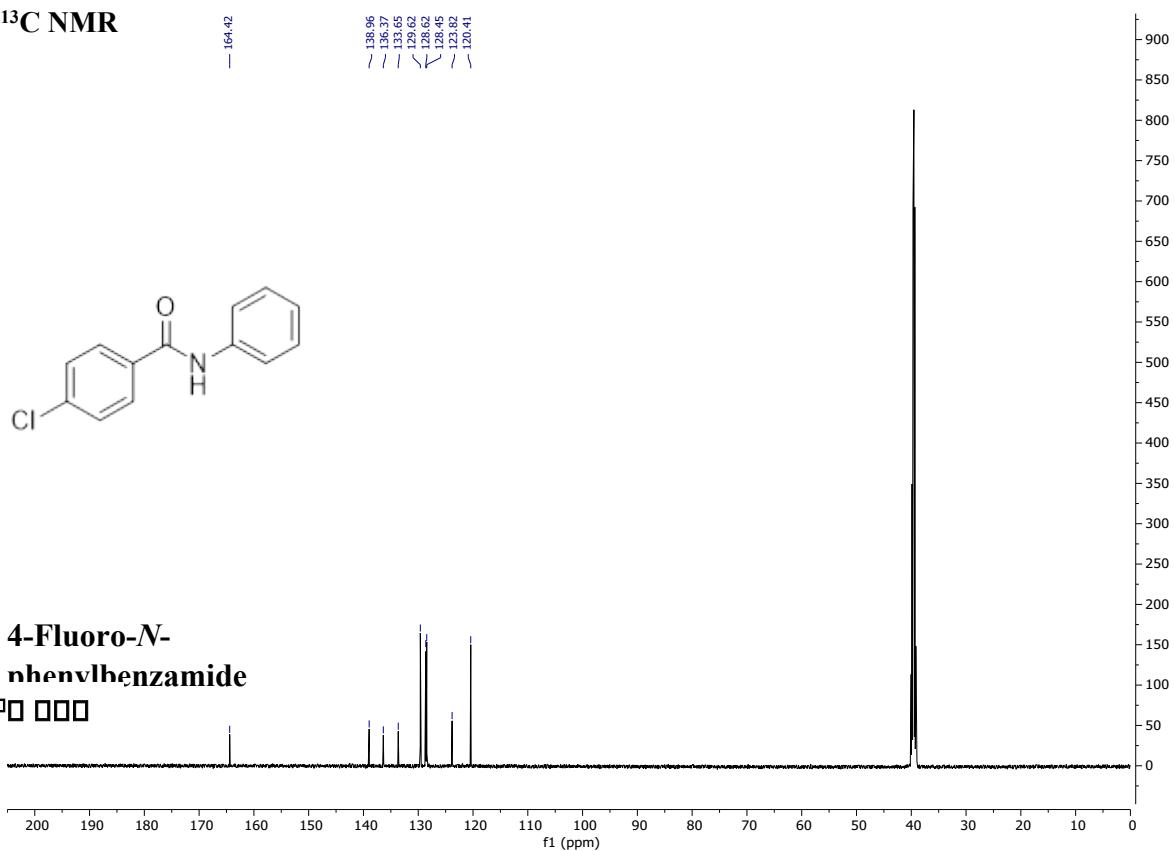
<sup>13</sup>C NMR

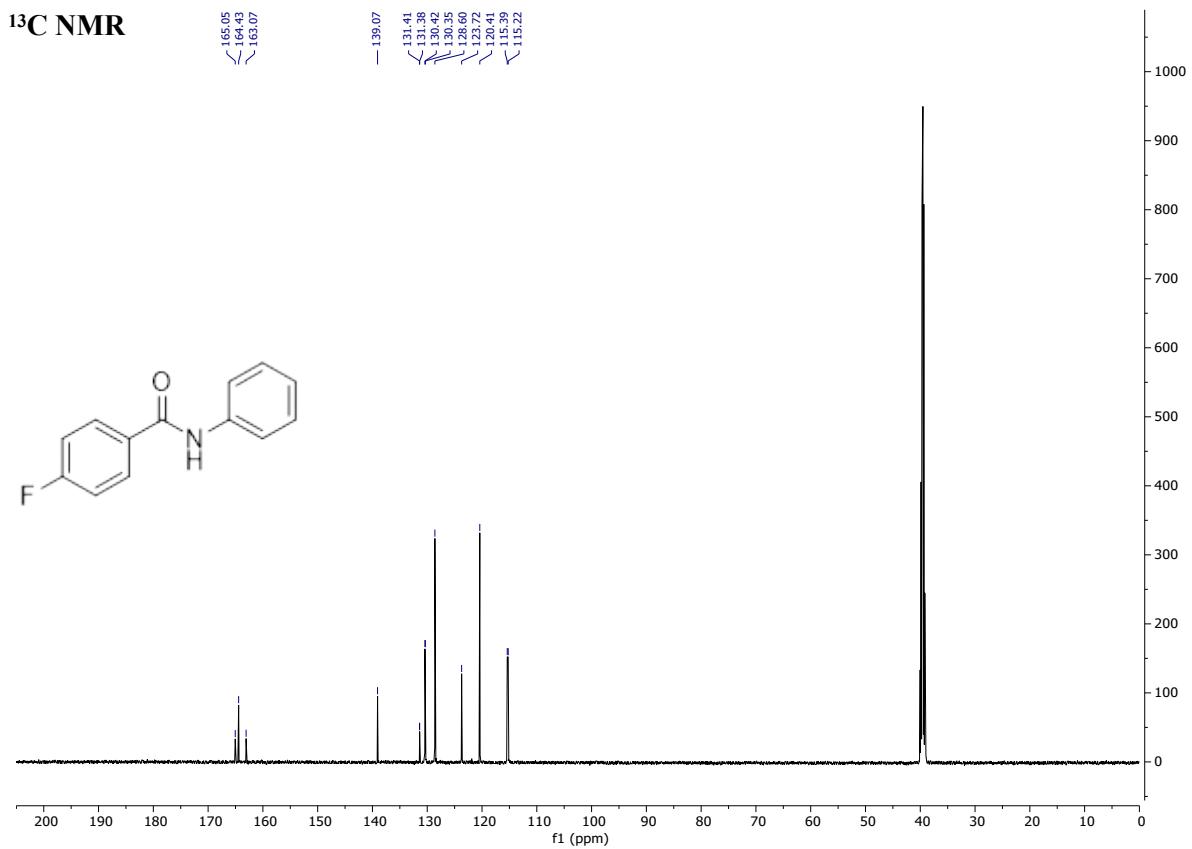
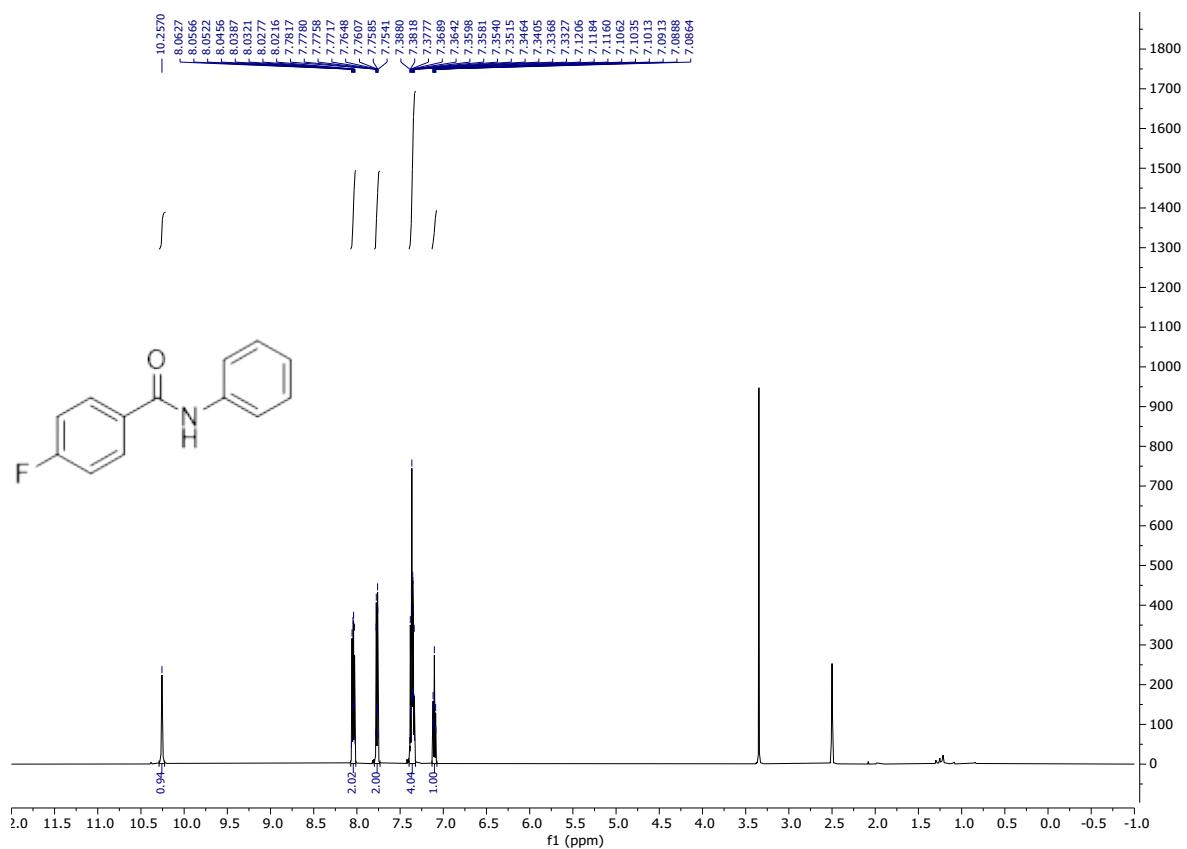


**4-Chloro-N-phenylbenzamide (3ma)**

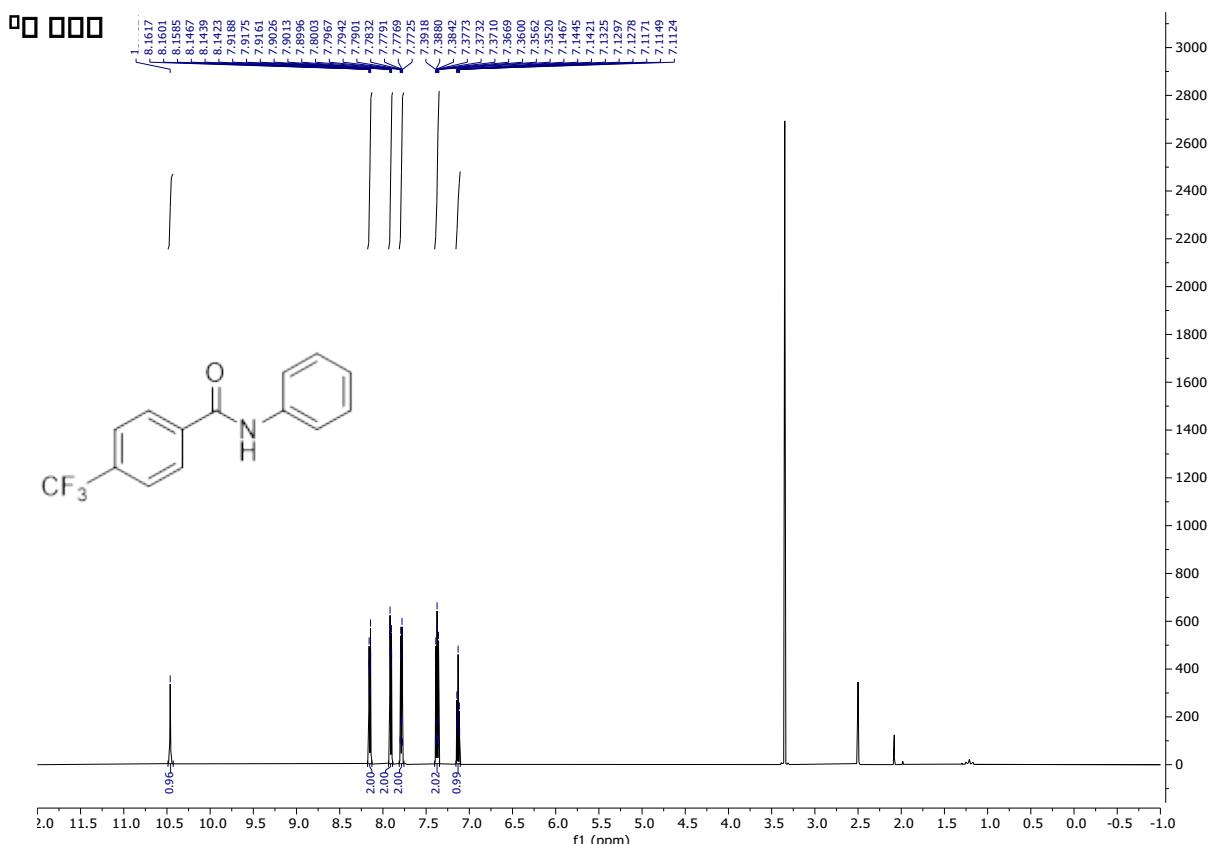


**<sup>13</sup>C NMR**

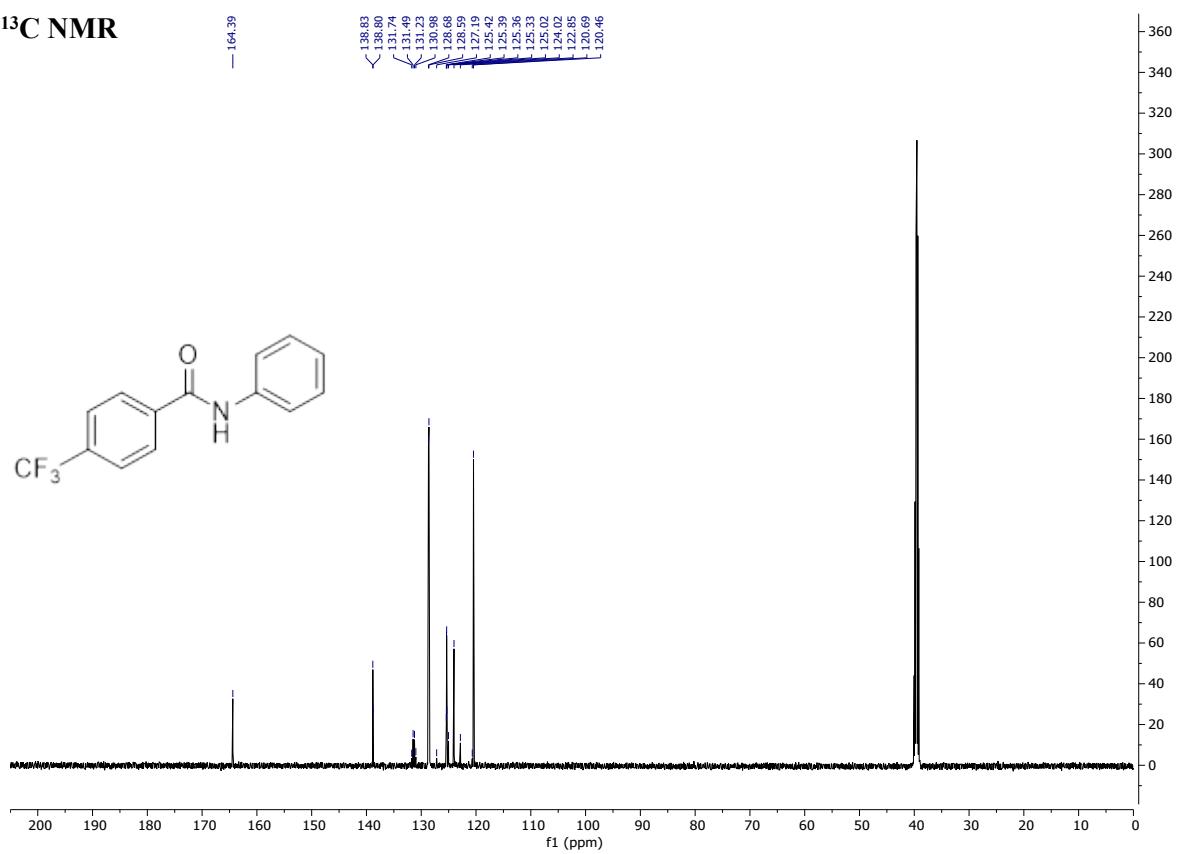




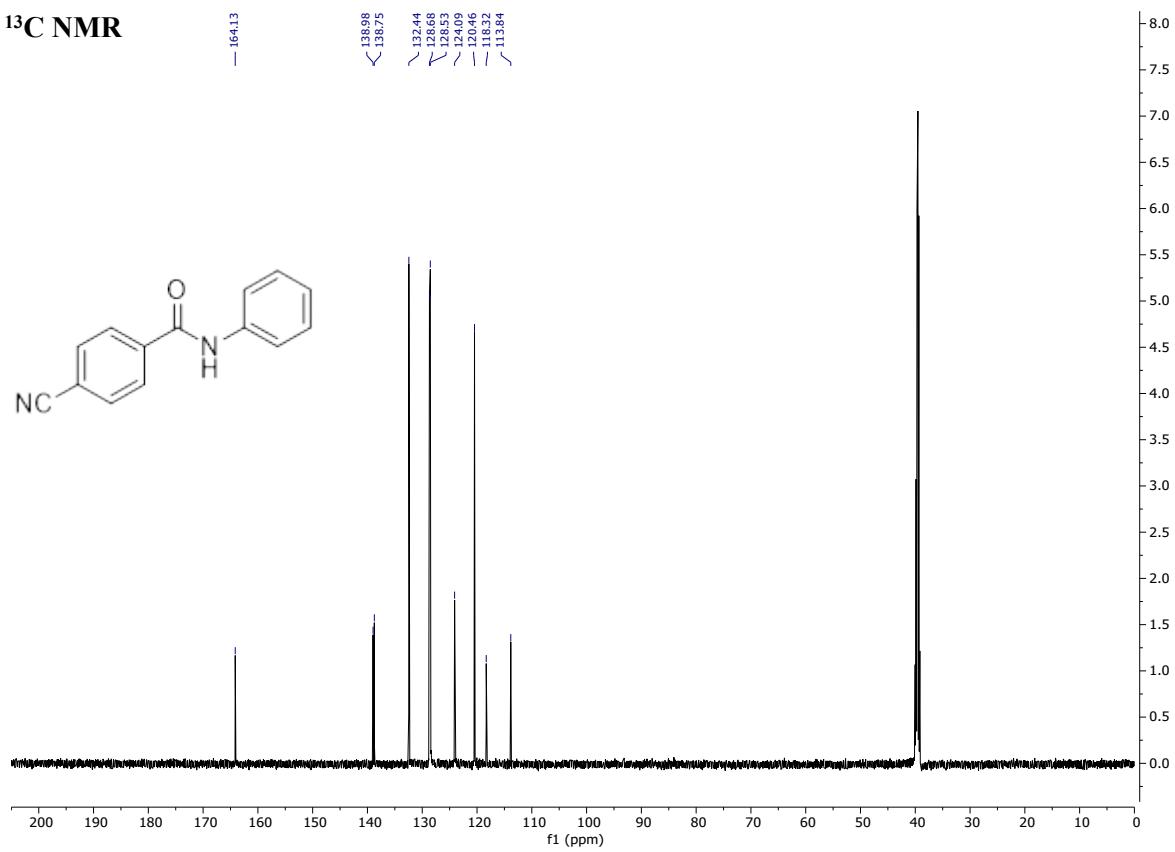
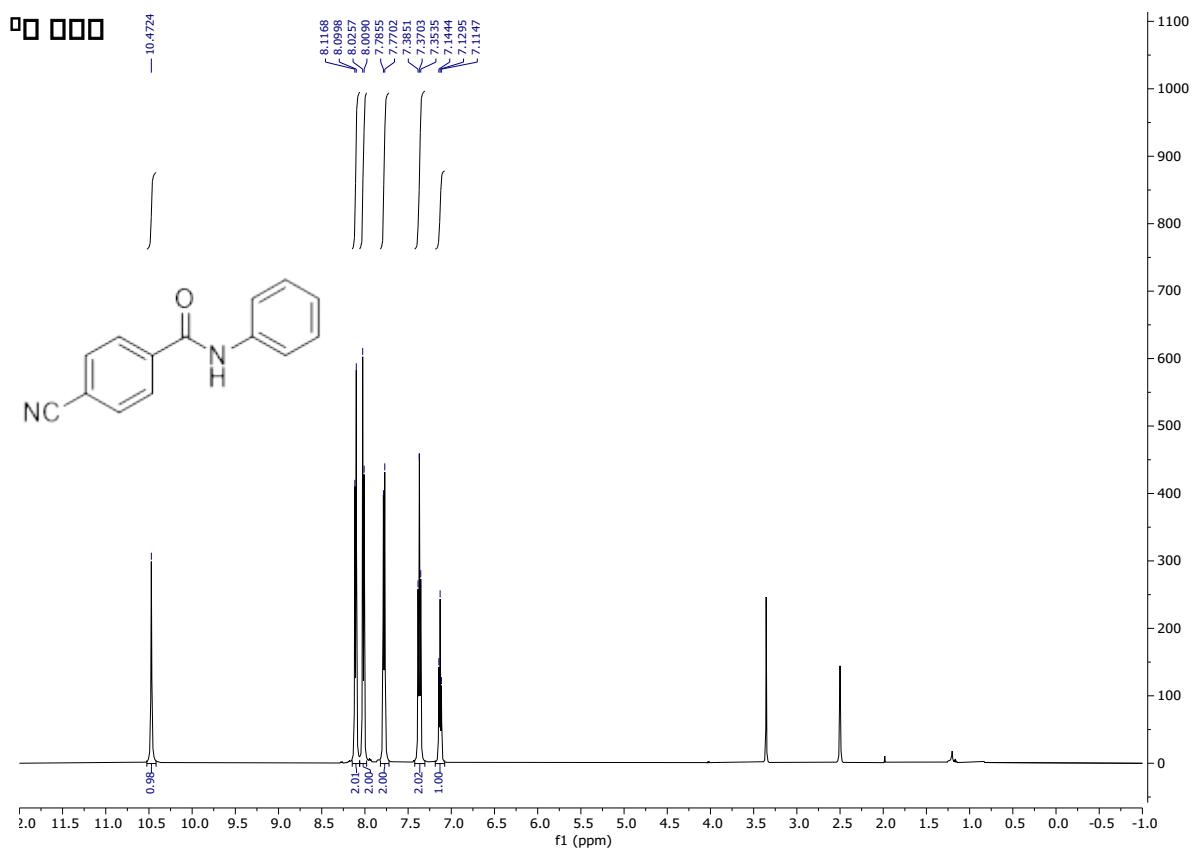
**N-Phenyl-4-(trifluoromethyl)benzamide (3oa)**



