

# Supporting Information

## Copper(I)/Lewis Acid Triggered Ring-Opening Coupling

### Reaction of Cyclopropenes with Nitriles

Huawen Huang\*, Xiaochen Ji, Fuhong Xiao and Guo-Jun Deng\*

Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry  
of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China.

E-mail: hwhuang@xtu.edu.cn; gjdeng@xtu.edu.cn.

### List of Contents

A. General method .....	S2
B. General procedure .....	S2
C. Analytical data for products prepared .....	S2
D. <sup>1</sup> H and <sup>13</sup> C NMR spectra .....	S11

## A. General method

Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. High-resolution mass spectra were obtained with Shimadzu LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. All the other chemicals were purchased without further purification.

## B. General procedure

**Procedure for the synthesis of  $\gamma$ -amino ketones from corresponding cyclopropyl ketones and nitriles.** To the mixture of cyclopropyl ketone (0.2 mmol, 1.0 equiv) and nitrile (aryl-carbonitrile: 3 equiv; alkyl-carbonitrile: 1.5 equiv), CuBr (5 mol%),  $\text{PBU}_3$  (10 mol%),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (1.0 equiv),  $\text{H}_2\text{O}$  (1.0 equiv), and  $\text{MeNO}_2$  (1.5 mL) were added successively. The mixture was stirred under 85 °C for 18 h. Upon completion, the crude product was directly separated by flash column chromatography on silica gel to give the pure product.

## C. Analytical data for products prepared

***N*-(4-Oxo-4-phenyl-butyl)-benzamide 4aa.** White solid, m.p: 118–120 °C. IR (KBr): 2970, 1643, 1406, 704  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 7.7$  Hz, 2H), 7.78 (d,  $J = 7.5$  Hz, 2H), 7.54 (t,  $J = 7.4$  Hz, 1H), 7.46–7.36 (m, 5H), 6.90 (br. s, 1H), 3.53 (q,  $J = 6.5$  Hz, 2H), 3.10 (t,  $J = 6.8$  Hz, 2H), 2.08 (p,  $J = 6.7$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.33, 167.55, 136.58, 134.43, 133.19, 131.23, 128.55, 128.40, 127.98, 126.84, 39.85, 36.25, 23.47. MS (EI)  $m/z$ : 77, 105, 148, 162, 267. Anal. calcd.

for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>: C 76.38, H 6.41, found: C 76.51, H 6.36.

**4-Methyl-N-(4-oxo-4-phenyl-butyl)-benzamide 4ab.** White solid, m.p: 128–130 °C. IR (KBr): 2922, 1740, 1644, 1540, 1364, 685 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.71 (br. s, 1H), 3.53 (q, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.7 Hz, 2H), 2.36 (s, 3H), 2.08 (p, *J* = 6.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.37, 167.50, 141.64, 136.63, 133.21, 131.62, 129.11, 128.58, 128.02, 126.84, 39.81, 36.29, 23.54, 21.35. MS (EI) *m/z*: 77, 91, 119, 162, 281. Anal. calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>: C 76.84, H 6.81, found: C 76.98, H 6.70.

**2-Methyl-N-(4-oxo-4-phenyl-butyl)-benzamide 4ac.** White solid, m.p: 112–114 °C. IR (KBr): 2923, 1644, 1522, 1408, 1289, 691 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19–7.14 (m, 2H), 6.20 (br. s, 1H), 3.52 (q, *J* = 6.6 Hz, 2H), 3.11 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 2.06 (p, *J* = 6.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.85, 170.28, 136.64, 136.40, 135.93, 133.20, 130.92, 129.74, 128.61, 128.00, 126.61, 125.65, 39.46, 36.03, 23.87, 19.73. MS (EI) *m/z*: 77, 105, 119, 162, 281. Anal. calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>: C 76.84, H 6.81, found: C 76.95, H 6.75.

**4-Methoxy-N-(4-oxo-4-phenyl-butyl)-benzamide 4ad.** White solid, m.p: 138–140 °C. IR (KBr): 2923, 1741, 1624, 1502, 1250, 681 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.69 (br. s, 1H), 3.82 (s, 3H), 3.53 (q, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.7 Hz, 2H), 2.08 (p, *J* = 6.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.48, 167.10, 162.01, 136.63, 133.22, 128.65, 128.59, 128.03, 126.76, 113.63, 55.32, 39.86, 36.34, 23.54. MS (EI) *m/z*: 77, 92, 107, 135, 297. Anal. calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>: C 72.71, H 6.44, found: C 72.88, H 6.31.

**3-Bromo-4-methyl-N-(4-oxo-4-phenyl-butyl)-benzamide 4ae.** White solid, m.p: 113–115 °C. IR (KBr): 2951, 1733, 1648, 1543, 1241, 1041, 689 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.94 (s, 1H), 7.64–7.51 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.78 (br. s, 1H), 3.53 (q, *J* = 6.5 Hz, 2H), 3.13 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 2.09 (p, *J* = 6.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ

200.49, 166.08, 141.42, 136.56, 133.75, 133.32, 130.98, 130.73, 128.63, 128.06, 125.63, 124.98, 40.04, 36.33, 23.35, 22.90. MS (EI) m/z: 77, 105, 162, 197, 359. Anal. calcd. for C<sub>18</sub>H<sub>18</sub>BrNO<sub>2</sub>: C 60.01, H 5.04, found: C 60.20, H 4.98.

**4-Fluoro-*N*-(4-oxo-4-phenyl-butyl)-benzamide 4af.** White solid, m.p: 129–131 °C. IR (KBr): 2922, 1647, 1503, 1234, 686 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.79 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.86 (br. s, 1H), 3.53 (q, *J* = 6.4 Hz, 2H), 3.13 (t, *J* = 6.6 Hz, 2H), 2.09 (p, *J* = 6.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.59, 166.47, 164.58, 136.56, 133.33, 130.62, 129.18, 128.63, 128.02, 115.44, 40.09, 36.41, 23.29. MS (EI) m/z: 77, 105, 123, 166, 285. Anal. calcd. for C<sub>17</sub>H<sub>16</sub>FNO<sub>2</sub>: C 71.56, H 5.65, found: C 71.58, H 5.57.