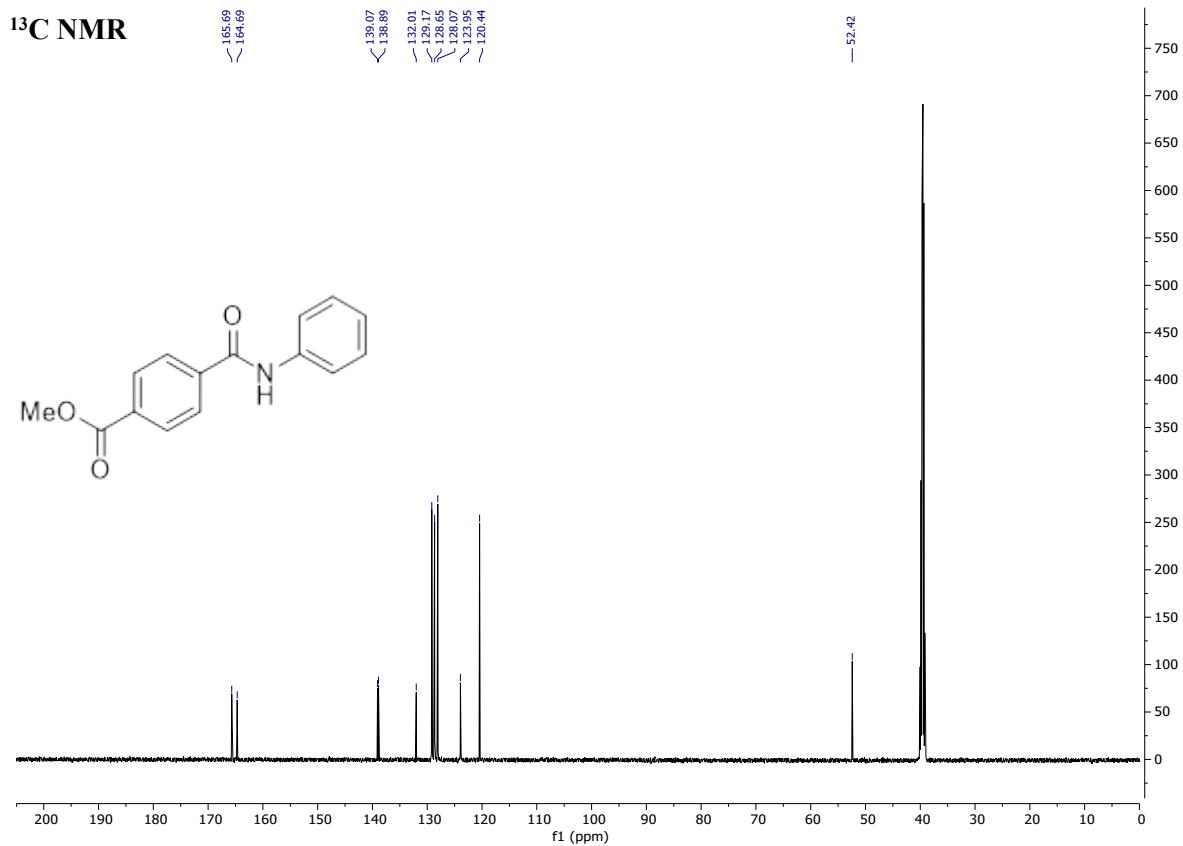
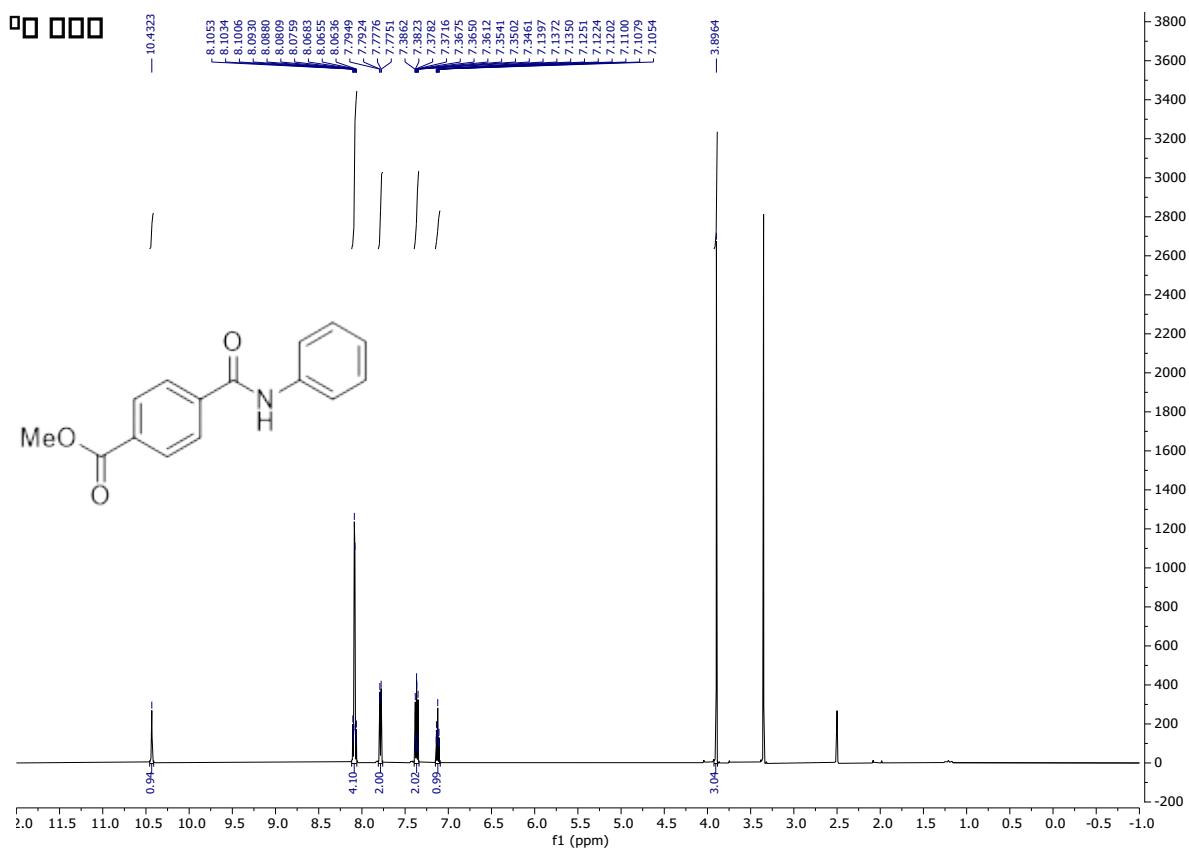
**<sup>13</sup>C NMR**



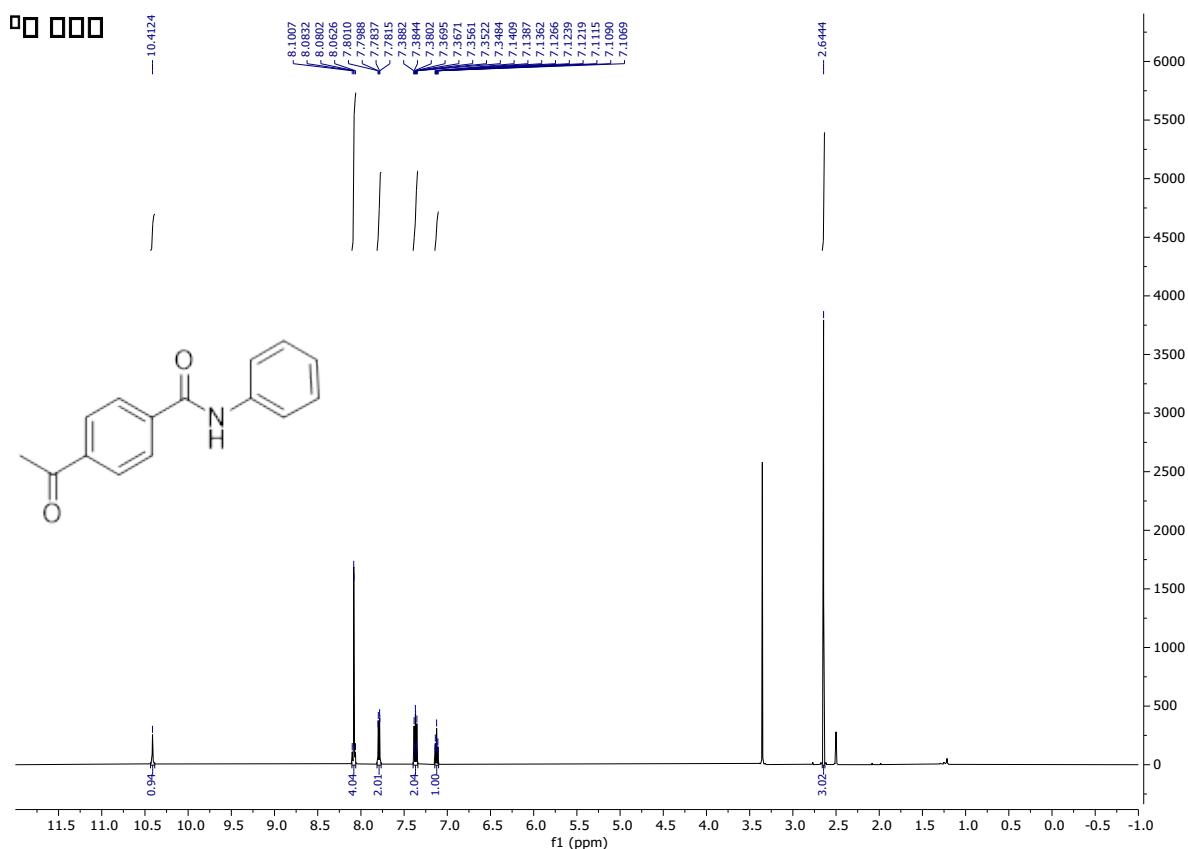
### **4-Cyano-N-phenylbenzamide (3pa)**



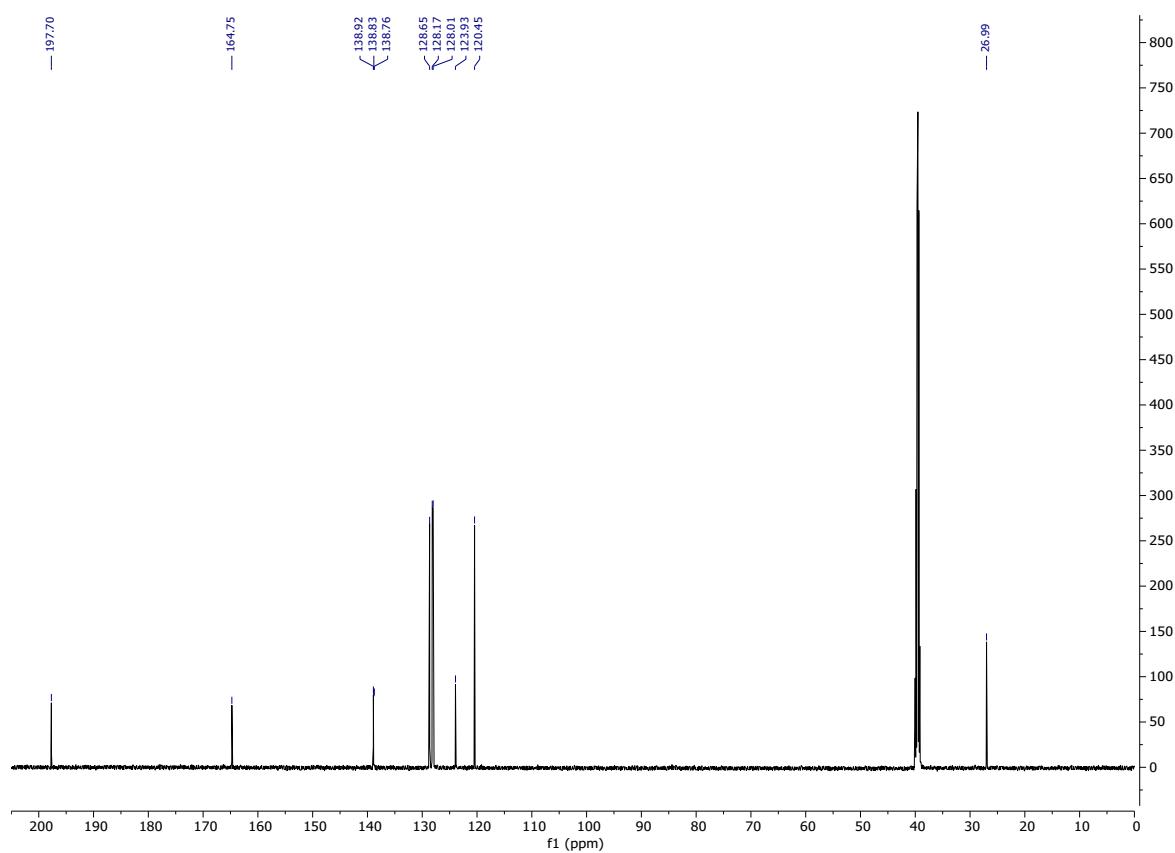
**Methyl-4-(phenylcarbamoyl)benzoate (3qa)**

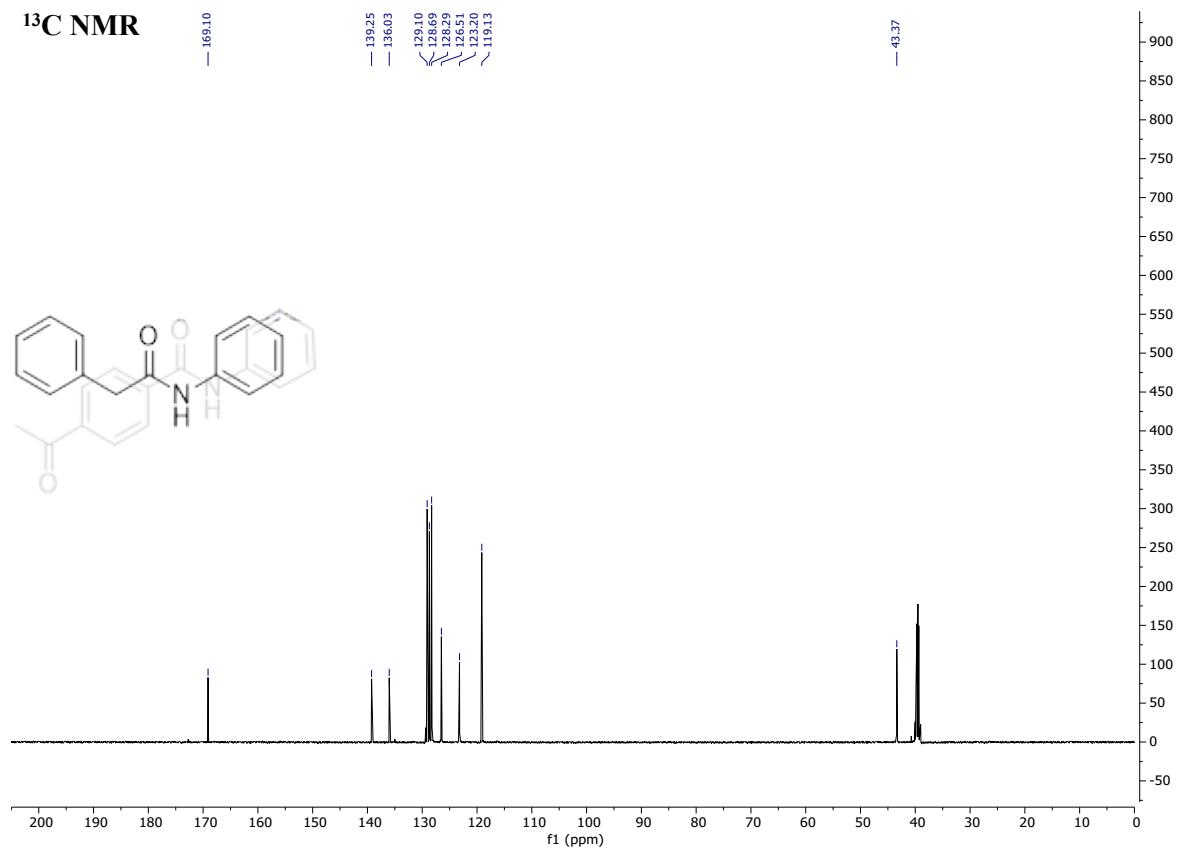
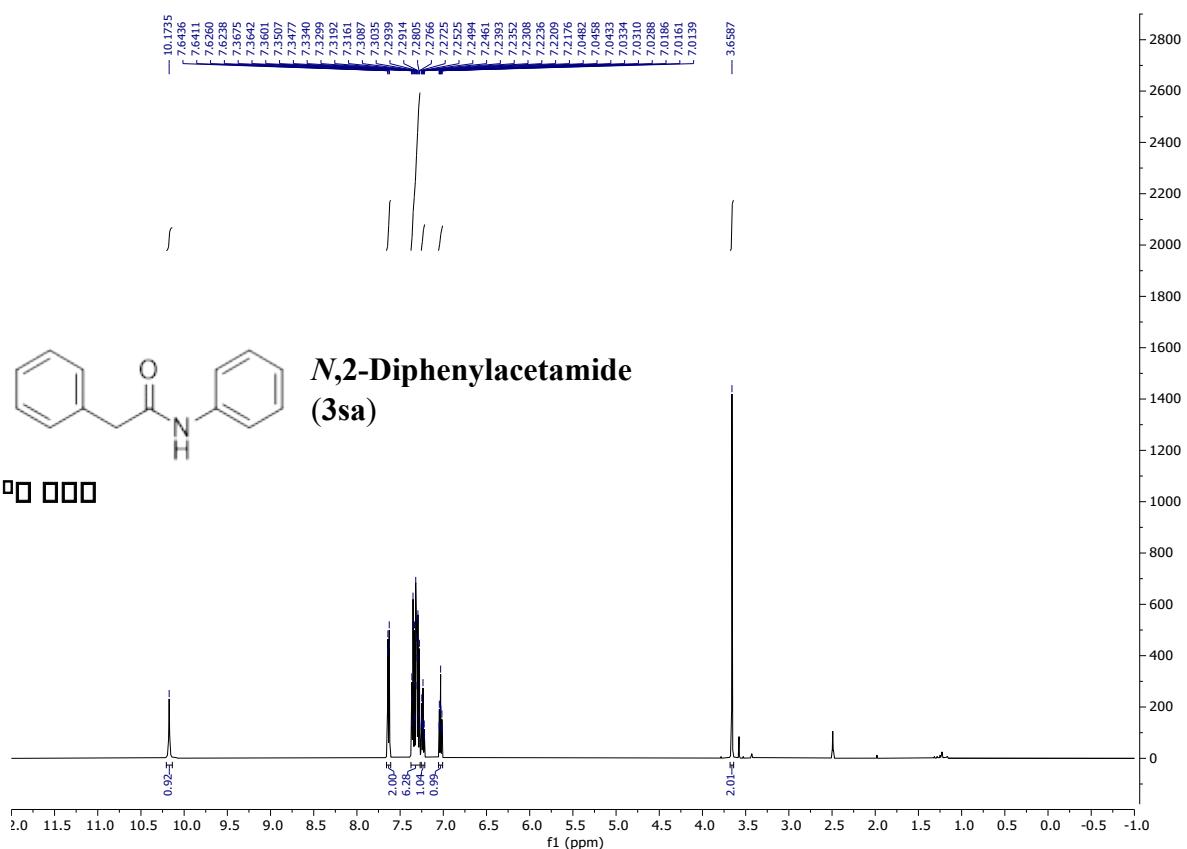