**4-Chloro-*N*-(4-oxo-4-phenyl-butyl)-benzamide 4ag.** White solid, m.p: 155–157 °C. IR (KBr): 2922, 1738, 1639, 1538, 1363, 686 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.85 (br. s, 1H), 3.53 (q, 6.4 Hz, 2H), 3.14 (t, *J* = 6.6 Hz, 2H), 2.10 (p, *J* = 6.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.63, 166.44, 137.51, 136.55, 133.38, 132.83, 128.71, 128.66, 128.33, 128.04, 40.17, 36.47, 23.21. MS (EI) m/z: 77, 105, 139, 182, 301. Anal. calcd. for C<sub>17</sub>H<sub>16</sub>ClNO<sub>2</sub>: C 67.66, H 5.34, found: C 67.52, H 5.41.

**4-Bromo-*N*-(4-oxo-4-phenyl-butyl)-benzamide 4ah.** White solid, m.p: 158–160 °C. IR (KBr): 2922, 1682, 1639, 1540, 1459, 686 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.59-7.53 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.82 (br. s, 1H), 3.54 (q, *J* = 6.2 Hz, 2H), 3.14 (t, *J* = 6.5 Hz, 2H), 2.10 (p, *J* = 6.5 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.64, 166.50, 136.55, 133.39, 133.30, 131.70, 128.67, 128.52, 128.05, 125.97, 40.19, 36.49, 23.19. MS (EI) m/z: 77, 105, 183, 226, 345. Anal. calcd. for C<sub>17</sub>H<sub>16</sub>BrNO<sub>2</sub>: C 58.97, H 4.66, found: C 58.68, H 4.71.

**4-Iodo-*N*-(4-oxo-4-phenyl-butyl)-benzamide 4ai.** White solid, m.p: 173–175 °C. IR (KBr): 2922, 1649, 1539, 1457, 1268, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.77–7.74 (m, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.51–7.43 (m, 4H),

6.87 (br. s, 1H), 3.52 (q,  $J = 6.3$  Hz, 2H), 3.16–3.12 (m, 2H), 2.12 – 2.06 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.62, 166.72, 137.67, 136.54, 133.86, 133.38, 128.66, 128.53, 128.05, 98.25, 40.16, 36.46, 23.20. MS (EI)  $m/z$ : 77, 105, 127, 230, 273, 393. Anal. calcd. for  $\text{C}_{17}\text{H}_{16}\text{INO}_2$ : C 51.93, H 4.10, found: C 52.08, H 4.06.

**Pentanoic acid [4-(4-fluoro-phenyl)-4-oxo-butyl]-amide 4bj.** White solid, m.p: 100–102 °C. IR (KBr): 2951, 1637, 1541, 1464, 1234, 833, 679  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 8.5, 5.6$  Hz, 2H), 7.11 (t,  $J = 8.5$  Hz, 2H), 5.83 (br. s, 1H), 3.33 (q,  $J = 6.5$  Hz, 2H), 3.00 (t,  $J = 6.9$  Hz, 2H), 2.13 (t,  $J = 7.6$  Hz, 2H), 1.95 (p,  $J = 6.9$  Hz, 2H), 1.56 (p,  $J = 7.6$  Hz, 2H), 1.35–1.25 (m, 2H), 0.87 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.37, 173.35, 165.77, 133.10, 130.64, 115.70, 39.04, 36.52, 35.93, 27.78, 23.80, 22.36, 13.72. MS (EI)  $m/z$ : 85, 95, 123, 164, 223, 265. Anal. calcd. for  $\text{C}_{15}\text{H}_{20}\text{FNO}_2$ : C 67.90, H 7.60, found: C 67.74, H 7.64.

**Pentanoic acid [4-(4-chloro-phenyl)-4-oxo-butyl]-amide 4cj.** White solid, m.p: 127–129 °C. IR (KBr): 2938, 1638, 1543, 1461, 1362, 820, 683  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.4$  Hz, 2H), 7.41 (d,  $J = 8.4$  Hz, 2H), 5.83 (br. s, 1H), 3.33 (q,  $J = 6.6$  Hz, 2H), 2.99 (t,  $J = 6.9$  Hz, 2H), 2.13 (t,  $J = 7.6$  Hz, 2H), 1.94 (p,  $J = 6.9$  Hz, 2H), 1.56 (p,  $J = 7.6$  Hz, 2H), 1.34–1.25 (m, 2H), 0.87 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.72, 173.35, 139.63, 134.96, 129.41, 128.91, 38.99, 36.50, 35.97, 27.77, 23.77, 22.36, 13.72. MS (EI)  $m/z$ : 85, 128, 139, 180, 239, 281. Anal. calcd. for  $\text{C}_{15}\text{H}_{20}\text{ClNO}_2$ : C 63.94, H 7.15, found: C 63.80, H 7.22.

**Pentanoic acid [4-(4-methoxy-phenyl)-4-oxo-butyl]-amide 4dj.** White solid, m.p: 115–117 °C. IR (KBr): 2933, 1666, 1513, 1458, 1255, 1171, 1027, 833  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.8$  Hz, 2H), 6.92 (d,  $J = 8.8$  Hz, 2H), 5.87 (br. s, 1H), 3.86 (s, 3H), 3.33 (q,  $J = 6.5$  Hz, 2H), 2.98 (t,  $J = 6.9$  Hz, 2H), 2.13 (t,  $J = 7.6$  Hz, 2H), 1.95 (p,  $J = 6.8$  Hz, 2H), 1.56 (p,  $J = 7.6$  Hz, 2H), 1.35–1.26 (m, 2H), 0.88 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.73, 173.36, 163.58, 130.32, 129.76, 113.75, 55.45, 39.24, 36.54, 35.72, 27.79, 23.85, 22.37, 13.73. MS (EI)  $m/z$ : 77, 92, 135, 150, 176, 235, 277. Anal. calcd. for  $\text{C}_{16}\text{H}_{23}\text{NO}_3$ : C 69.29, H 8.36, found: C 69.38, H 8.25.