**4-Acetyl-N-phenylbenzamide (3ra)**



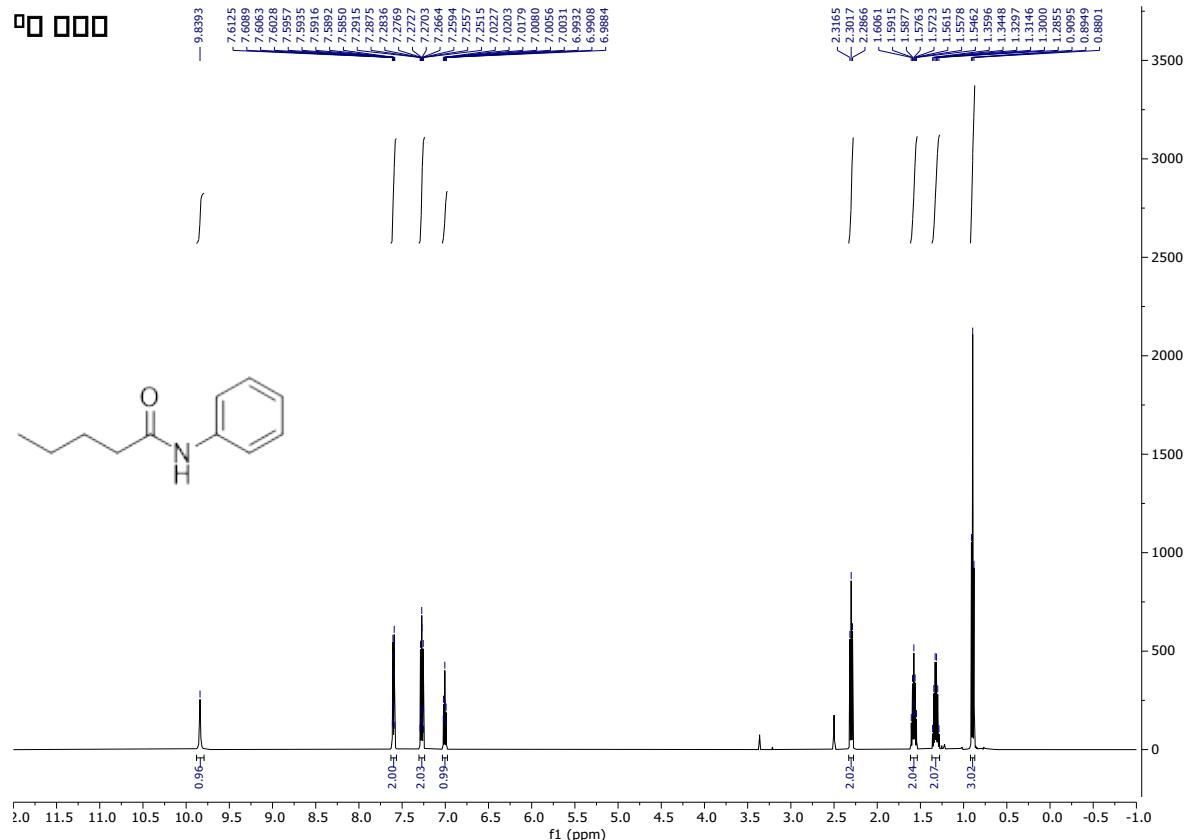
**<sup>13</sup>C NMR**



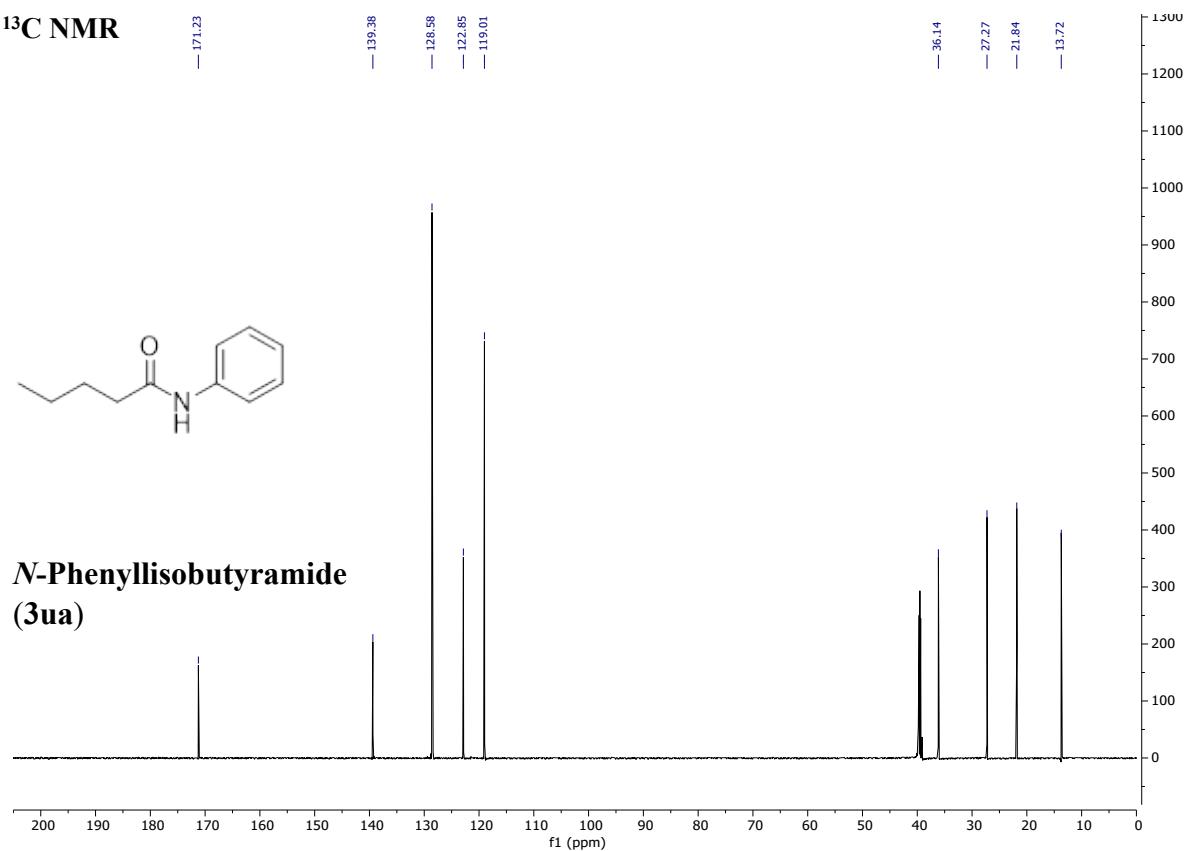




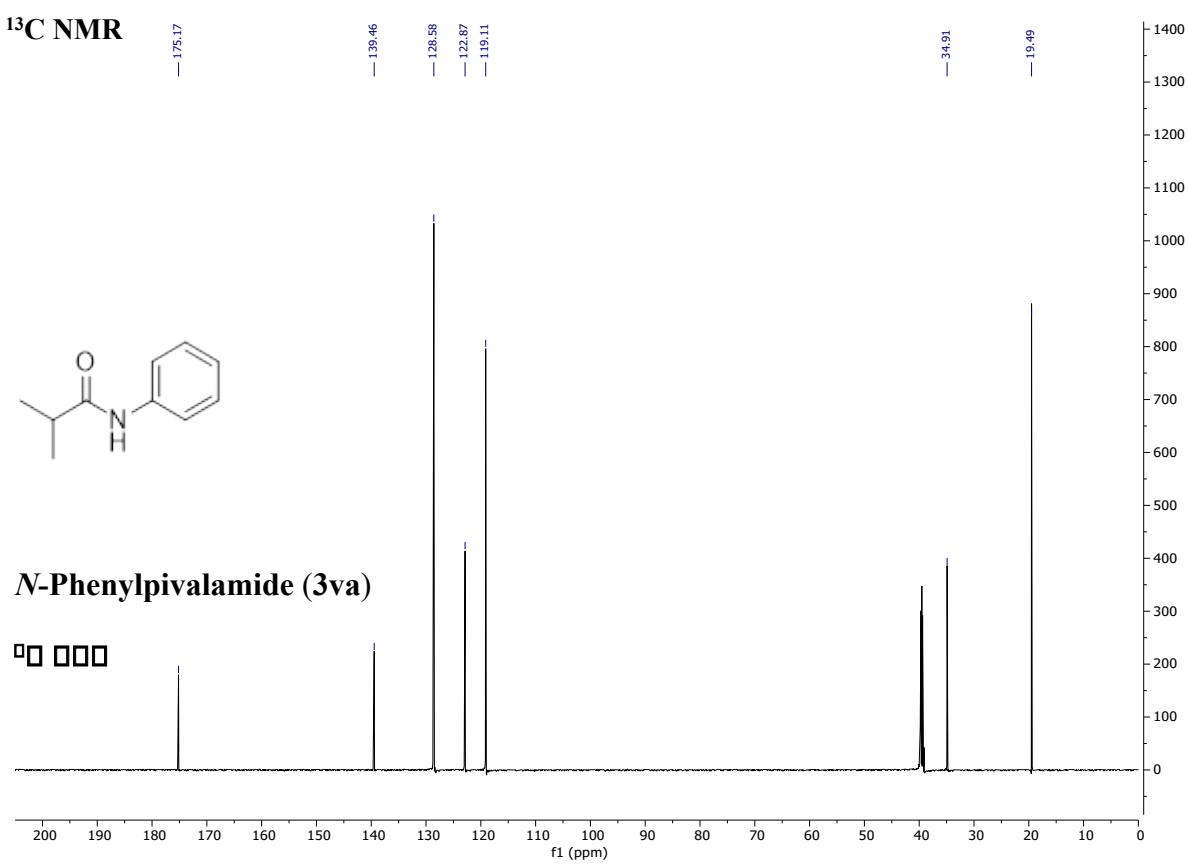
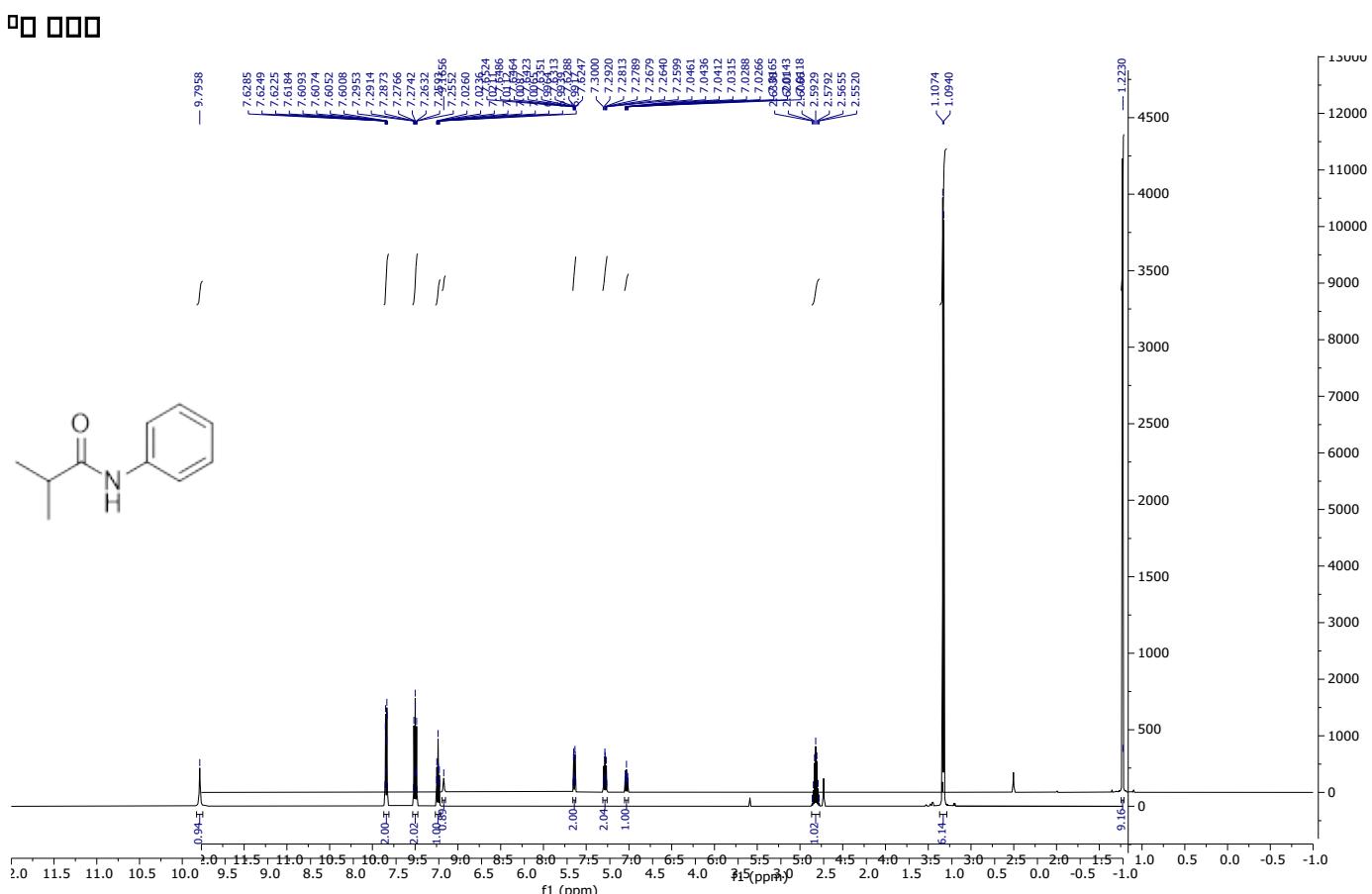
**N-Phenylpentanamide (3ta)**