**Dodecanoic acid (4-oxo-4-phenyl-butyl)-amide 4ak.** White solid, m.p: 91–93 °C. IR

(KBr): 2919, 1684, 1640, 1459, 1362, 683  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.1$  Hz, 2H), 7.55 (t,  $J = 7.3$  Hz, 1H), 7.44 (t,  $J = 7.7$  Hz, 2H), 5.90 (br. s, 1H), 3.34 (q,  $J = 6.5$  Hz, 2H), 3.03 (t,  $J = 6.9$  Hz, 2H), 2.12 (t,  $J = 7.6$  Hz, 2H), 1.96 (p,  $J = 6.8$  Hz, 2H), 1.62–1.53 (m, 2H), 1.32–1.17 (m, 16H), 0.86 (t,  $J = 6.7$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.04, 173.36, 136.66, 133.17, 128.59, 127.98, 39.10, 36.80, 36.03, 31.84, 29.56, 29.54, 29.43, 29.30, 29.27, 29.26, 25.72, 23.74, 22.62, 14.05. MS (EI)  $m/z$ : 77, 105, 146, 205, 345. Anal. calcd. for  $\text{C}_{22}\text{H}_{35}\text{NO}_2$ : C 76.47, H 10.21, found: C 76.57, H 10.15.

**Cyclopropanecarboxylic acid (4-oxo-4-phenyl-butyl)-amide 4al.** White solid, m.p: 112–114  $^\circ\text{C}$ . IR (KBr): 2927, 1680, 1646, 1546, 1448, 1241, 691  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 7.6$  Hz, 2H), 7.54 (t,  $J = 7.3$  Hz, 1H), 7.43 (t,  $J = 7.7$  Hz, 2H), 6.20 (br. s, 1H), 3.34 (q,  $J = 6.6$  Hz, 2H), 3.03 (t,  $J = 7.0$  Hz, 2H), 1.99–1.92 (m, 2H), 1.37–1.30 (m, 1H), 0.91–0.87 (m, 2H), 0.69–0.64 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.09, 173.72, 136.65, 133.11, 128.55, 127.96, 39.29, 35.97, 23.88, 14.59, 6.91. MS (EI)  $m/z$ : 69, 77, 105, 146, 185, 231. Anal. calcd. for  $\text{C}_{14}\text{H}_{17}\text{NO}_2$ : C 72.70, H 7.41, found: C 72.82, H 7.32.

**Adamantane-1-carboxylic acid (4-oxo-4-phenyl-butyl)-amide 4am.** White solid, m.p: 116–118  $^\circ\text{C}$ . IR (KBr): 2908, 1683, 1642, 1520, 1449, 1273, 745, 690  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.8$  Hz, 2H), 7.54 (t,  $J = 7.3$  Hz, 1H), 7.44 (t,  $J = 7.5$  Hz, 2H), 5.94 (br. s, 1H), 3.33 (q,  $J = 6.2$  Hz, 2H), 3.02 (t,  $J = 6.7$  Hz, 2H), 2.00–1.93 (m, 5H), 1.79 (s, 6H), 1.68 (q,  $J = 12.3$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.16, 178.11, 136.67, 133.13, 128.57, 128.01, 40.52, 39.16, 39.05, 36.47, 36.12, 28.09, 23.65. MS (EI)  $m/z$ : 77, 105, 135, 180, 206, 281, 325. Anal. calcd. for  $\text{C}_{21}\text{H}_{27}\text{NO}_2$ : C 77.50, H 8.36, found: C 77.44, H 8.39.

***N*-(4-Oxo-4-phenyl-butyl)-4-phenyl-butyramide 4an.** White solid, m.p: 72–74  $^\circ\text{C}$ . IR (KBr): 2933, 1679, 1543, 1449, 1247, 744, 695  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.0$  Hz, 2H), 7.55 (t,  $J = 7.2$  Hz, 1H), 7.44 (t,  $J = 7.6$  Hz, 2H), 7.25 (t,  $J = 7.4$  Hz, 2H), 7.18–7.13 (m, 3H), 5.92 (br. s, 1H), 3.33 (q,  $J = 6.5$  Hz, 2H), 3.03 (t,  $J = 6.9$  Hz, 2H), 2.62 (t,  $J = 7.5$  Hz, 2H), 2.15 (t,  $J = 7.5$  Hz, 2H), 1.99–1.89 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.98, 172.87, 141.43, 136.61, 133.15, 128.57,

128.38, 128.28, 127.95, 125.84, 39.11, 35.98, 35.87, 35.15, 27.04, 23.72. MS (EI) m/z: 77, 91, 105, 146, 205, 309. Anal. calcd. for C<sub>20</sub>H<sub>23</sub>NO<sub>2</sub>: C 77.64, H 7.49, found: C 77.75, H 7.46.

***N*-[4-(4-Fluoro-phenyl)-4-oxo-butyl]-2-phenyl-acetamide 4bo.** White solid, m.p: 96–98 °C. IR (KBr): 2922, 1676, 1627, 1550, 1459, 1357, 1239, 826, 691 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93–7.89 (m, 2H), 7.34–7.22 (m, 5H), 7.11 (t, *J* = 8.6 Hz, 2H), 5.80 (br. s, 1H), 3.53 (s, 2H), 3.30 (q, *J* = 6.7 Hz, 2H), 2.92 (t, *J* = 7.0 Hz, 2H), 1.88 (p, *J* = 6.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.01, 171.17, 165.70, 134.90, 133.02, 130.59, 129.29, 128.91, 127.23, 115.62, 43.79, 39.14, 35.62, 23.63. MS (EI) m/z: 77, 91, 125, 223, 299. Anal. calcd. for C<sub>18</sub>H<sub>18</sub>FNO<sub>2</sub>: C 72.22, H 6.06, found: C 72.05, H 6.12.

***N*-(4-Oxo-4-phenyl-butyl)-acrylamide 4ap.** White solid, m.p: 68–70 °C. IR (KBr): 2930, 1673, 1543, 1449, 1243, 691 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.27–6.05 (m, 3H), 5.60 (dd, *J* = 10.2, 1.3 Hz, 1H), 3.43 (q, *J* = 6.7 Hz, 2H), 3.07 (t, *J* = 6.9 Hz, 2H), 2.01 (p, *J* = 6.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.15, 165.77, 136.63, 133.24, 130.89, 128.62, 128.01, 126.18, 39.28, 36.08, 23.59. MS (EI) m/z: 77, 105, 146, 217. Anal. calcd. for C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>: C 71.87, H 6.96, found: C 71.64, H 7.07.