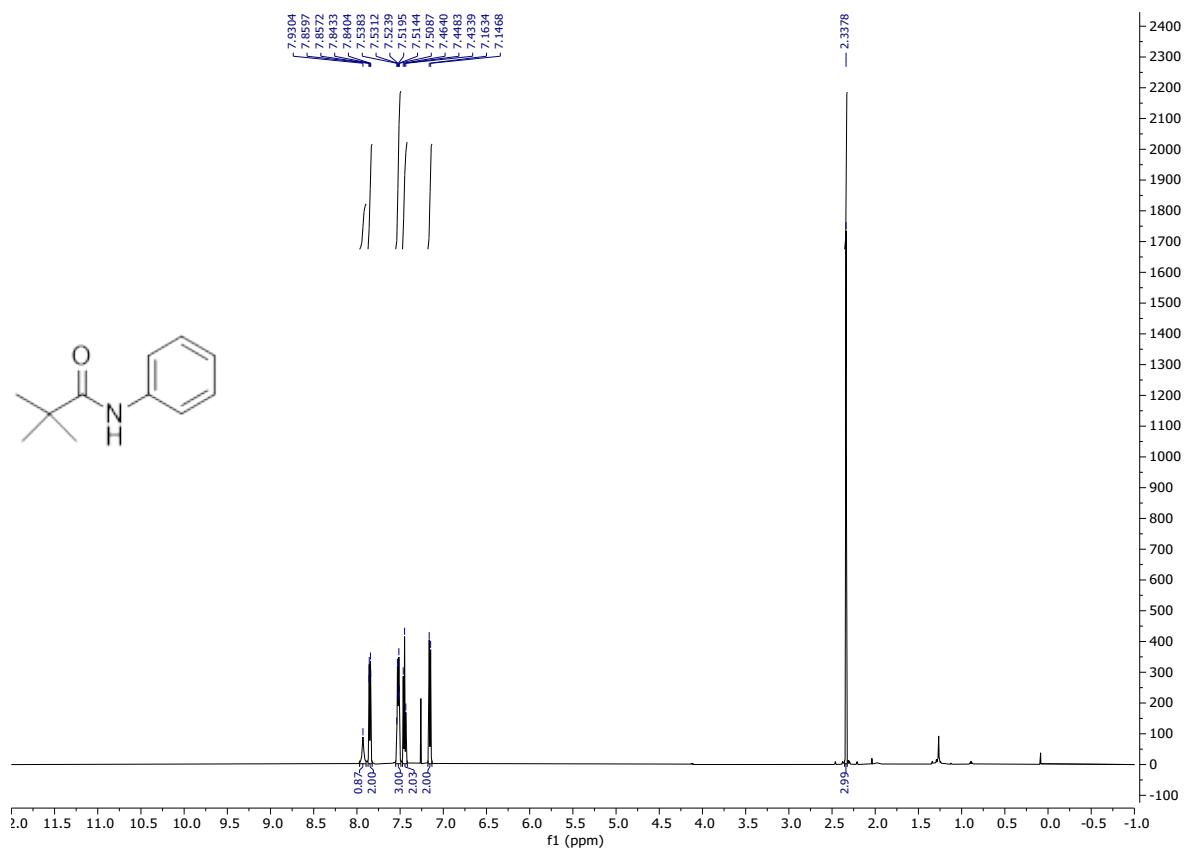


**<sup>13</sup>C NMR**

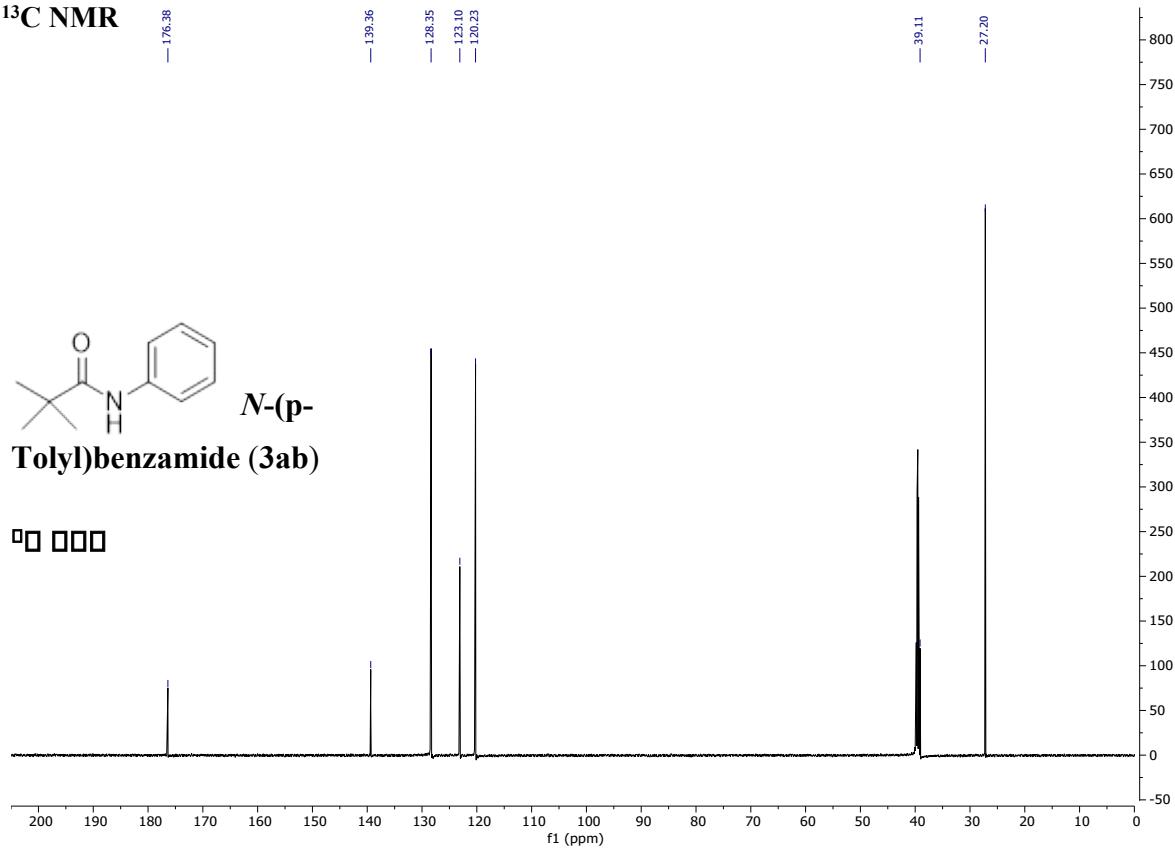


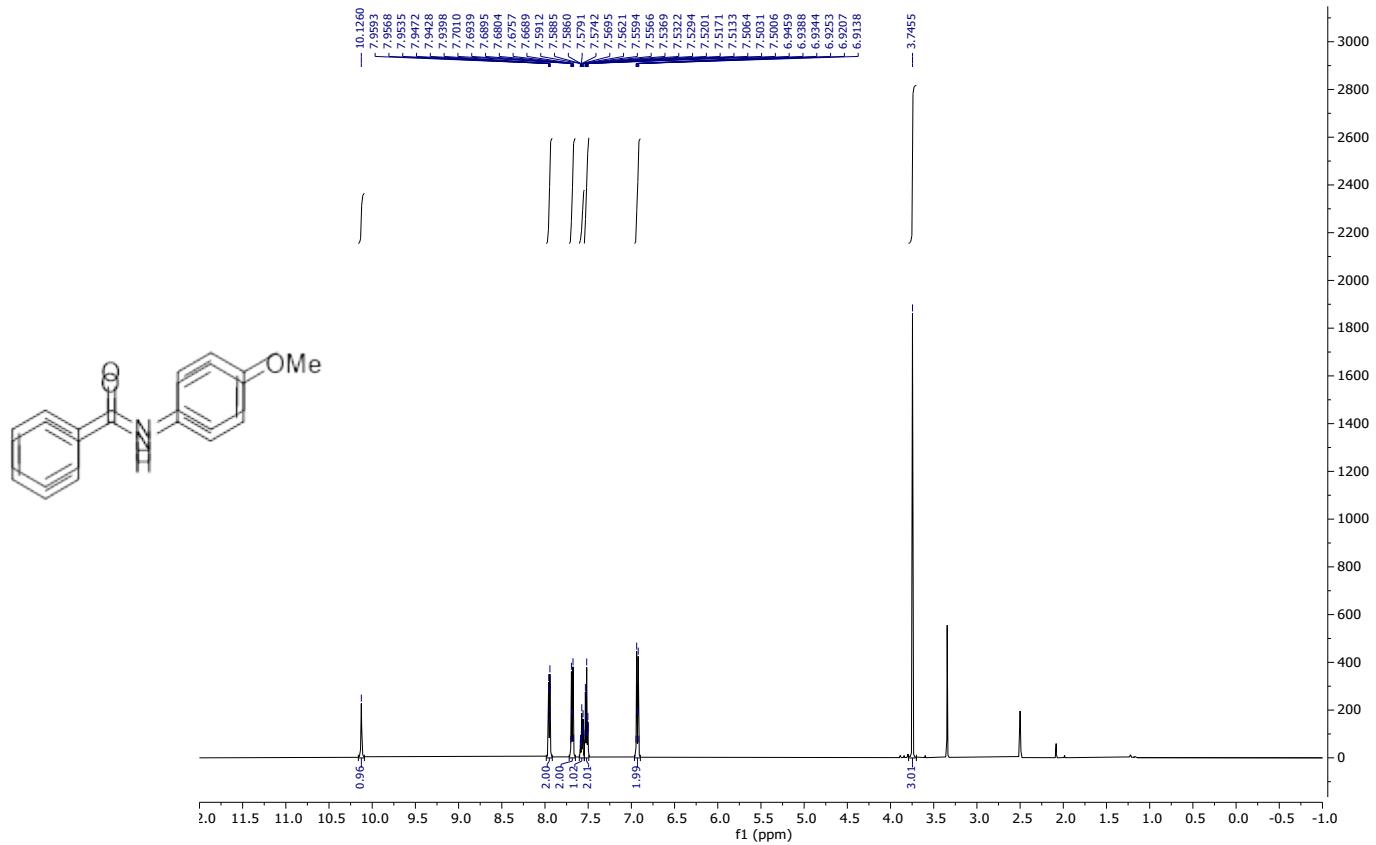
**N-Phenyllisobutyramide  
(3ua)**



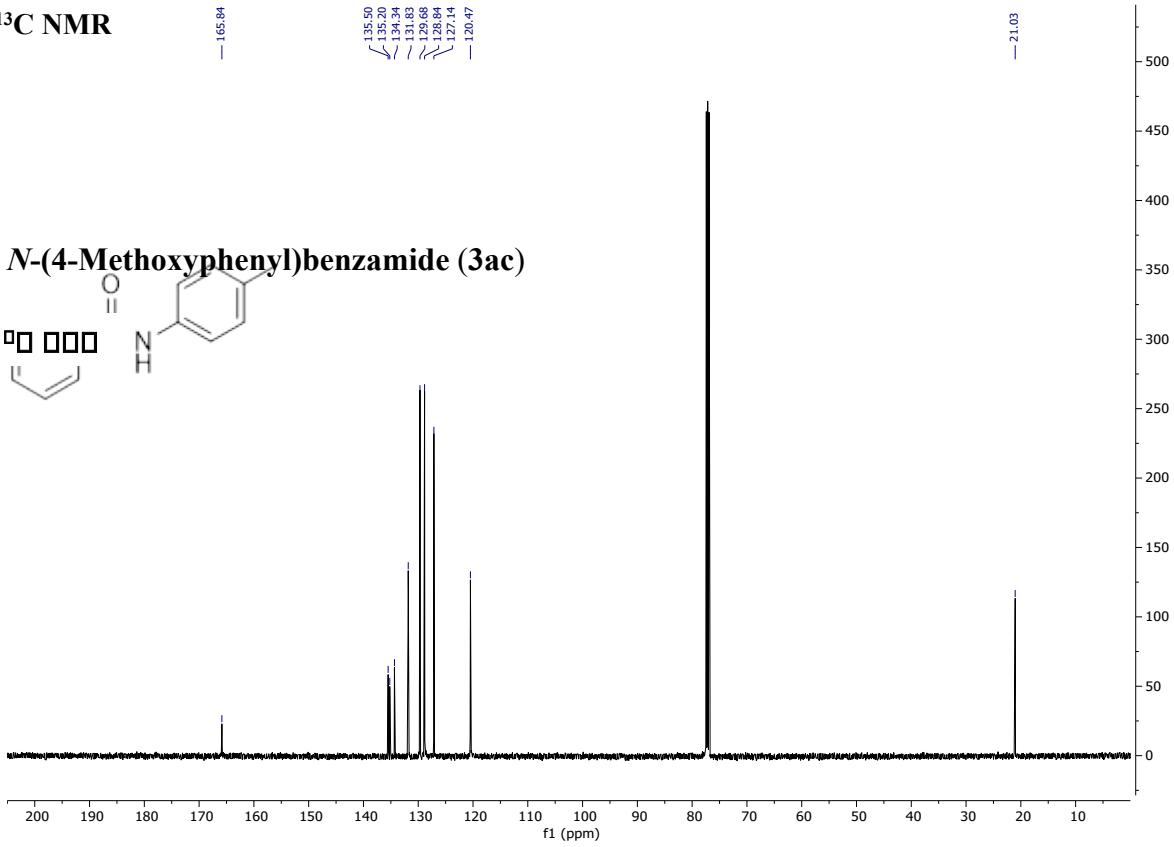


### <sup>13</sup>C NMR

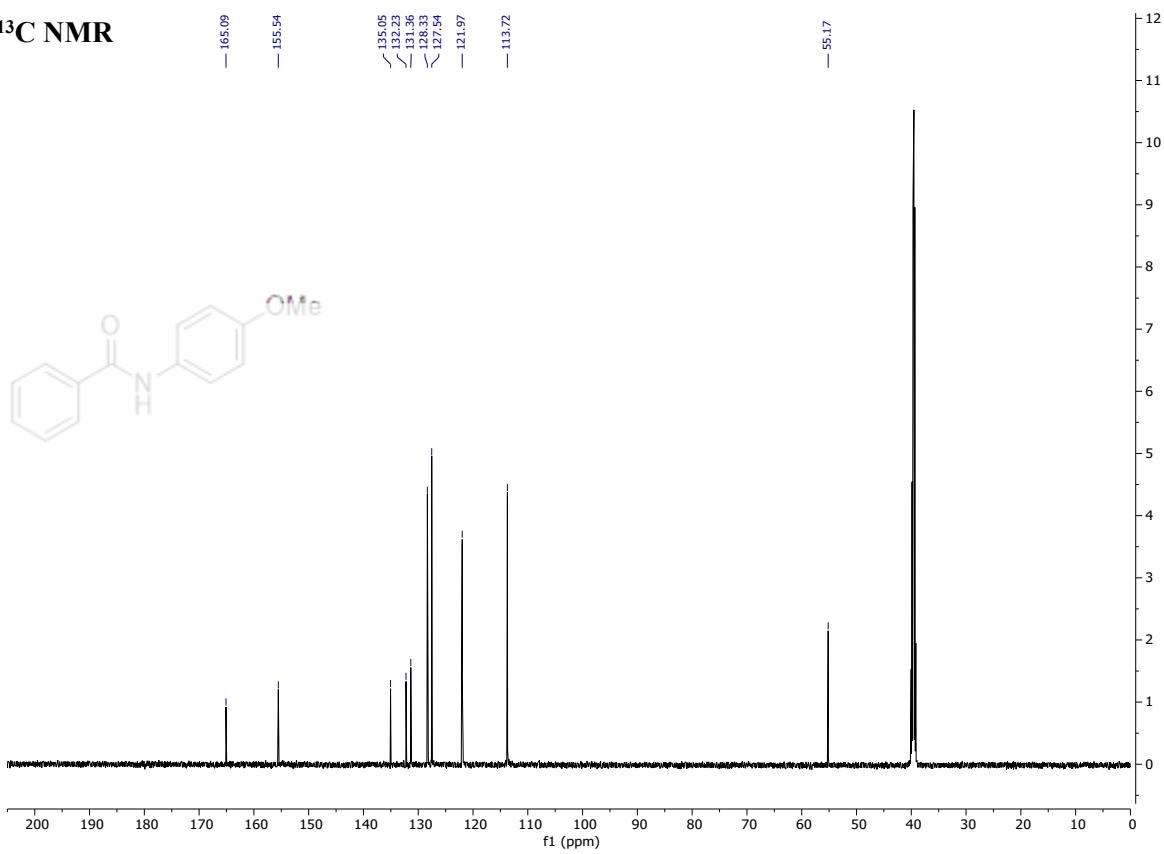




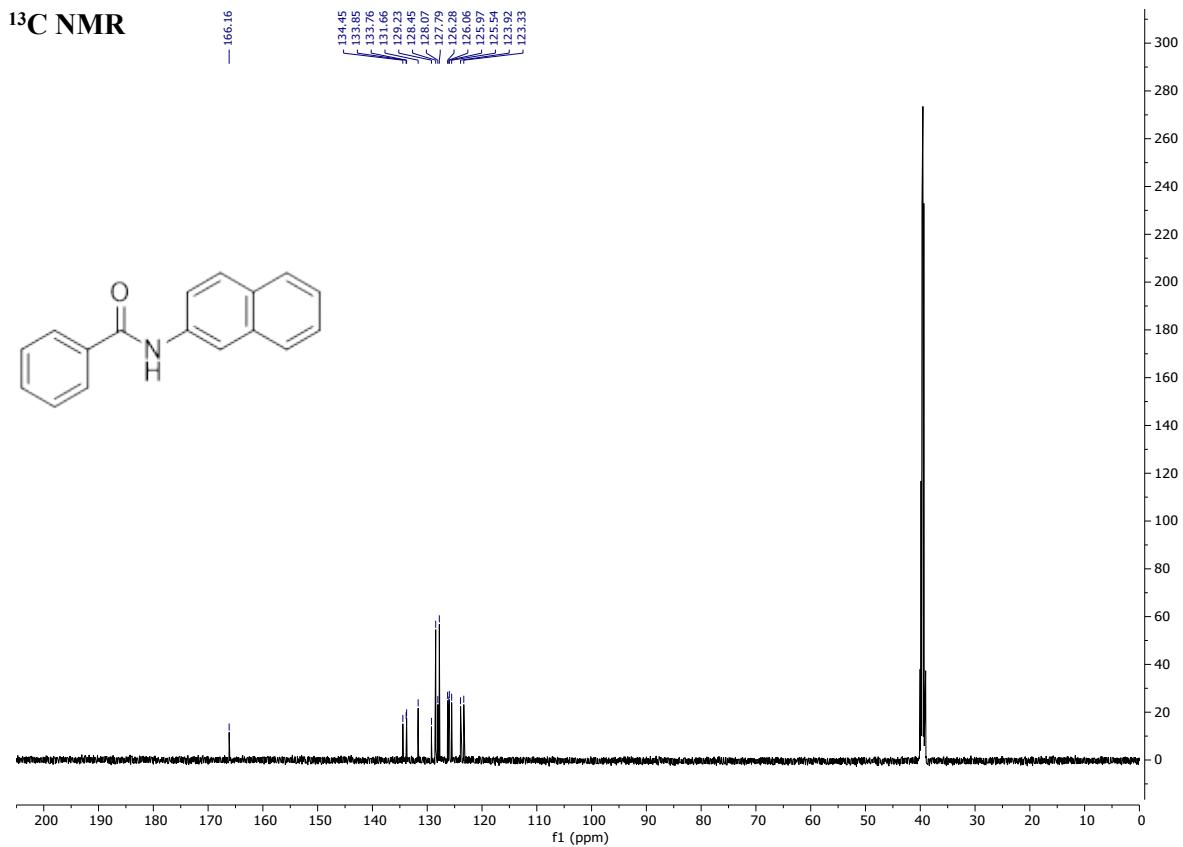
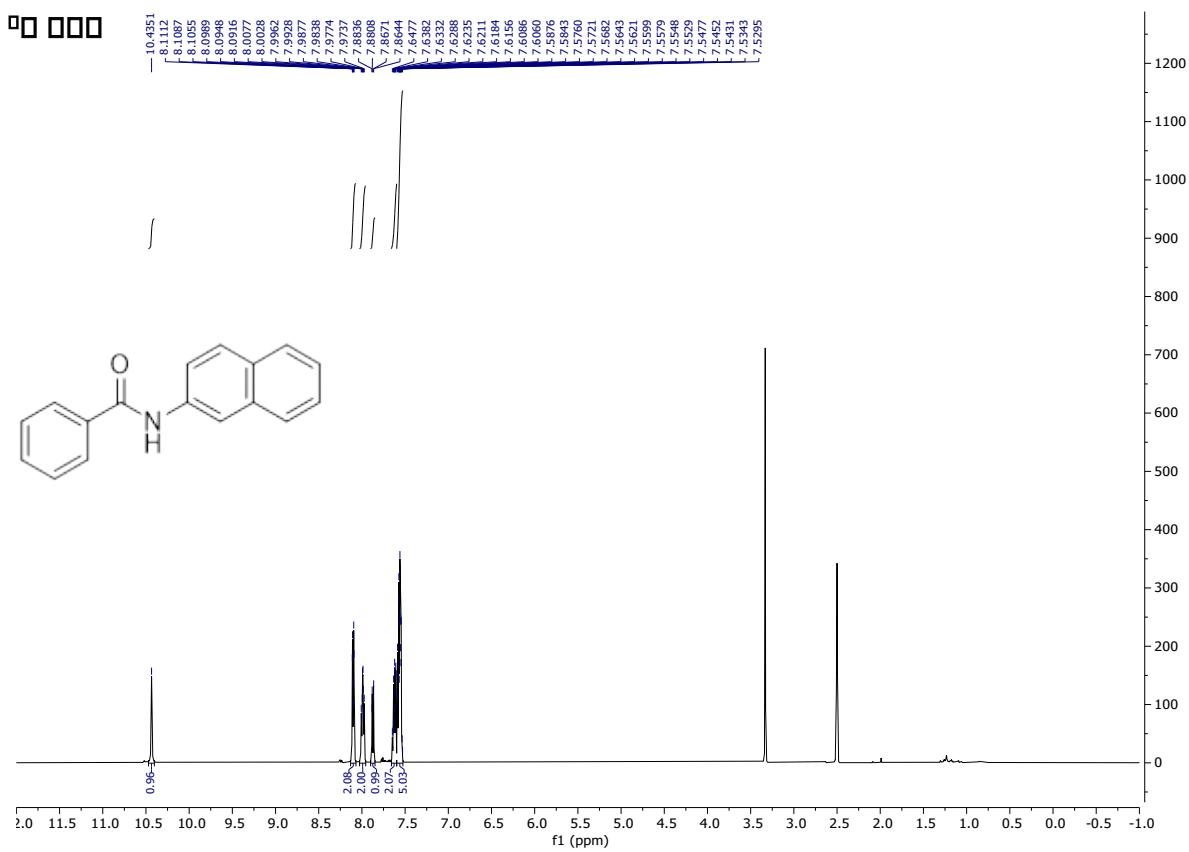
**<sup>13</sup>C NMR**