**Hex-5-enoic acid (4-oxo-4-phenyl-butyl)-amide 4aq.** Yellowish oil. IR (KBr): 2933, 1648, 1544, 1447, 1250, 1208, 994, 745, 691 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.07 (br. s, 1H), 5.81–5.71 (m, 1H), 5.02–4.94 (m, 2H), 3.34 (q, *J* = 6.4 Hz, 2H), 3.04 (t, *J* = 6.9 Hz, 2H), 2.16 (t, *J* = 7.6 Hz, 2H), 2.06 (q, *J* = 7.1 Hz, 2H), 1.97 (p, *J* = 6.8 Hz, 2H), 1.71 (p, *J* = 7.5 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.97, 173.00, 137.78, 136.62, 133.11, 128.54, 127.92, 115.09, 39.06, 35.96, 35.83, 33.06, 24.67, 23.74. MS (EI) m/z: 77, 105, 146, 205, 259. Anal. calcd. for C<sub>16</sub>H<sub>21</sub>NO<sub>2</sub>: C 74.10, H 8.16, found: C 74.23, H 8.14.

**3-Methoxy-*N*-(4-oxo-4-phenyl-butyl)-propionamide 4ar.** Yellowish oil. IR (KBr): 2930, 1680, 1546, 1448, 1209, 1113, 692 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.41 (br. s, 1H),

3.59 (t,  $J = 5.8$  Hz, 2H), 3.36–3.32 (m, 5H), 3.02 (t,  $J = 7.0$  Hz, 2H), 2.41 (t,  $J = 5.8$  Hz, 2H), 1.95 (p,  $J = 7.0$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.79, 171.49, 136.70, 133.08, 128.55, 127.96, 68.61, 58.70, 38.88, 36.97, 35.82, 23.84. MS (EI)  $m/z$ : 77, 105, 146, 205, 249. Anal. calcd. for  $\text{C}_{14}\text{H}_{19}\text{NO}_3$ : C 67.45, H 7.68, found: C 67.28, H 7.75.

***N*-[4-(4-Chloro-phenyl)-4-oxo-butyl]-3-methoxy-propionamide 4cr.** Yellowish oil. IR (KBr): 2936, 1672, 1553, 1403, 1115, 817, 753  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.5$  Hz, 2H), 7.42 (d,  $J = 8.5$  Hz, 2H), 6.36 (br. s, 1H), 3.60 (t,  $J = 5.8$  Hz, 2H), 3.37–3.32 (m, 5H), 2.99 (t,  $J = 7.0$  Hz, 2H), 2.42 (t,  $J = 5.8$  Hz, 2H), 1.95 (p,  $J = 7.0$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.53, 171.61, 139.56, 135.05, 129.43, 128.90, 68.63, 58.76, 38.81, 37.00, 35.82, 23.88. MS (EI)  $m/z$ : 77, 105, 146, 205, 283. Anal. calcd. for  $\text{C}_{14}\text{H}_{18}\text{ClNO}_3$ : C 59.26, H 6.39, found: C 59.13, H 6.45.

**4-Chloro-*N*-(4-oxo-4-phenyl-butyl)-butyramide 4as.** Yellowish oil. IR (KBr): 2931, 1648, 1505, 1232, 833, 698  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.8$  Hz, 2H), 7.56 (t,  $J = 7.3$  Hz, 1H), 7.45 (t,  $J = 7.7$  Hz, 2H), 6.00 (br. s, 1H), 3.56 (t,  $J = 6.2$  Hz, 2H), 3.34 (q,  $J = 6.6$  Hz, 2H), 3.04 (t,  $J = 6.9$  Hz, 2H), 2.32 (t,  $J = 7.1$  Hz, 2H), 2.07 ((p,  $J = 6.8$  Hz, 2H), 1.97 (p,  $J = 6.9$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.99, 171.79, 136.62, 133.23, 128.62, 127.99, 44.47, 39.23, 35.98, 33.19, 28.07, 23.68. MS (EI)  $m/z$ : 77, 105, 146, 205, 233, 267. Anal. calcd. for  $\text{C}_{14}\text{H}_{18}\text{ClNO}_2$ : C 62.80, H 6.78, found: C 62.55, H 6.91.

**Hex-5-ynoic acid (4-oxo-4-phenyl-butyl)-amide 4at.** White solid, m.p: 77–79 °C. IR (KBr): 2933, 1678, 1545, 1447, 1366, 1248, 691  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.6$  Hz, 2H), 7.56 (t,  $J = 7.3$  Hz, 1H), 7.45 (t,  $J = 7.7$  Hz, 2H), 5.93 (br. s, 1H), 3.34 (q,  $J = 6.6$  Hz, 2H), 3.04 (t,  $J = 6.9$  Hz, 2H), 2.30–2.20 (m, 4H), 2.01–1.93 (m, 3H), 1.86–1.78 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.99, 172.35, 136.64, 133.20, 128.61, 127.99, 83.46, 69.11, 39.16, 35.97, 35.03, 24.09, 23.74, 17.79. MS (EI)  $m/z$ : 77, 95, 105, 138, 146, 257. Anal. calcd. for  $\text{C}_{16}\text{H}_{19}\text{NO}_2$ : C 74.68, H 7.44, found: C 74.53, H 7.50.

**5-Cyano-pentanoic acid (4-oxo-4-phenyl-butyl)-amide 4au.** Yellowish oil. IR (KBr): 2936, 1679, 1545, 1449, 1242, 693  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93



(d,  $J = 8.2$  Hz, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.44 (t,  $J = 7.7$  Hz, 2H), 6.10 (br. s, 1H), 3.32 (q,  $J = 6.5$  Hz, 2H), 3.03 (t,  $J = 6.8$  Hz, 2H), 2.31 (t,  $J = 6.9$  Hz, 2H), 2.18 (t,  $J = 7.1$  Hz, 2H), 1.95 (p,  $J = 6.8$  Hz, 2H), 1.77–1.61 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.05, 172.04, 136.56, 133.23, 128.61, 127.94, 119.47, 39.21, 36.00, 35.31, 24.82, 24.50, 23.57, 16.87. MS (EI)  $m/z$ : 77, 105, 110, 162, 272. Anal. calcd. for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$ : C 70.56, H 7.40, found: C 70.62, H 7.35.

**2-(4-Methoxy-phenyl)-*N*-(4-oxo-4-phenyl-butyl)-acetamide 4av.** White solid, m.p: 109–111 °C. IR (KBr): 2925, 1648, 1448, 1203, 696  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 7.7$  Hz, 2H), 7.57 (t,  $J = 7.3$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 7.14 (d,  $J = 8.3$  Hz, 2H), 6.86 (d,  $J = 8.3$  Hz, 2H), 5.64 (br. s, 1H), 3.79 (s, 3H), 3.48 (s, 2H), 3.30 (q,  $J = 6.5$  Hz, 2H), 2.96 (t,  $J = 6.9$  Hz, 2H), 1.89 (p,  $J = 6.8$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.67, 171.60, 158.76, 136.58, 133.12, 130.42, 128.55, 127.95, 126.82, 114.34, 55.19, 42.87, 39.18, 35.71, 23.61. MS (EI)  $m/z$ : 77, 105, 146, 205, 311. Anal. calcd. for  $\text{C}_{19}\text{H}_{21}\text{NO}_3$ : C 73.29, H 6.80, found: C 73.12, H 6.87.