<sup>13</sup>C NMR

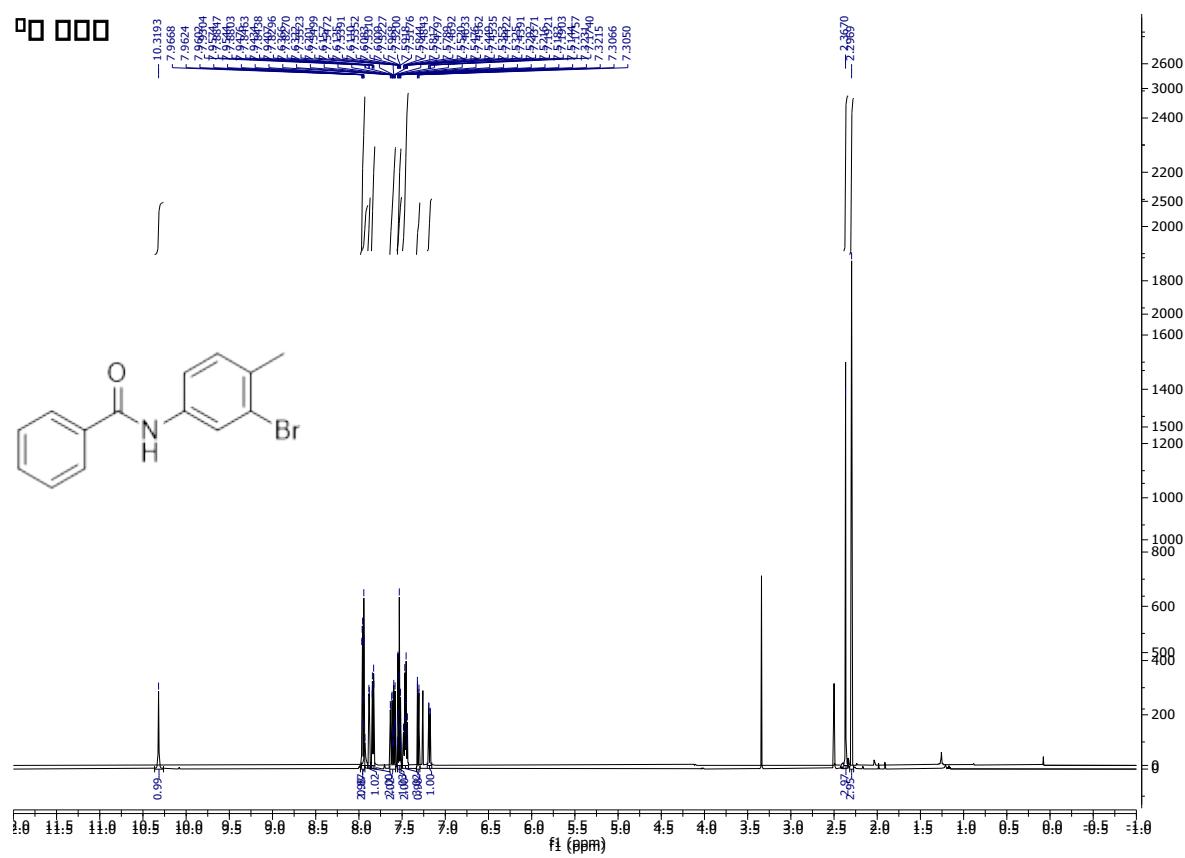


***N*-(Naphthalen-2-yl)benzamide (**3ad**)**

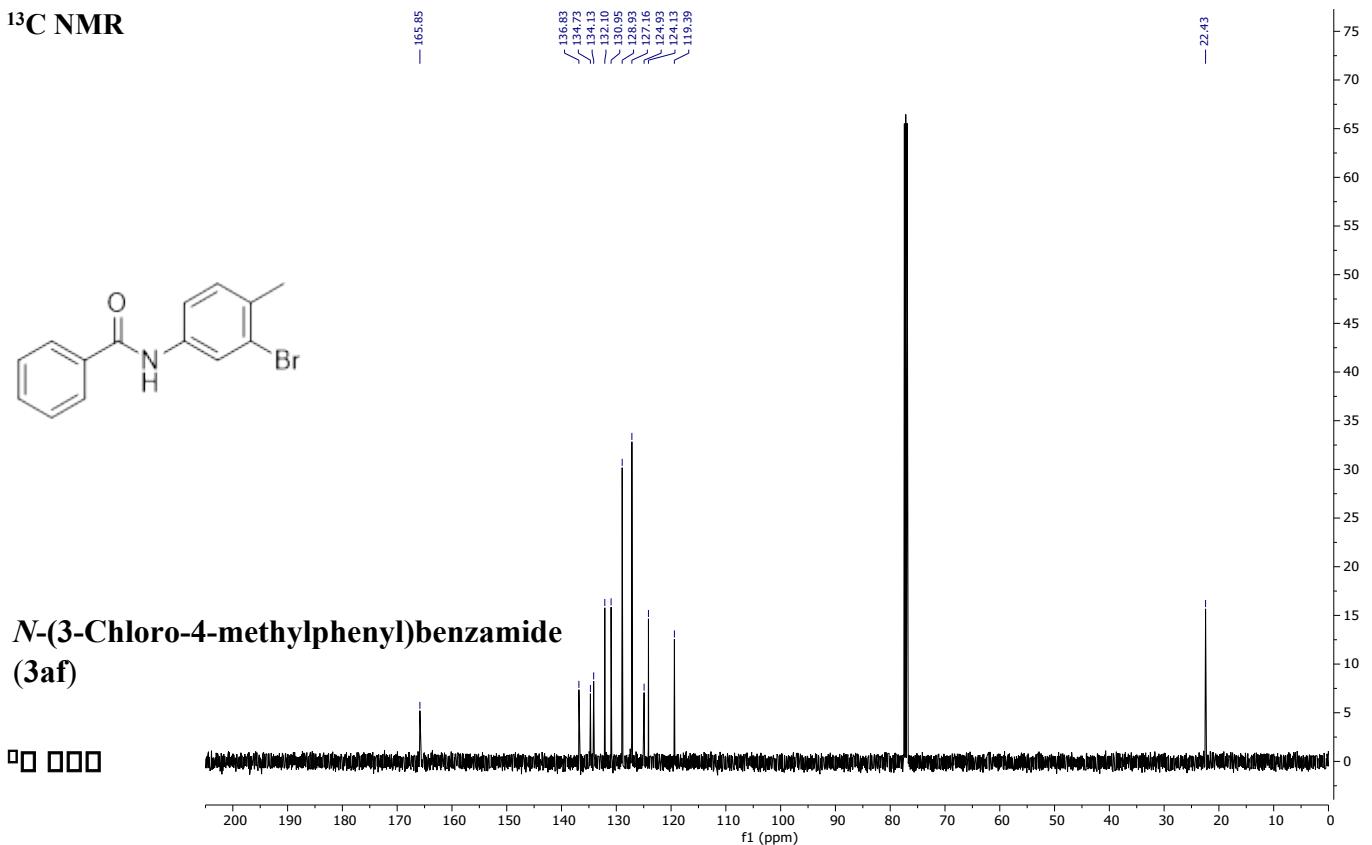


***N*-(3-Bromo-4-methylphenyl)benzamide (3ae)**

■ ■ ■

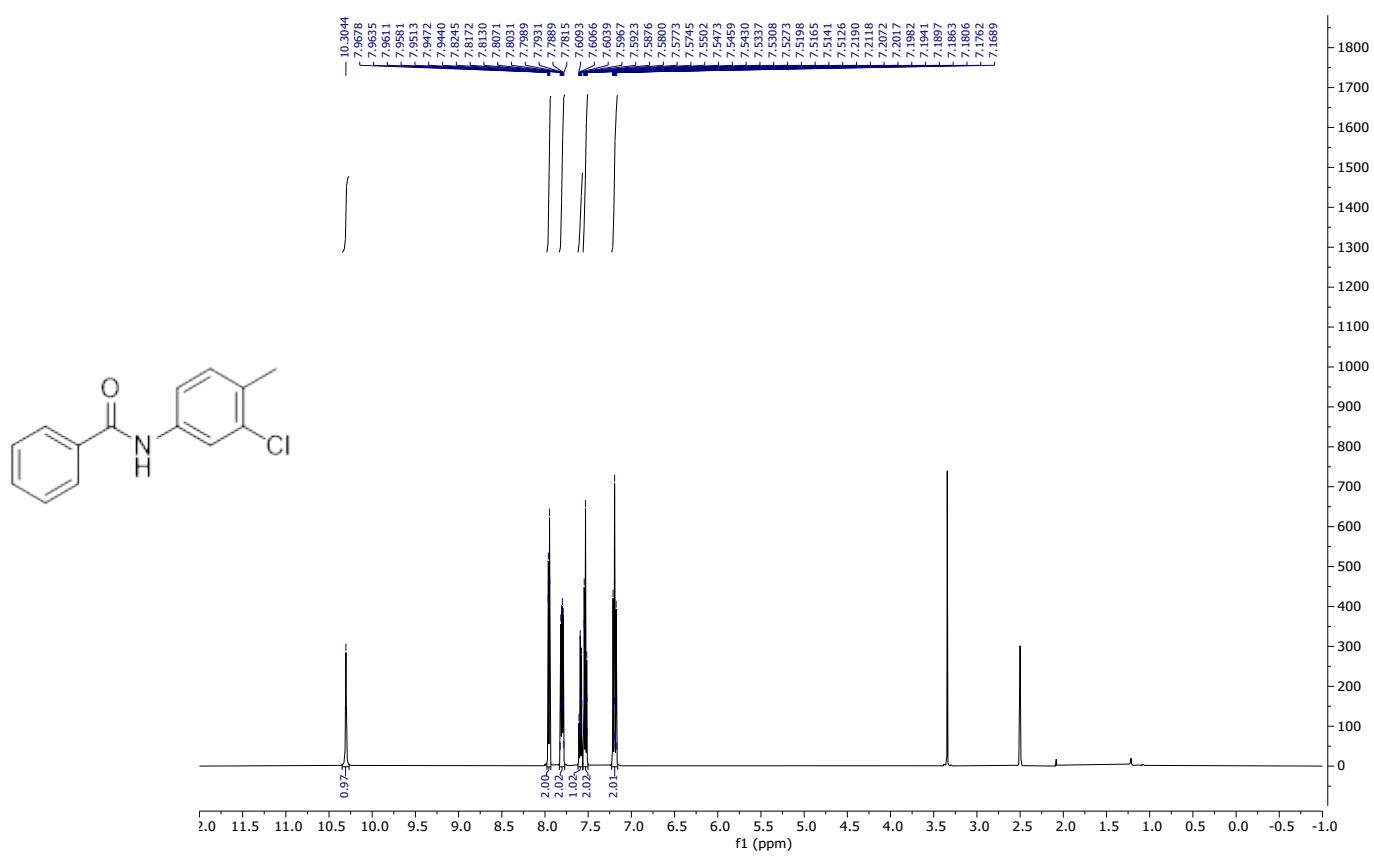


**<sup>13</sup>C NMR**

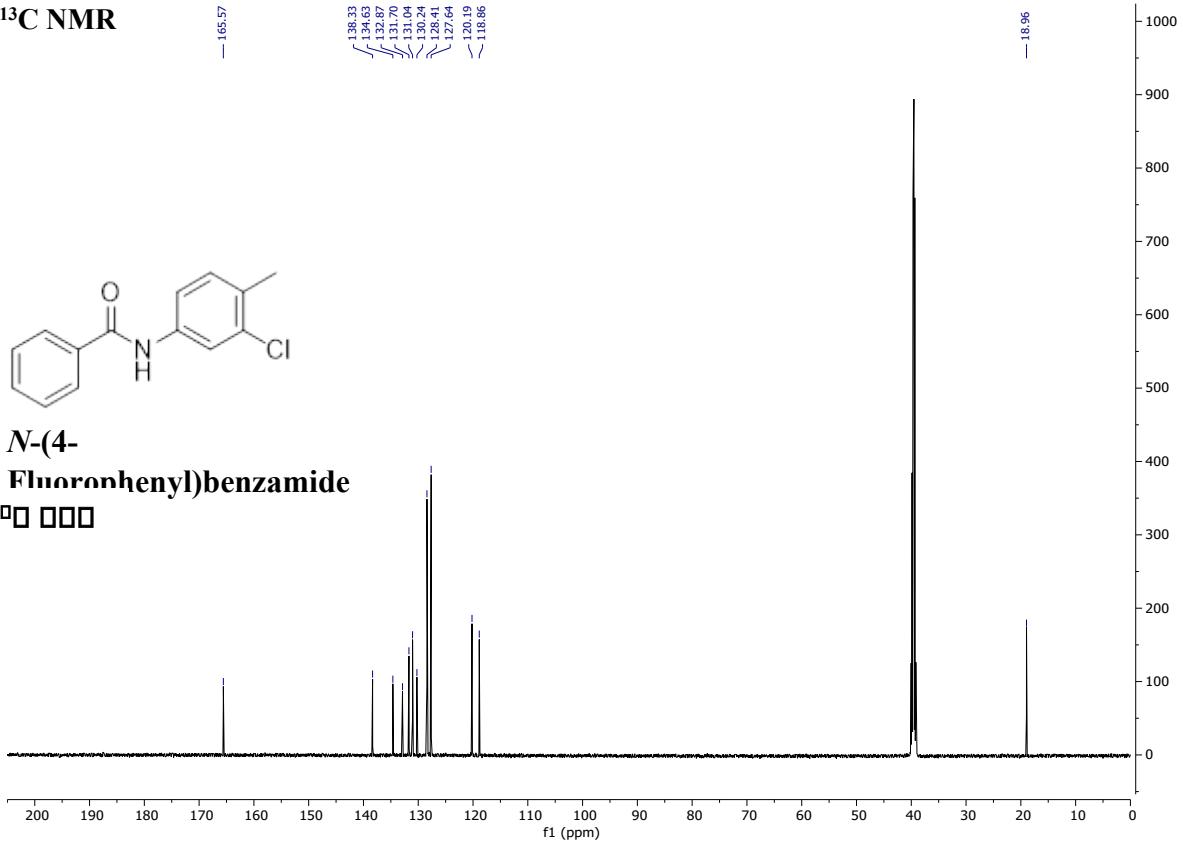


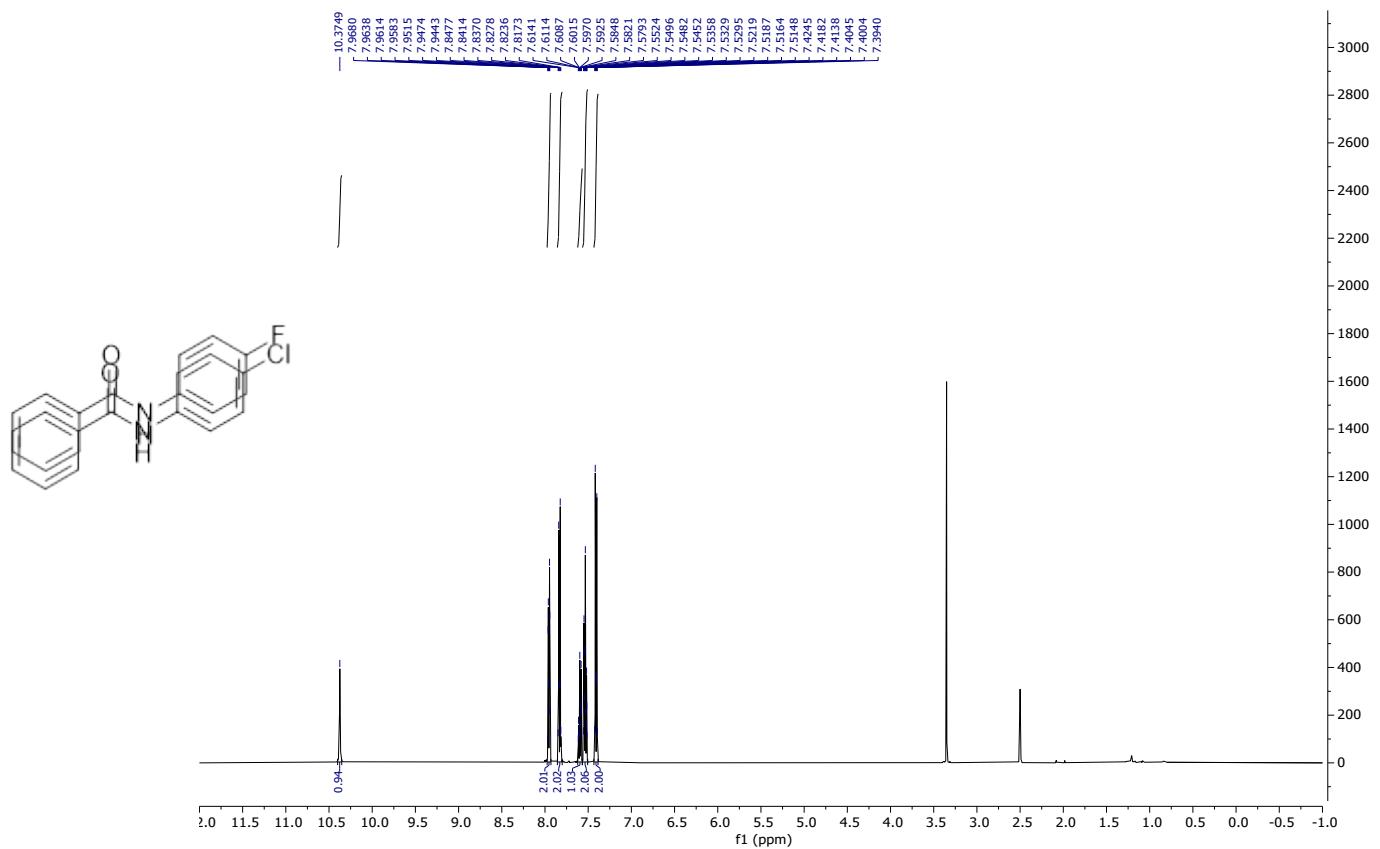
***N*-(3-Chloro-4-methylphenyl)benzamide  
(3af)**

■ ■ ■

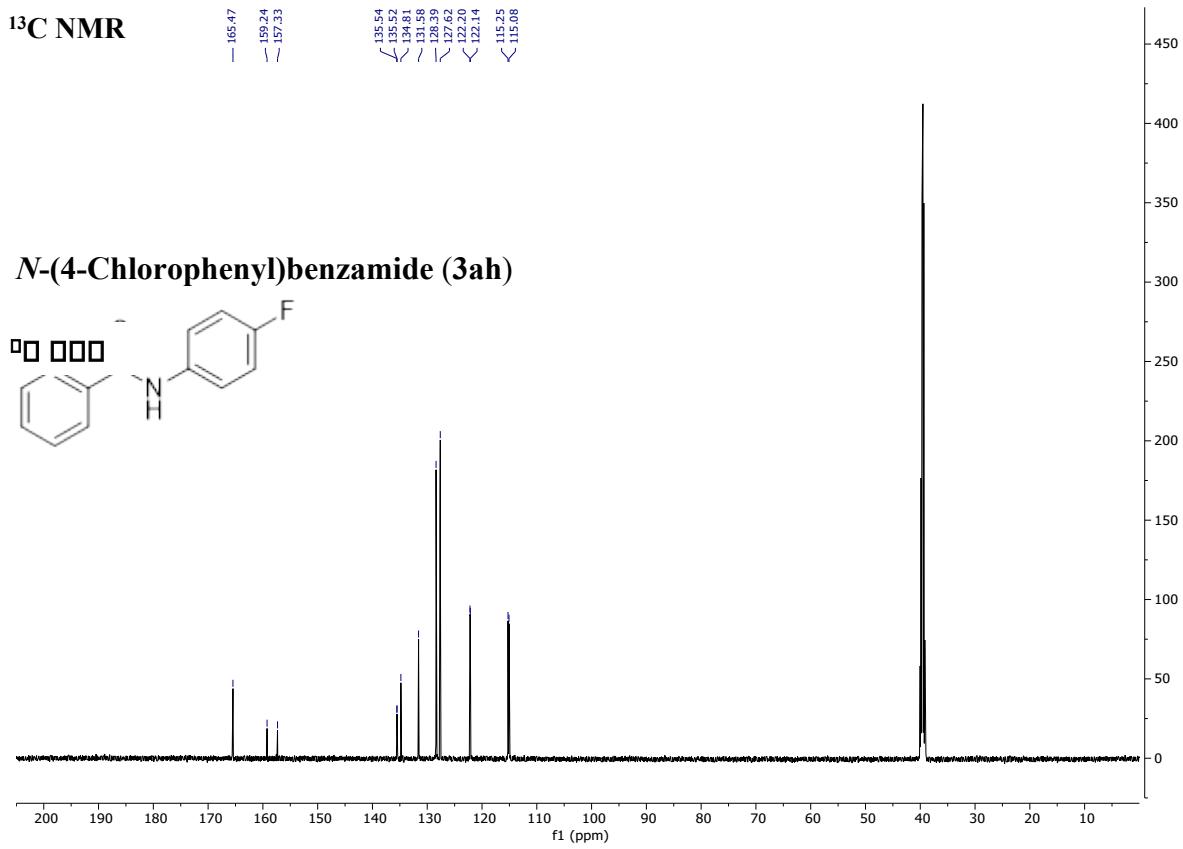


<sup>13</sup>C NMR

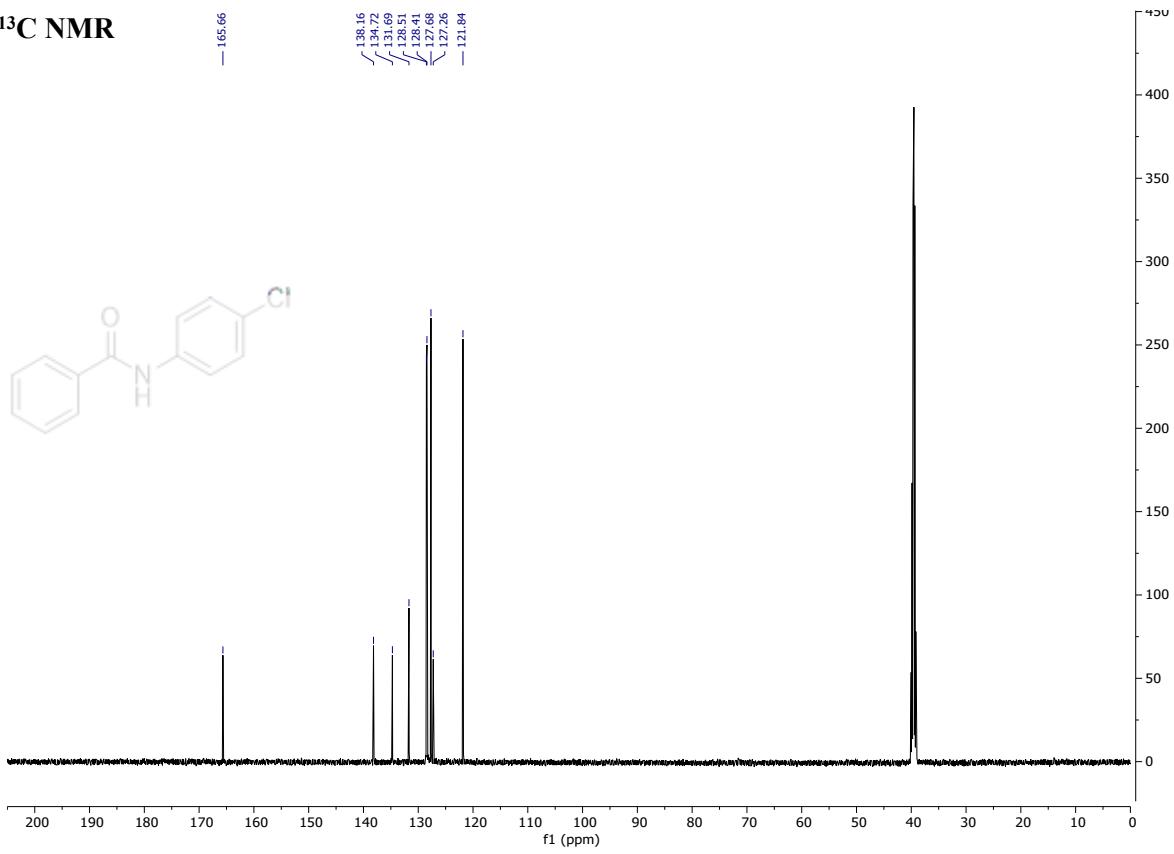




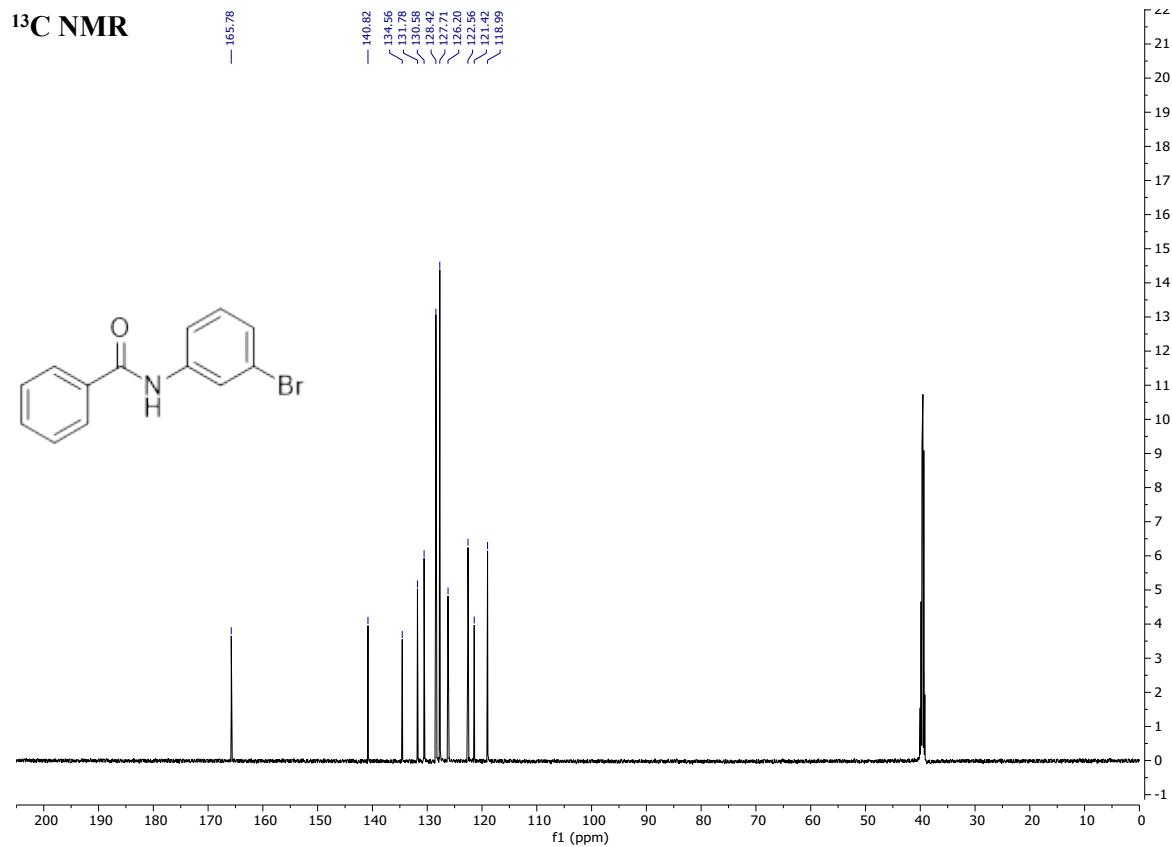
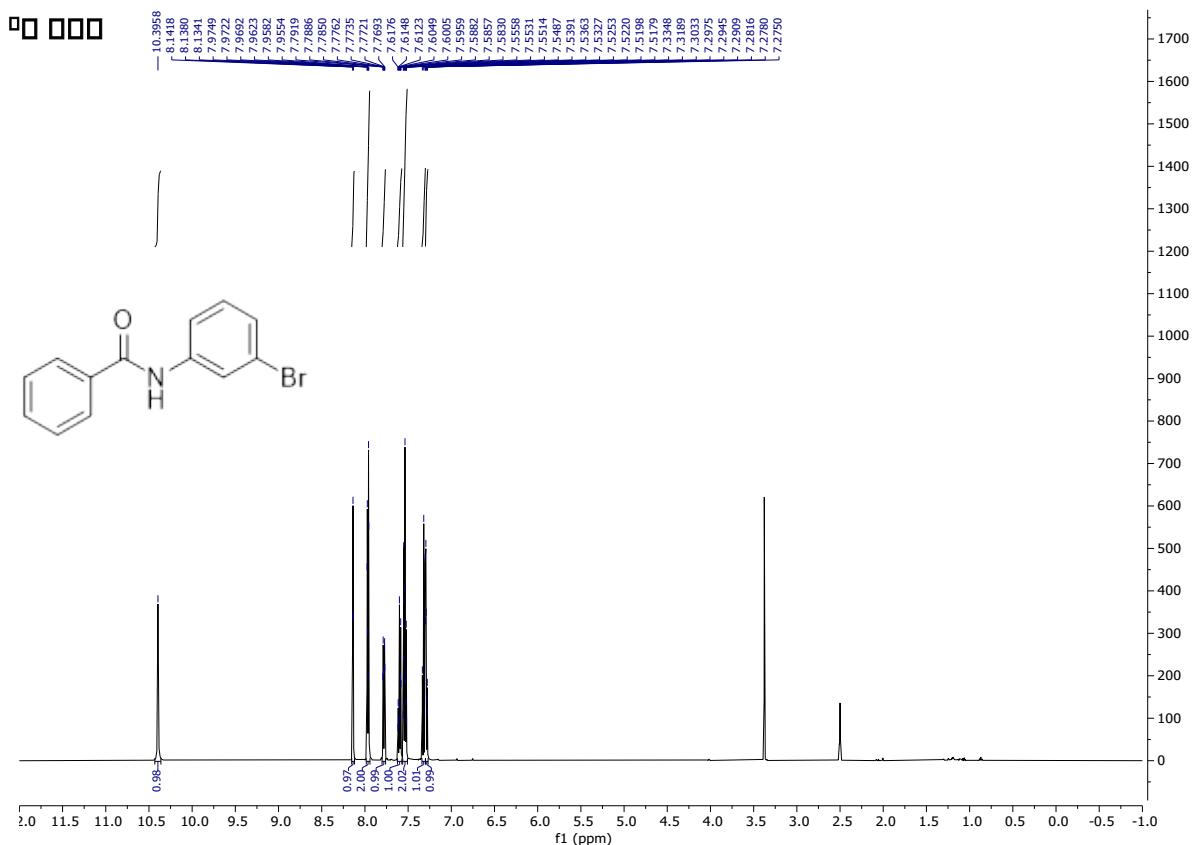
### <sup>13</sup>C NMR



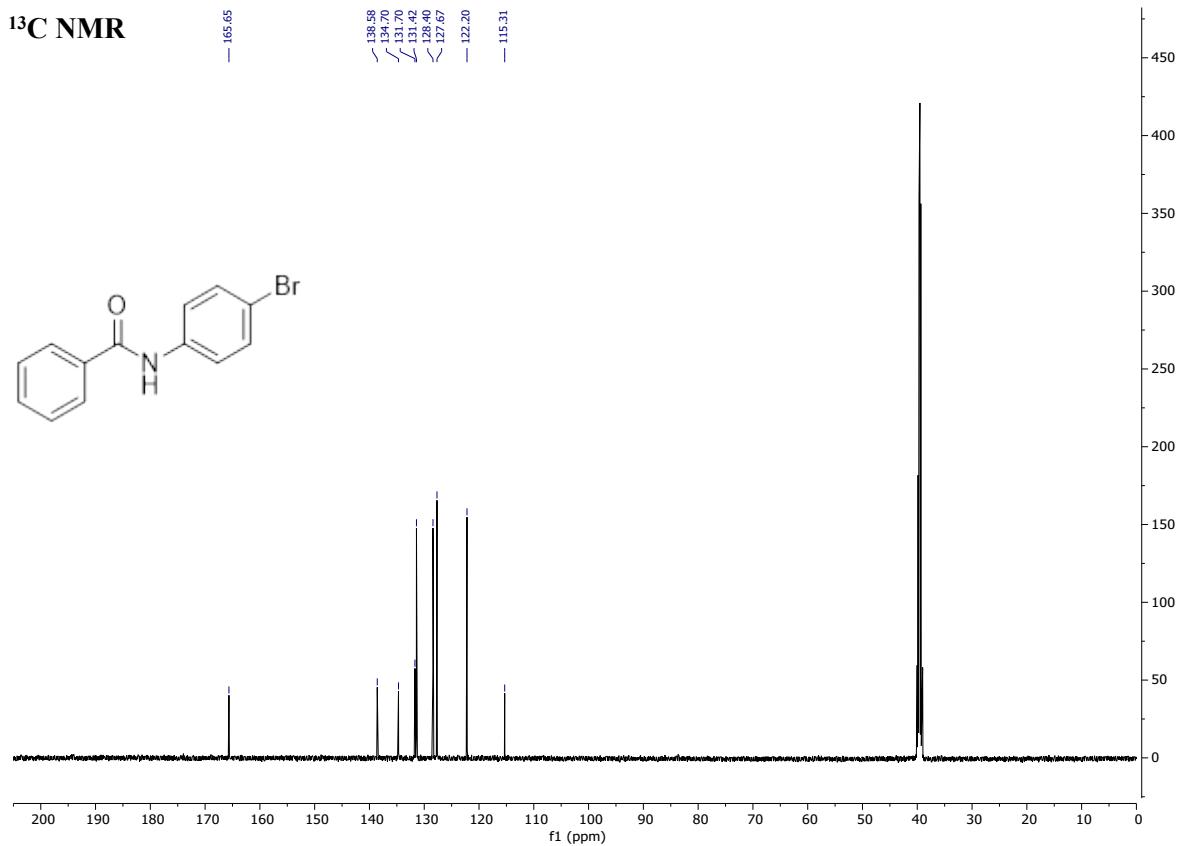
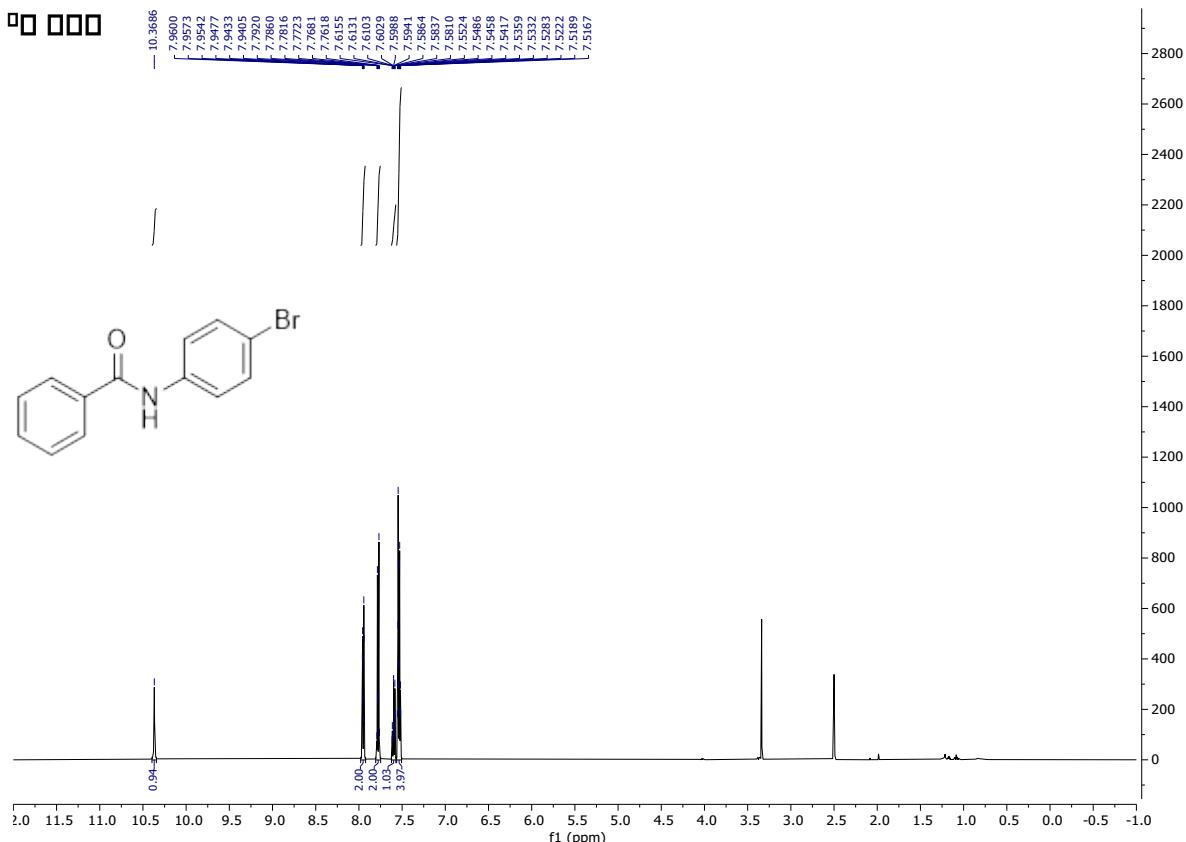
<sup>13</sup>C NMR



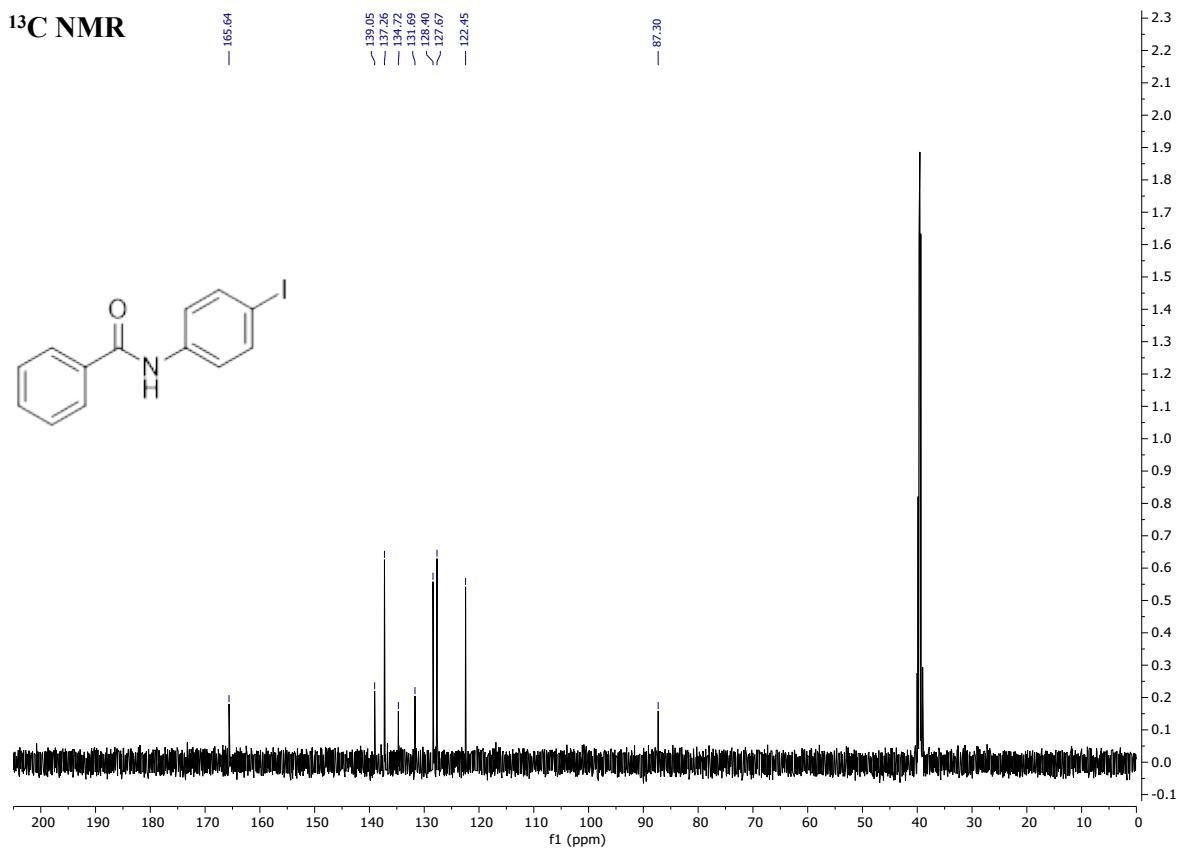
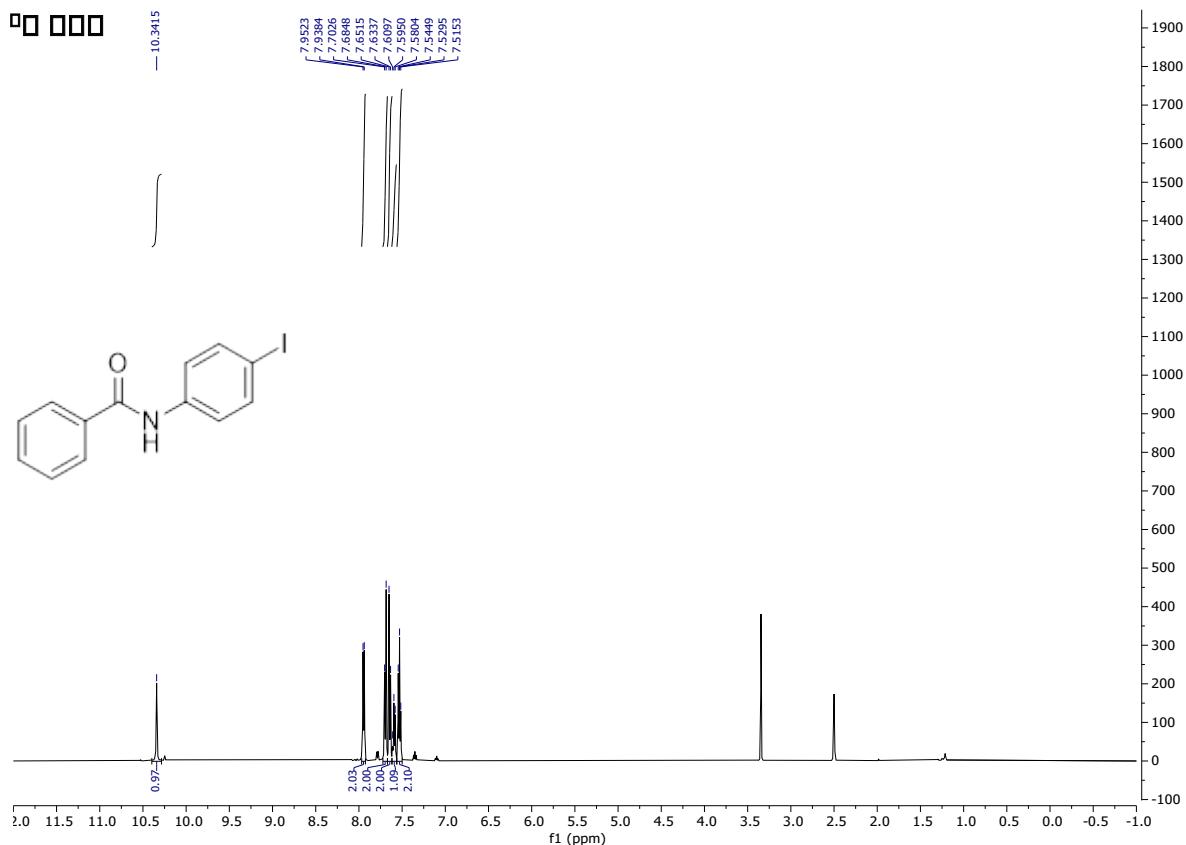
***N*-(3-Bromophenyl)benzamide (3ai)**