**8,9-Dimethoxy-10b-phenyl-1,2,3,10b-tetrahydropyrrolo[2,1-a]isoquinolin-5(6H)-one 4aw.** White solid, m.p: 135–137 °C. IR (KBr): 2948, 1644, 1505, 1463, 1229, 834, 699  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.17 (m, 5H), 7.07 (s, 1H), 6.59 (s, 1H), 4.00 (s, 3H), 3.90–3.81 (m, 4H), 3.69 (dd,  $J = 19.1, 11.0$  Hz, 1H), 3.37 (q,  $J = 18.2$  Hz, 2H), 2.69 (dd,  $J = 11.6, 6.1$  Hz, 1H), 2.52–2.44 (m, 1H), 2.04–1.98 (m, 1H), 1.86–1.71 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.19, 148.48, 147.77, 142.78, 133.11, 128.41, 126.94, 125.08, 124.89, 110.50, 108.30, 71.11, 56.43, 55.92, 45.39, 40.43, 38.33, 20.87. HRMS (ESI) calc.  $\text{C}_{20}\text{H}_{21}\text{NO}_3$   $[\text{M}+\text{H}]^+$ : 324.1600, found: 324.1594.

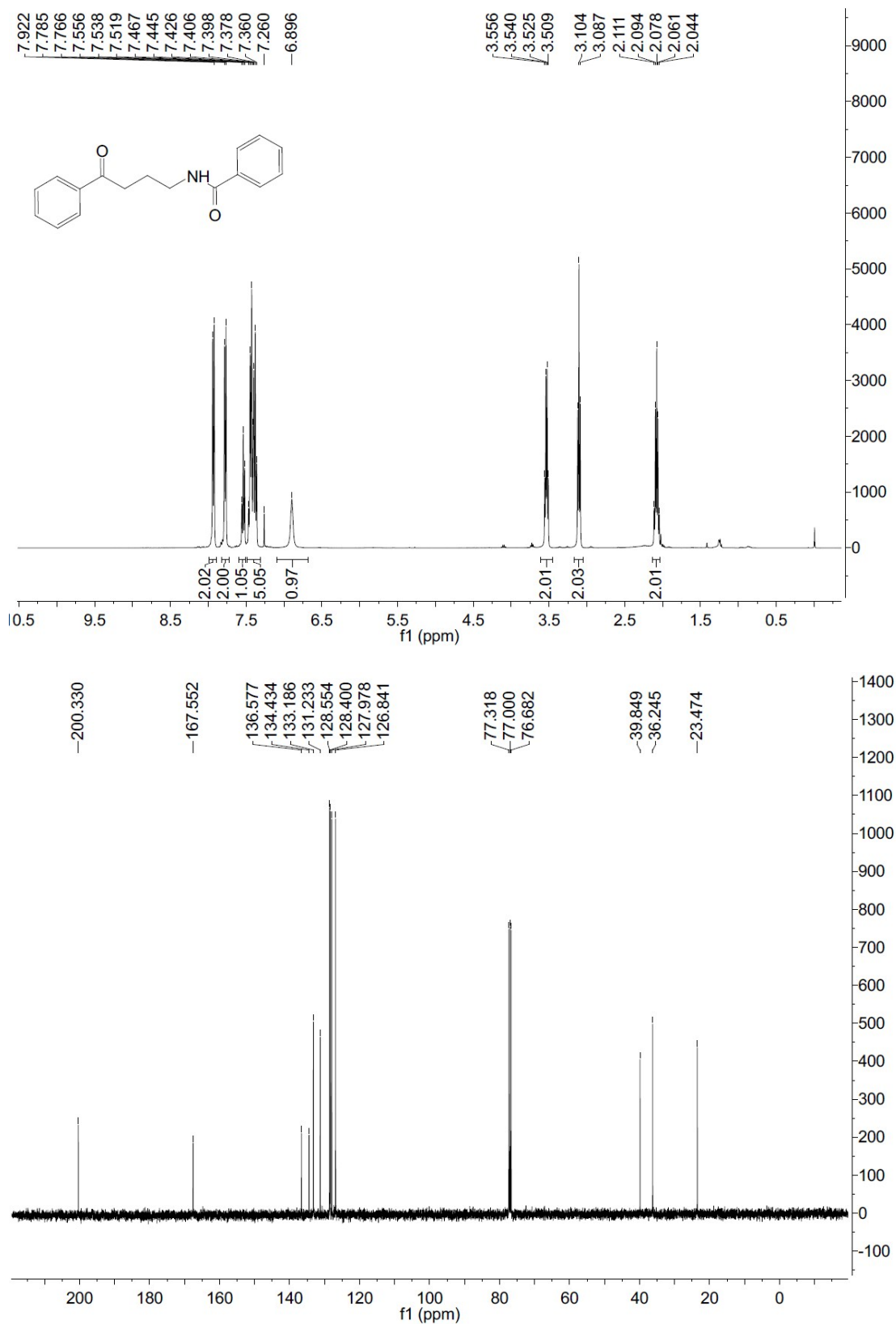
**11b-Phenyl-1,2,3,11b-tetrahydrobenzo[4,5]thieno[3,2-g]indolizin-5(6H)-one 4ax.** White solid, m.p: 175–177 °C. IR (KBr): 2923, 1646, 1508, 1407, 1231, 1160, 833, 671  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 7.9$  Hz, 1H), 7.54 (d,  $J = 7.7$  Hz, 1H), 7.42–7.28 (m, 6H), 7.23 (t,  $J = 7.2$  Hz, 1H), 3.95–3.82 (m, 2H), 3.67 (t,  $J = 10.7$  Hz, 1H), 3.55 (d,  $J = 19.5$  Hz, 1H), 2.85 (dd,  $J = 11.8, 6.4$  Hz, 1H), 2.45–2.36 (m, 1H), 2.08–2.01 (m, 1H), 1.78–1.65 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.03, 142.11, 139.29, 138.99, 136.93, 128.82, 127.45, 125.47, 124.93, 124.67, 124.66, 122.63, 121.25, 69.88, 44.67, 40.11, 32.38, 20.80. HRMS (ESI) calc.  $\text{C}_{20}\text{H}_{17}\text{NOS}$   $[\text{M}+\text{Na}]^+$ :

342.0929, found: 342.0923.