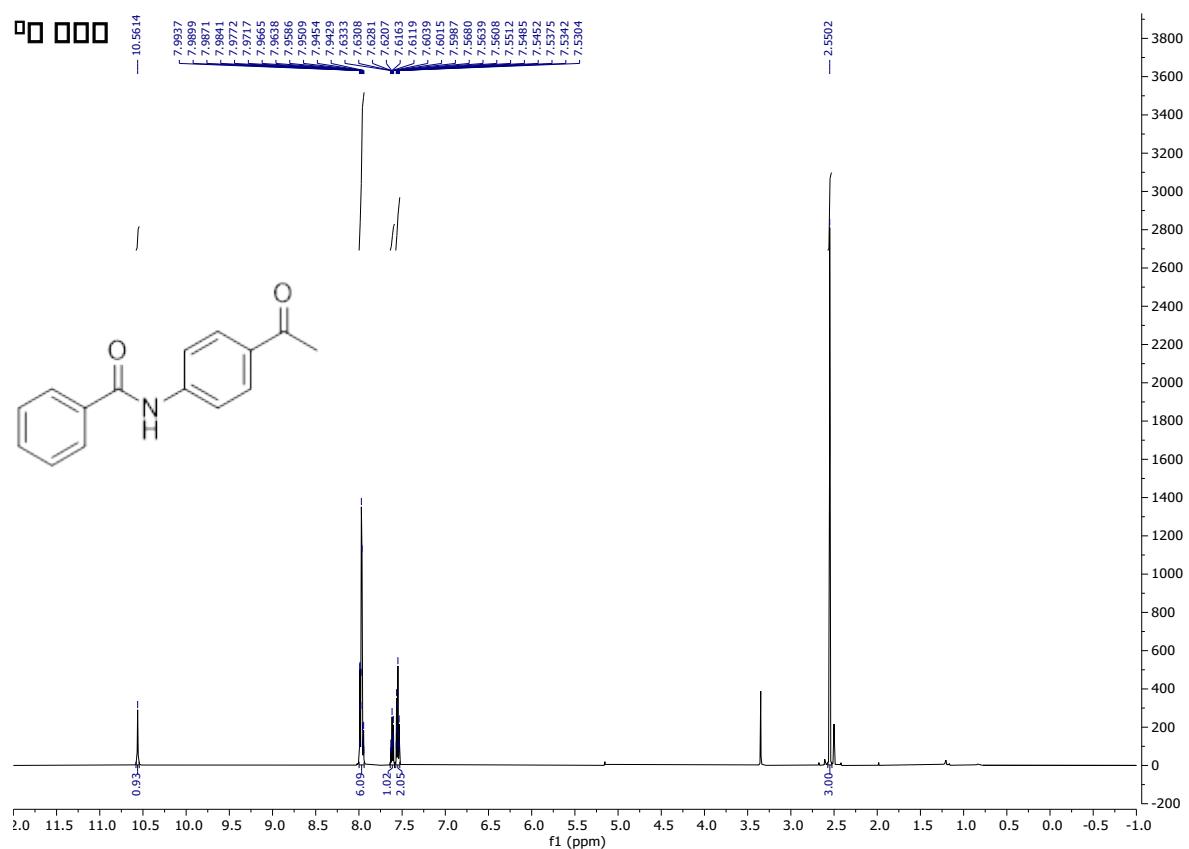
**N-(4-Bromophenyl)benzamide (3aj)**



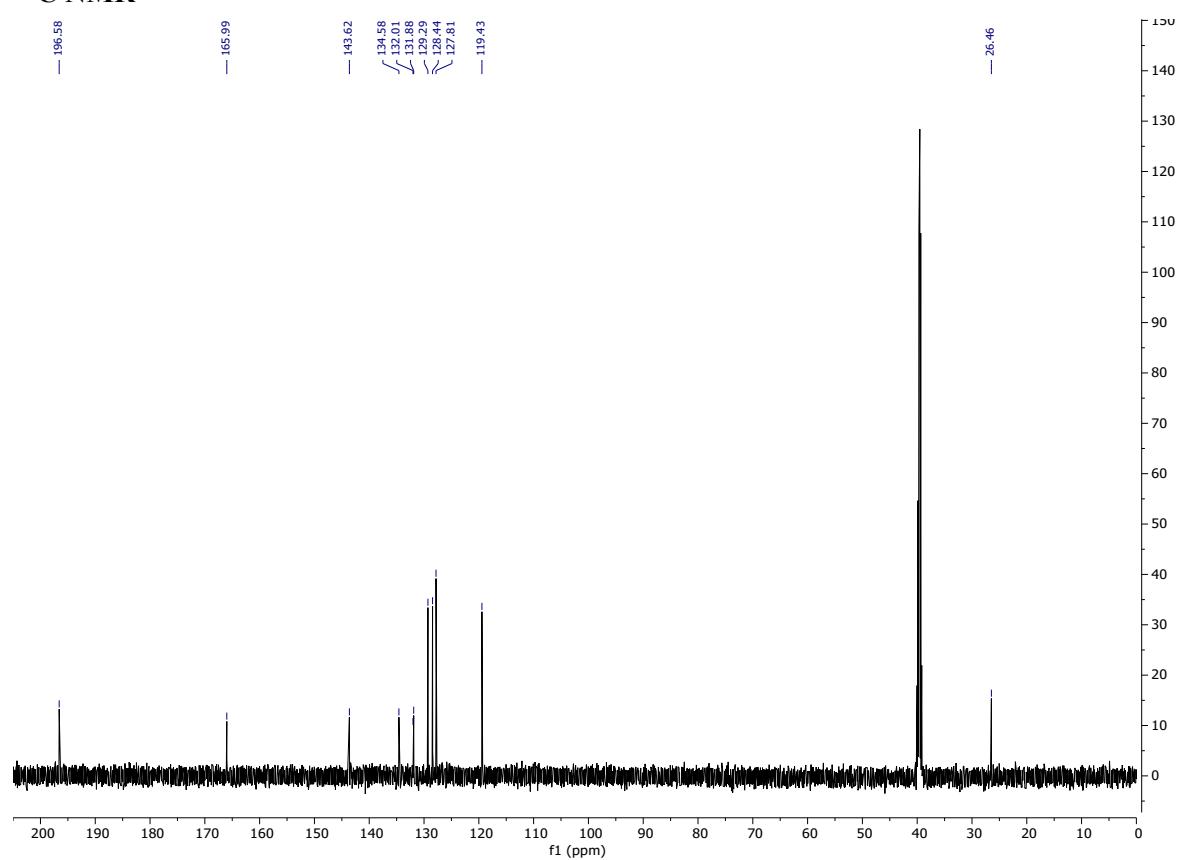
***N*-(4-Iodophenyl)benzamide (3ak)**

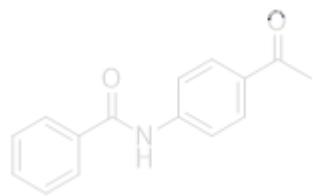
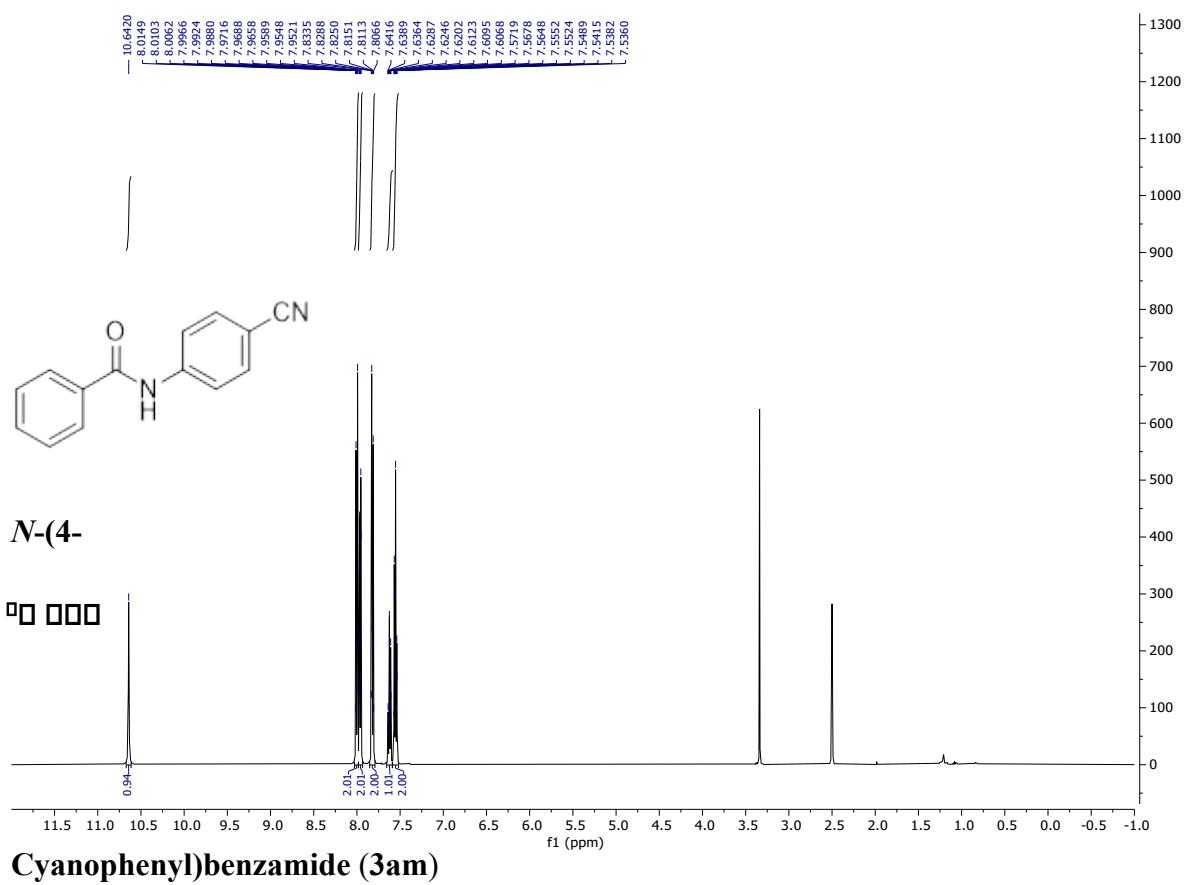


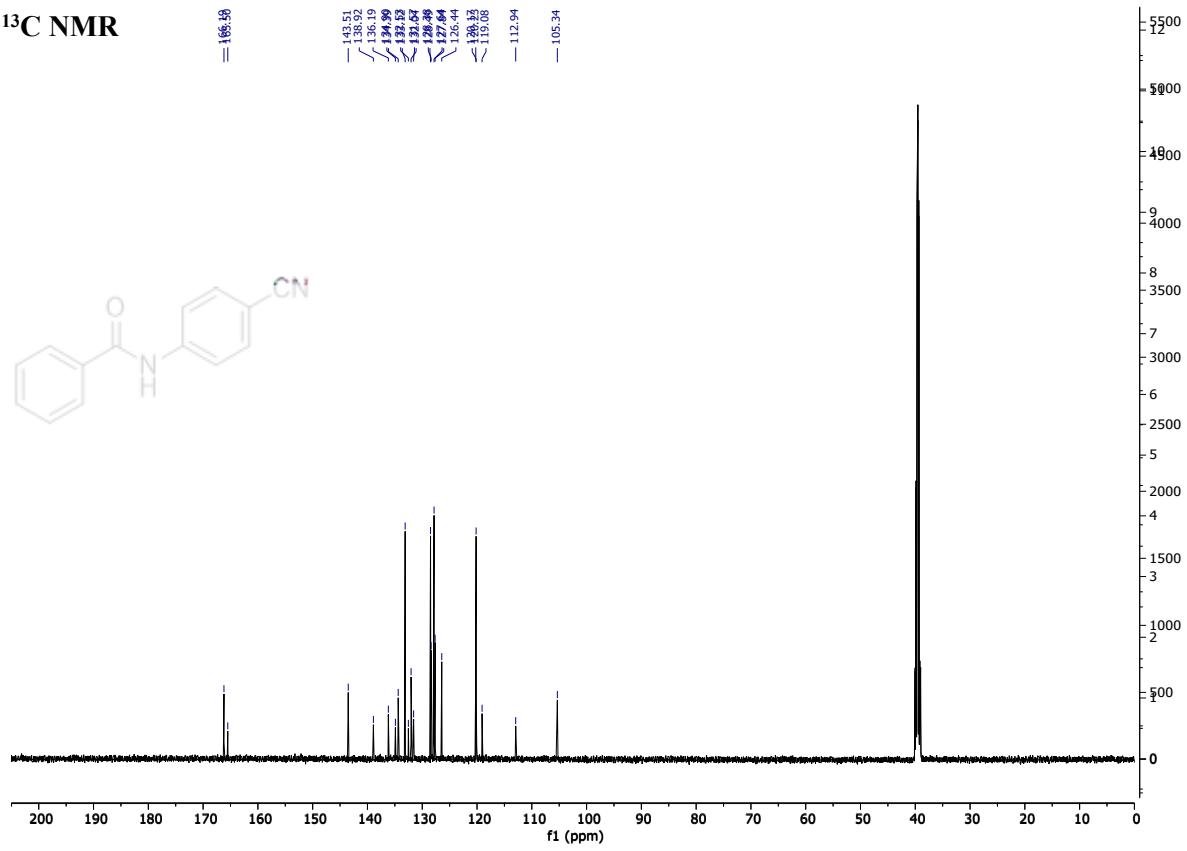
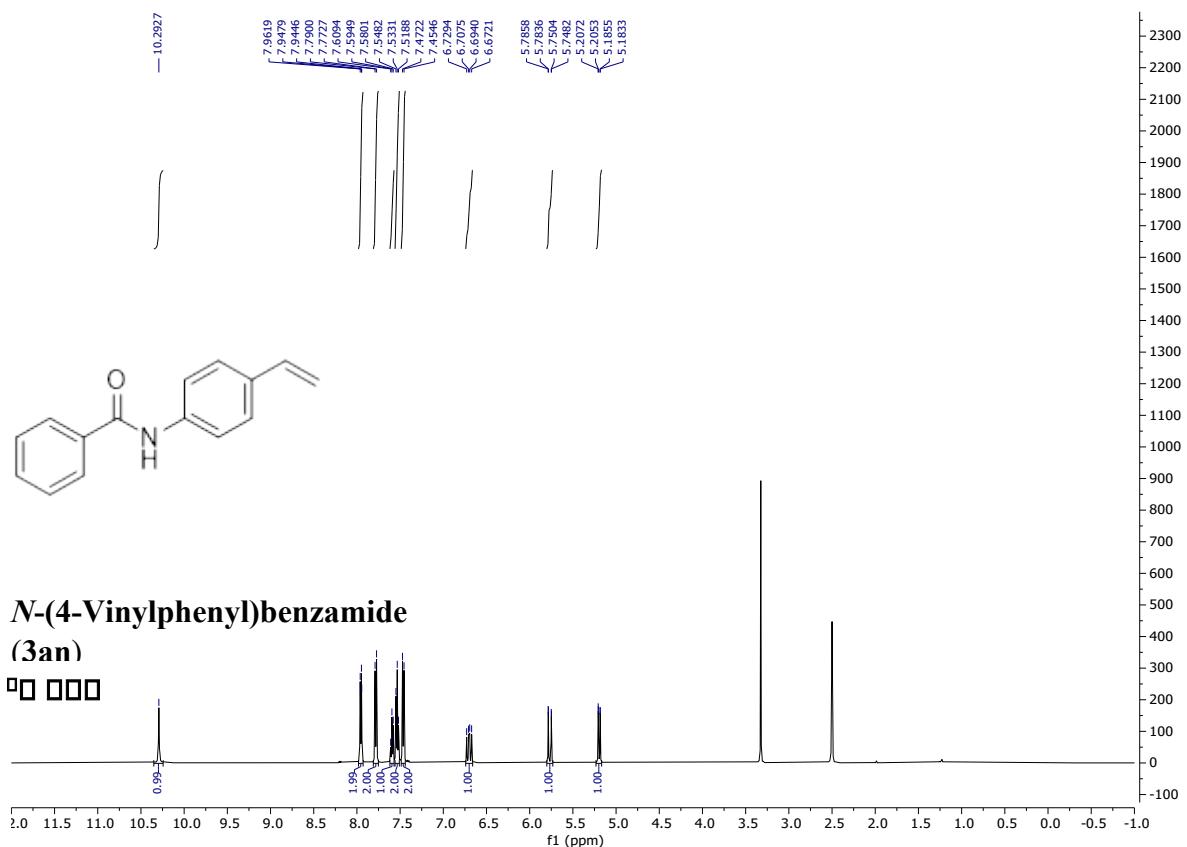
***N*-(4-Acetylphenyl)benzamide (3al)**