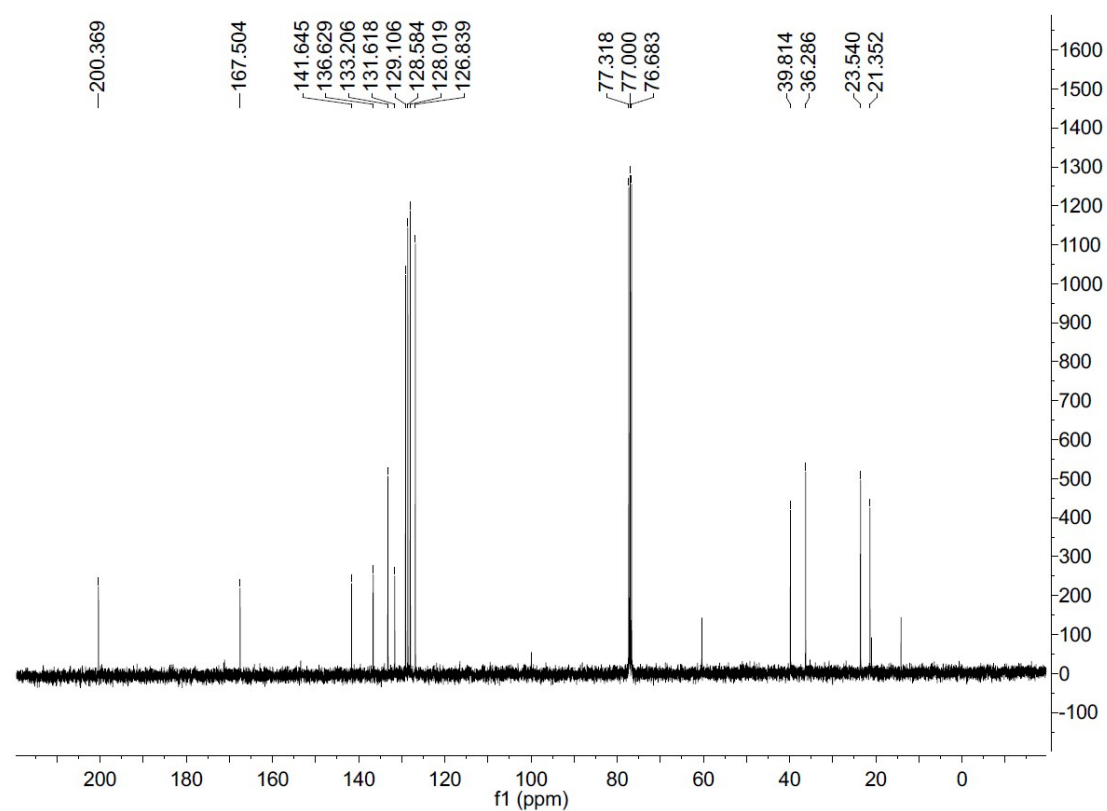
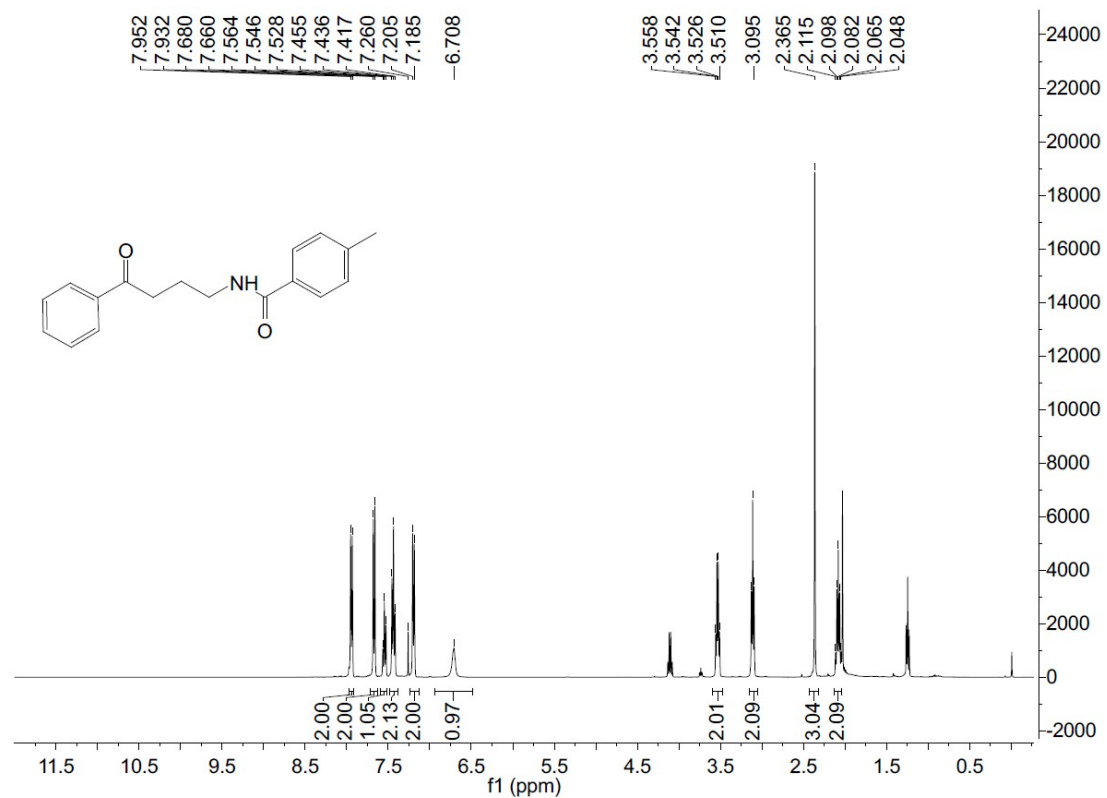
**7,8a-Diphenylhexahydroindolizin-5(1H)-one 5.** Yellowish oil. IR (KBr): 2930, 1647, 1418, 763, 701  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (t,  $J = 7.5$  Hz, 2H), 7.29–7.17 (m, 6H), 7.06 (d,  $J = 7.1$  Hz, 2H), 4.01 (dd,  $J = 20.7, 8.6$  Hz, 1H), 3.46 (t,  $J = 10.2$  Hz, 1H), 2.70–2.62 (m, 2H), 2.52–2.38 (m, 2H), 2.28–2.21 (m, 1H), 2.16–2.06 (m, 1H), 1.90–1.84 (m, 2H), 1.58–1.48 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.15, 146.56, 143.13, 128.83, 128.62, 126.90, 126.75, 126.70, 124.47, 68.16, 44.69, 44.30, 40.75, 39.59, 37.74, 20.32. MS (EI)  $m/z$ : 77, 91, 103, 131, 186, 214, 262, 291. Anal. calcd. for  $\text{C}_{20}\text{H}_{21}\text{NO}$ : C 82.44, H 7.26, found: C 82.57, H 7.23.