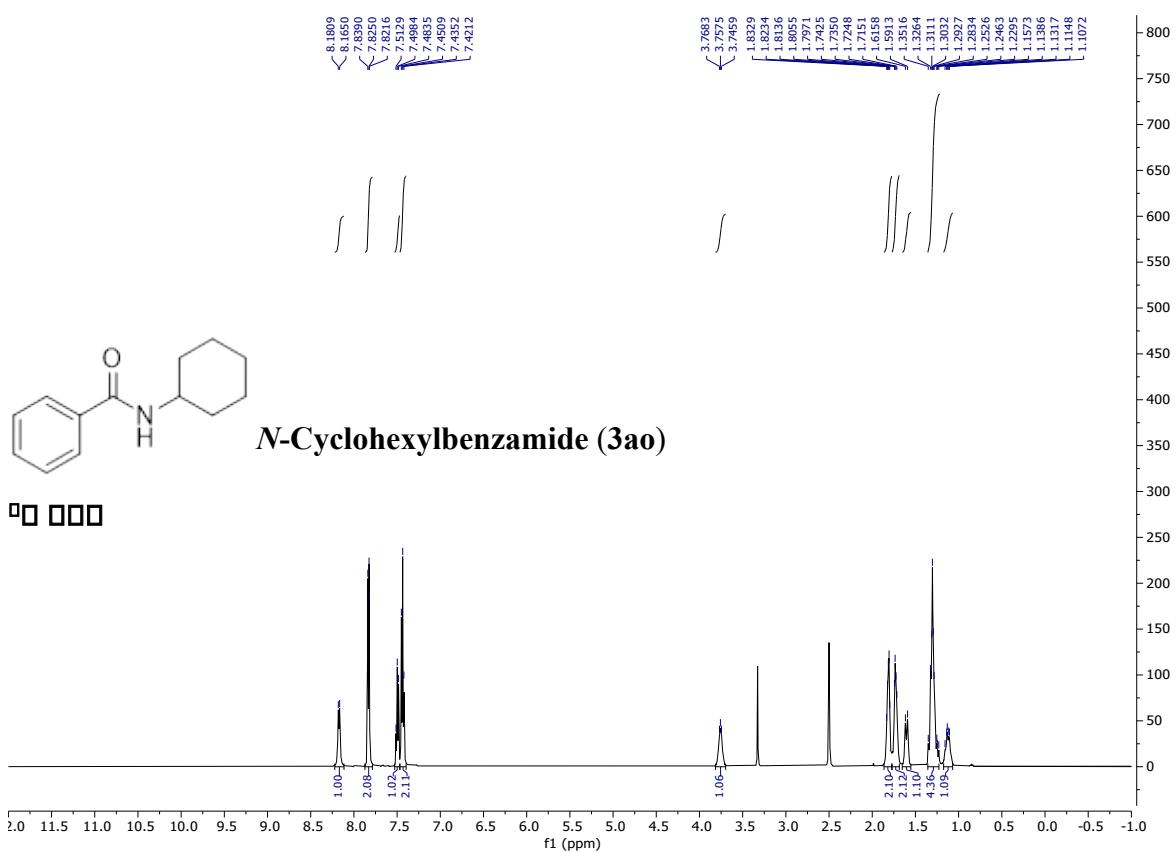


**<sup>13</sup>C NMR**

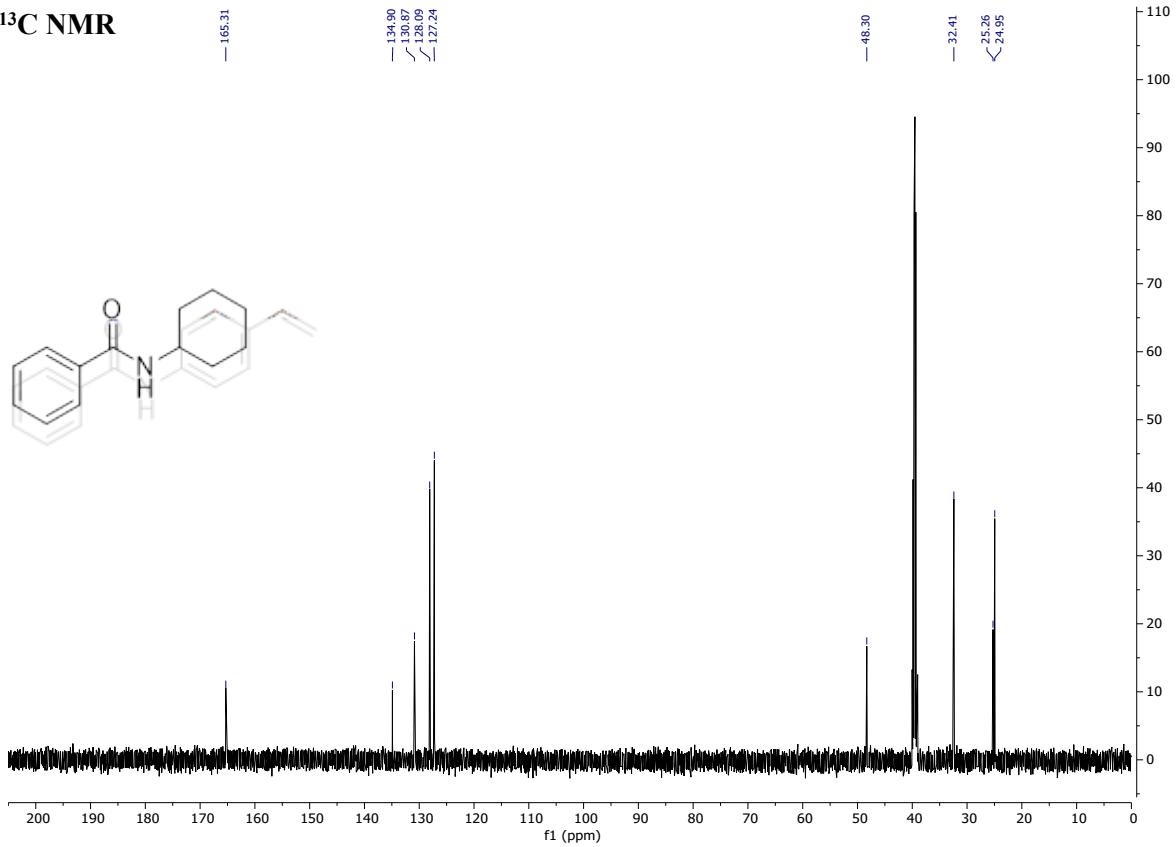




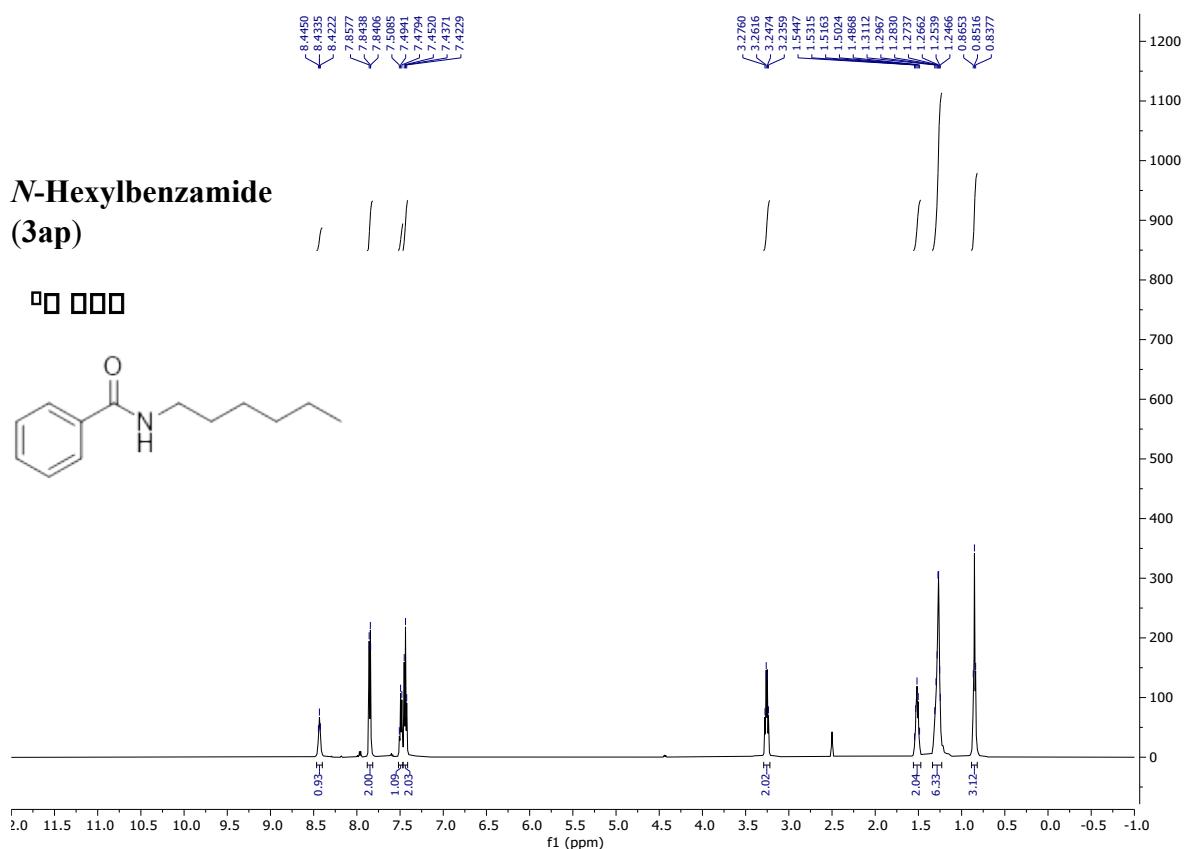




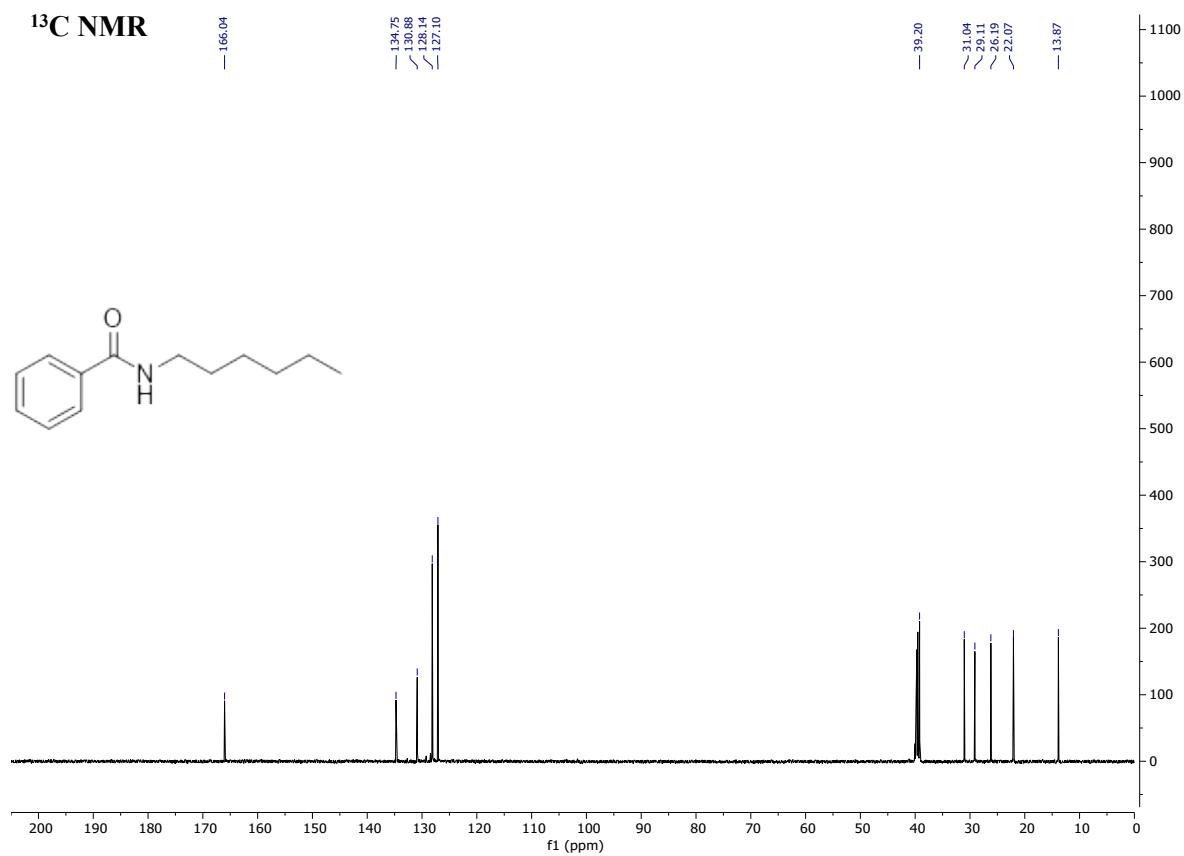
### <sup>13</sup>C NMR

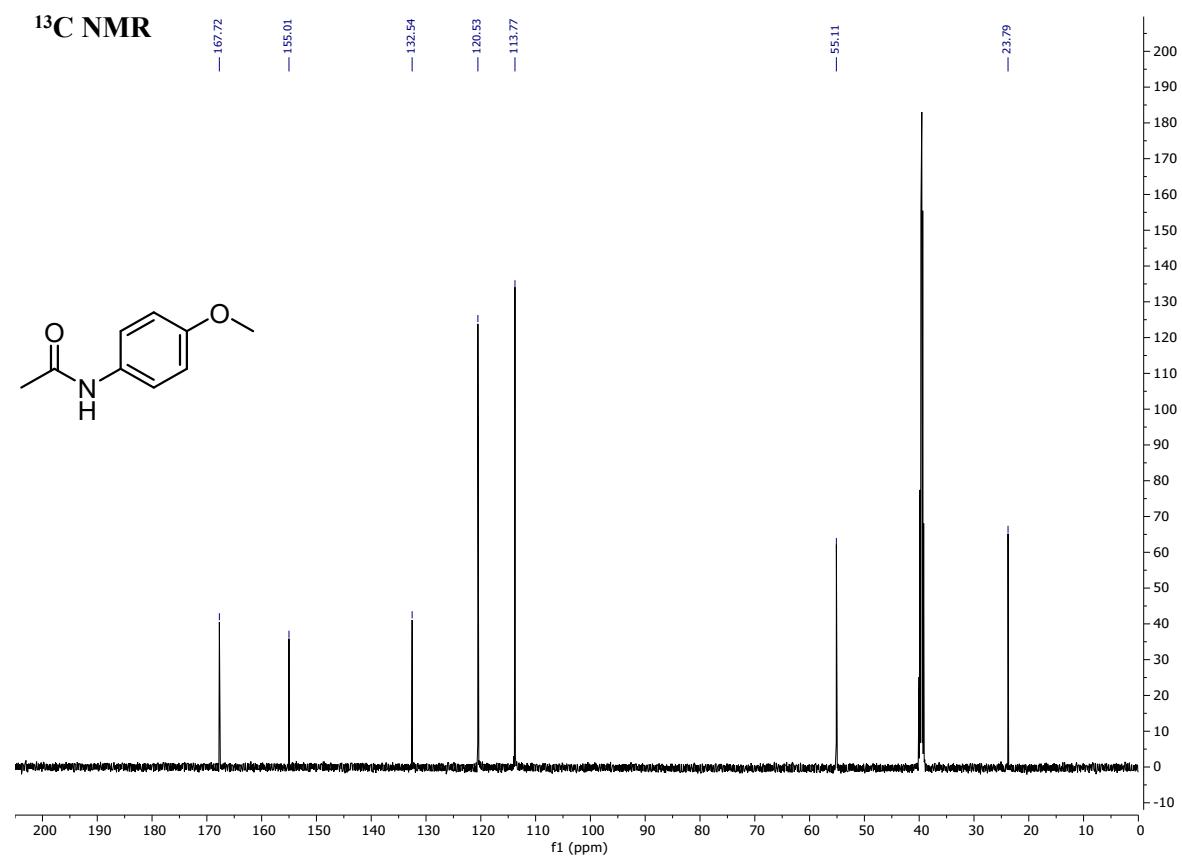
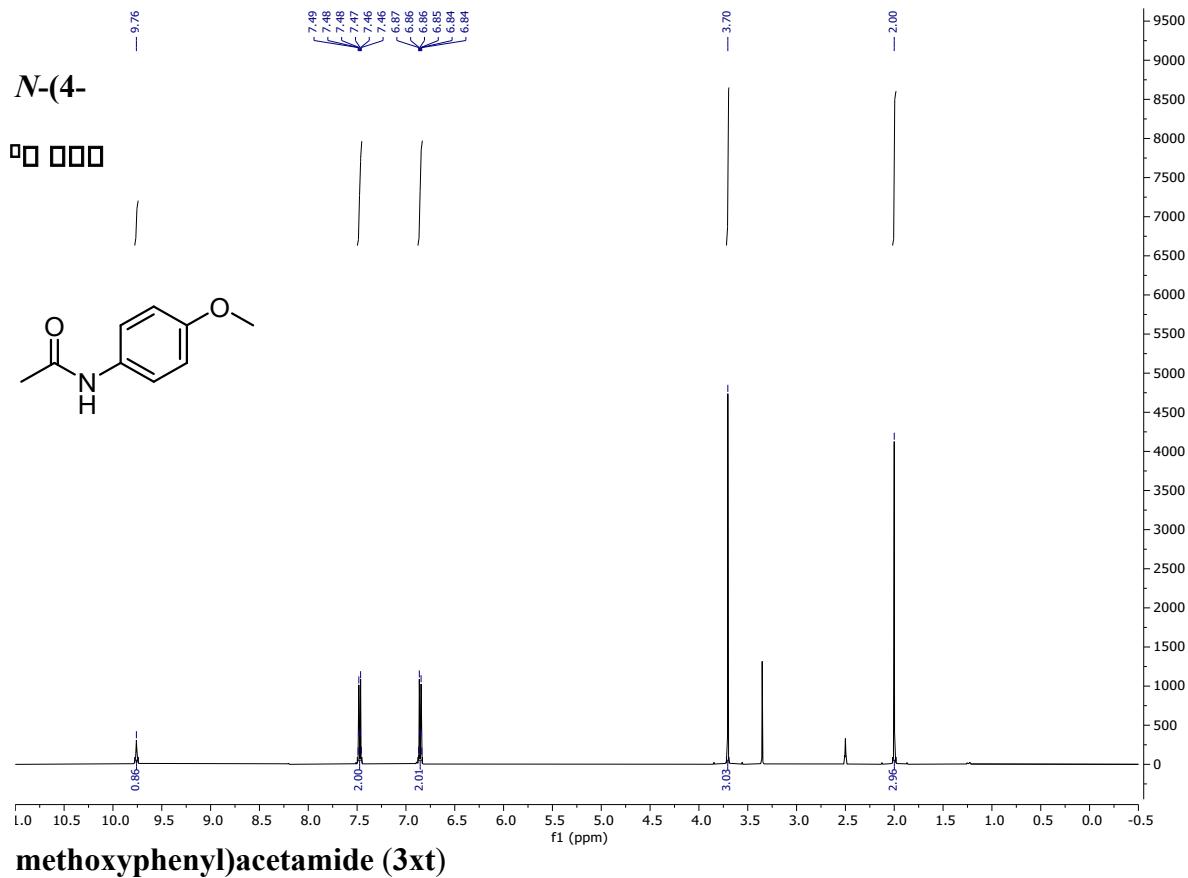


**N-Hexylbenzamide**  
**(3ap)**

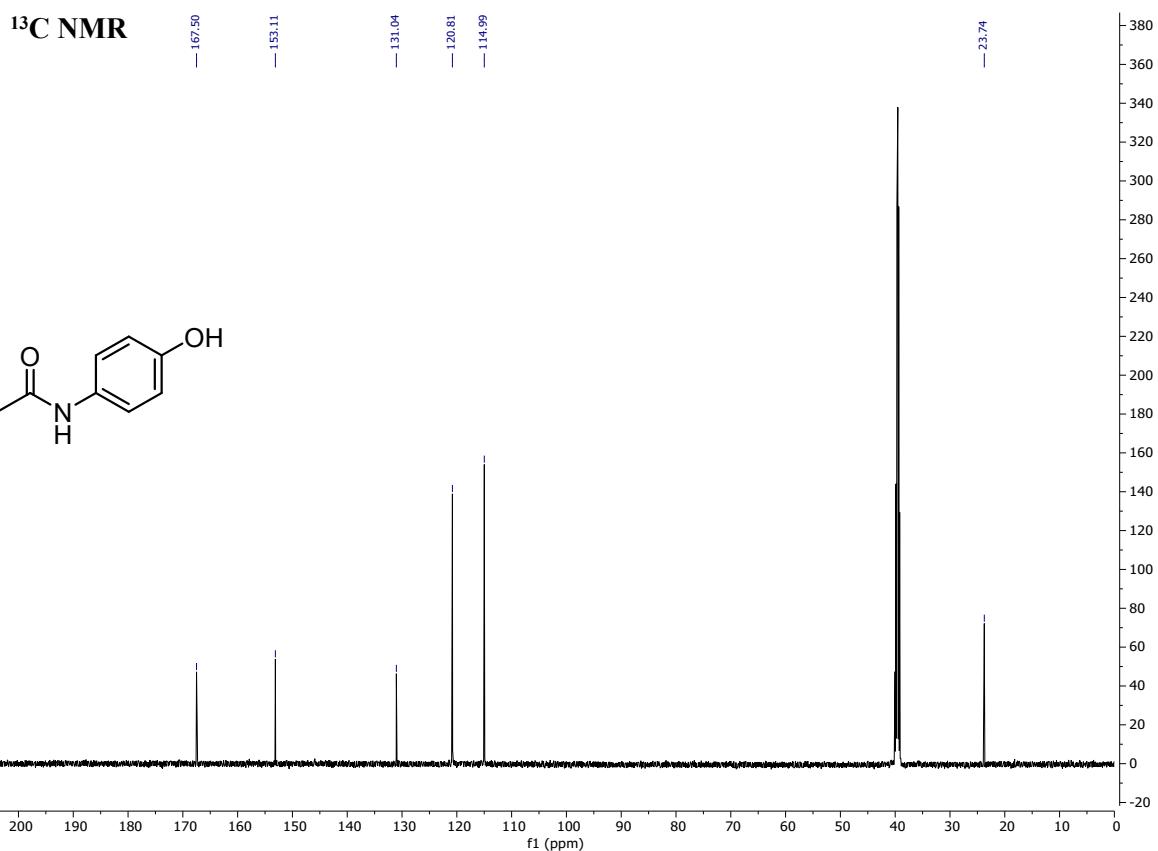
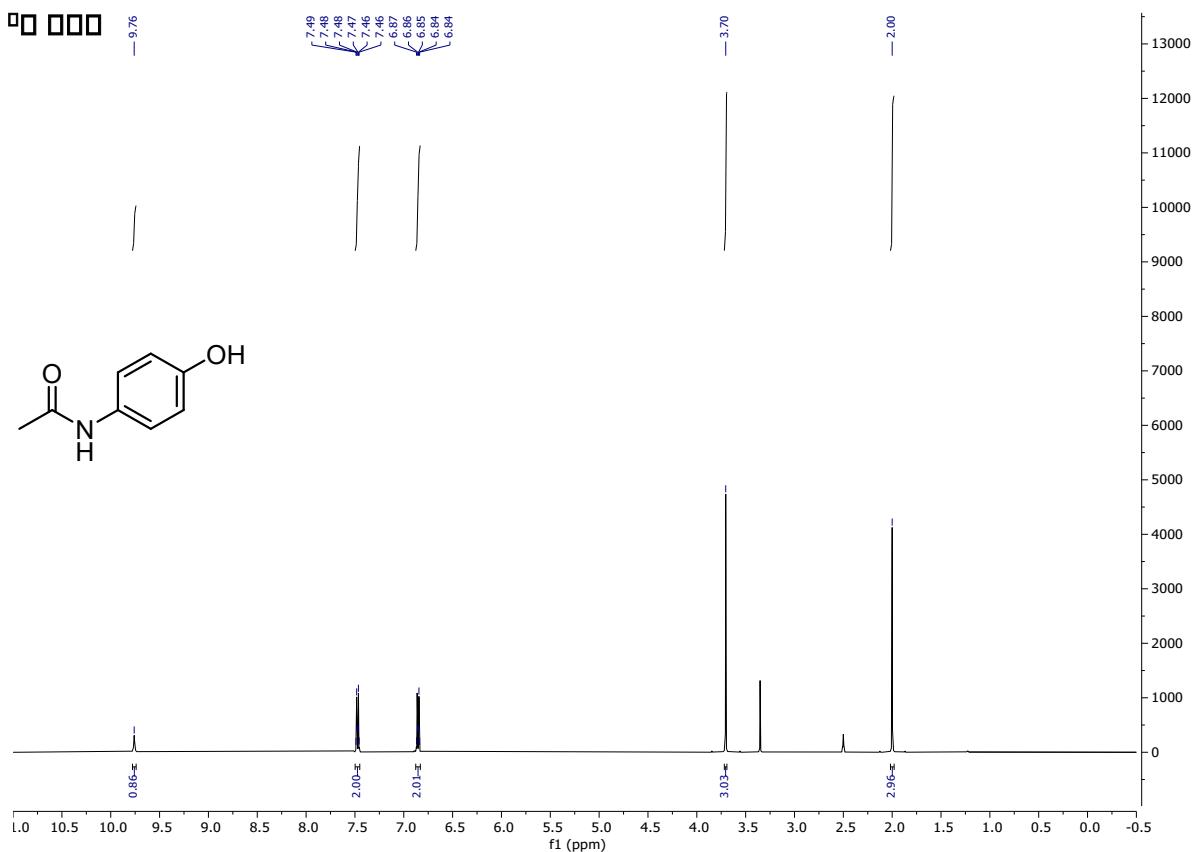


**<sup>13</sup>C NMR**

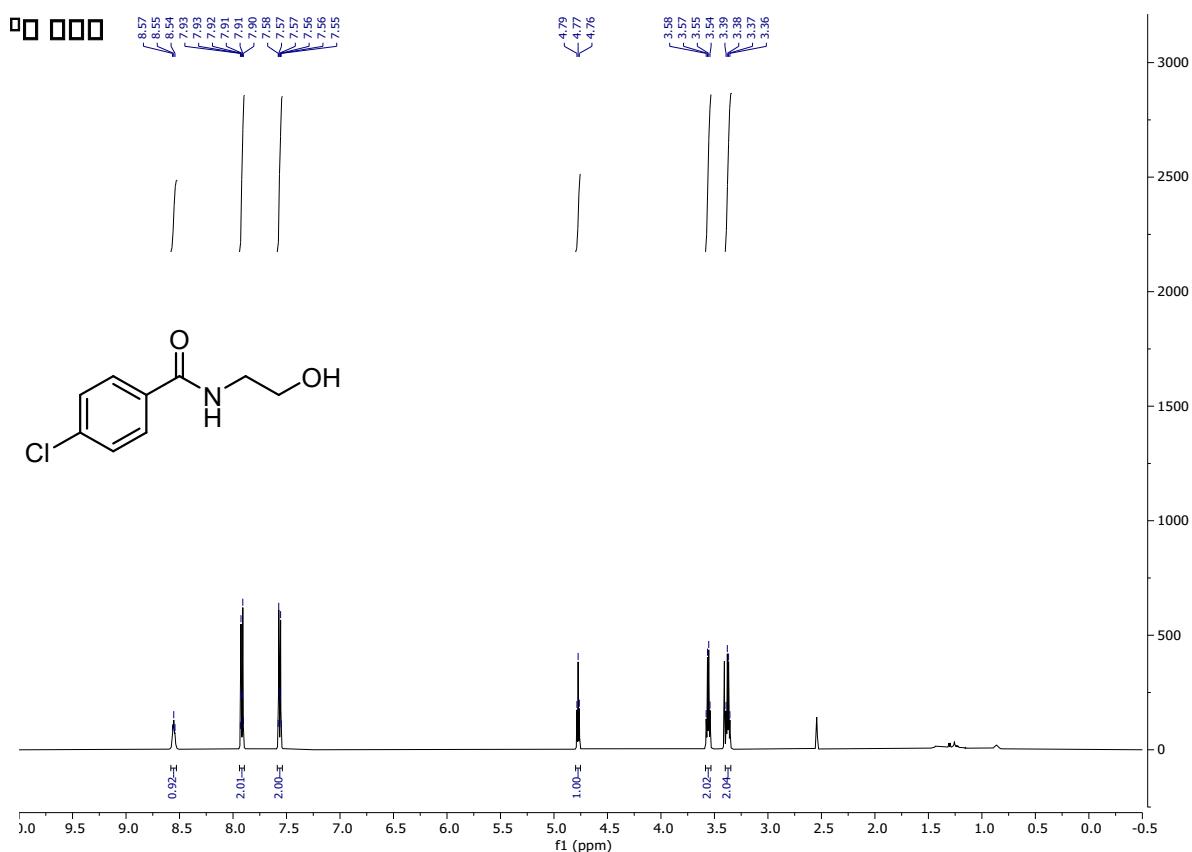




***N*-(4-hydroxyphenyl)acetamide (3xu)**



**4-chloro-N-(2-hydroxyethyl)cyclohexa-2,4-diene-1-carboxamide (3mv)**



**<sup>13</sup>C NMR**