## D. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

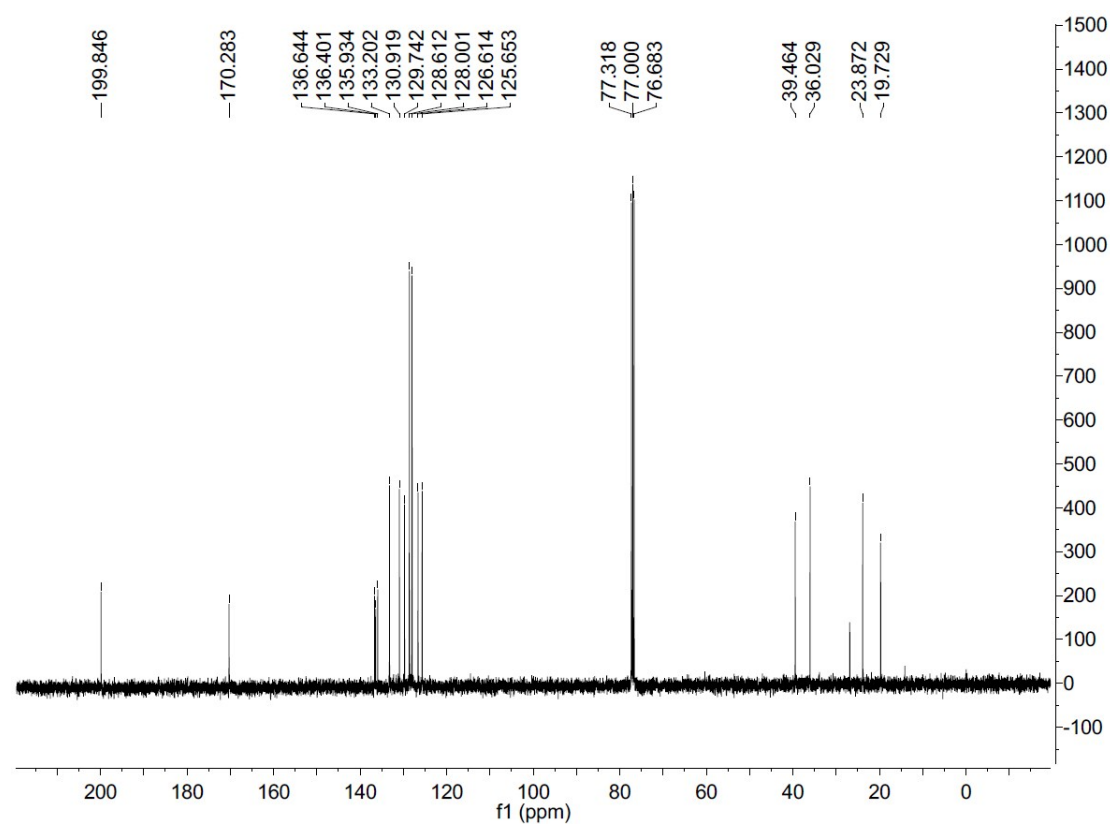
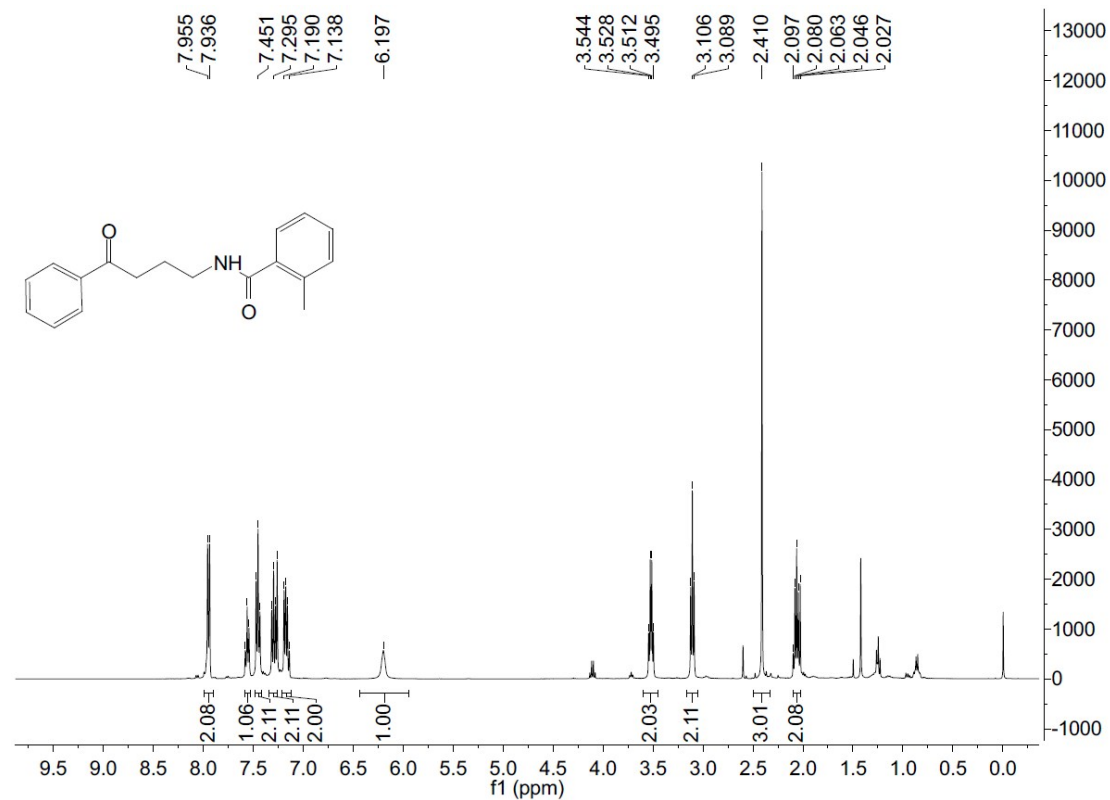
### 4aa



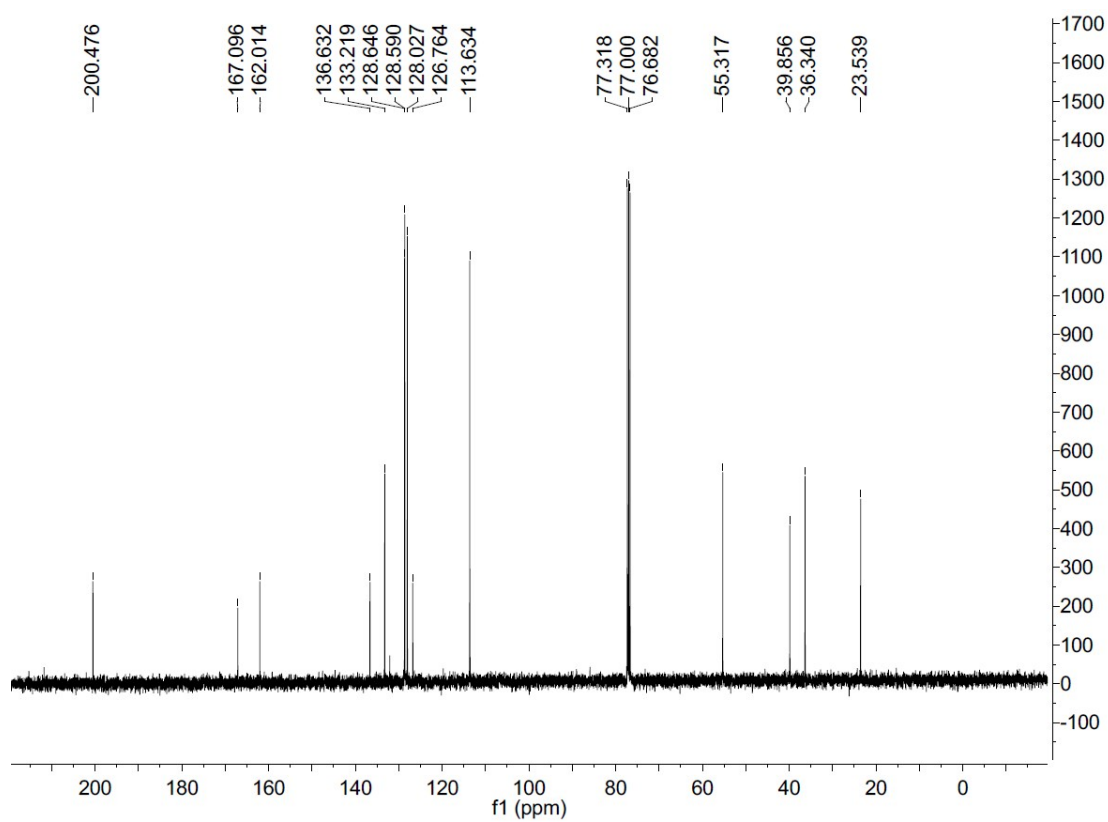
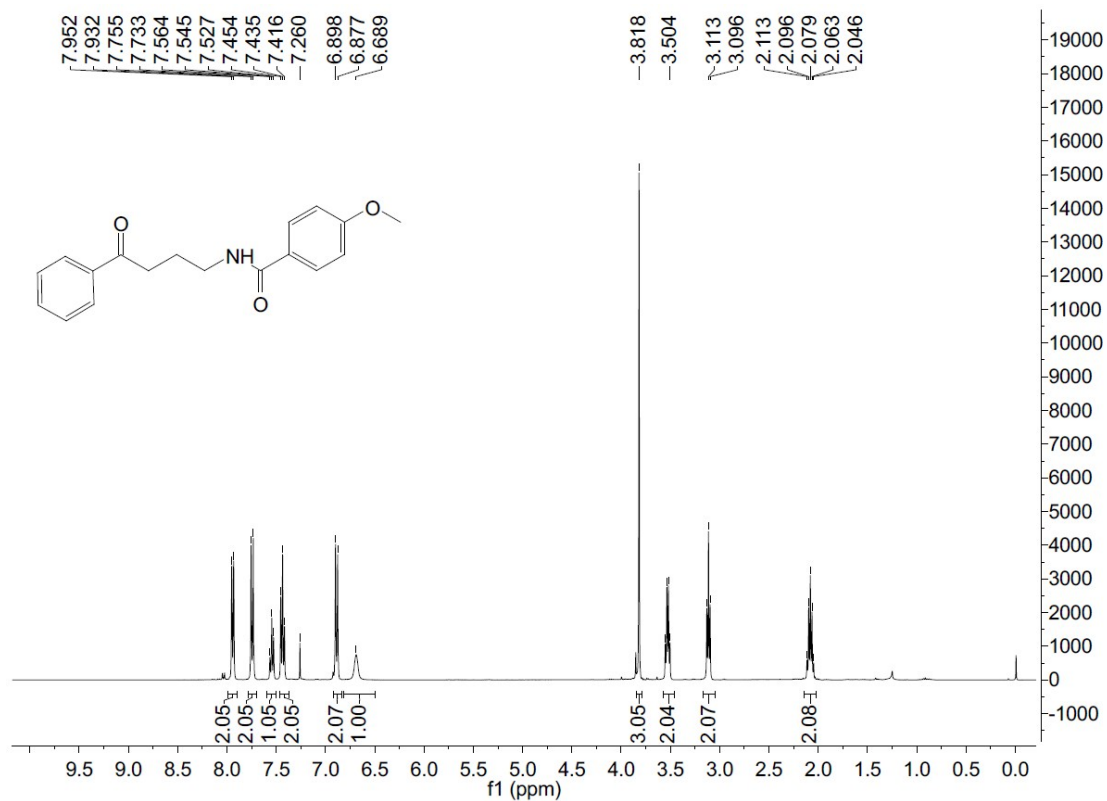
4ab



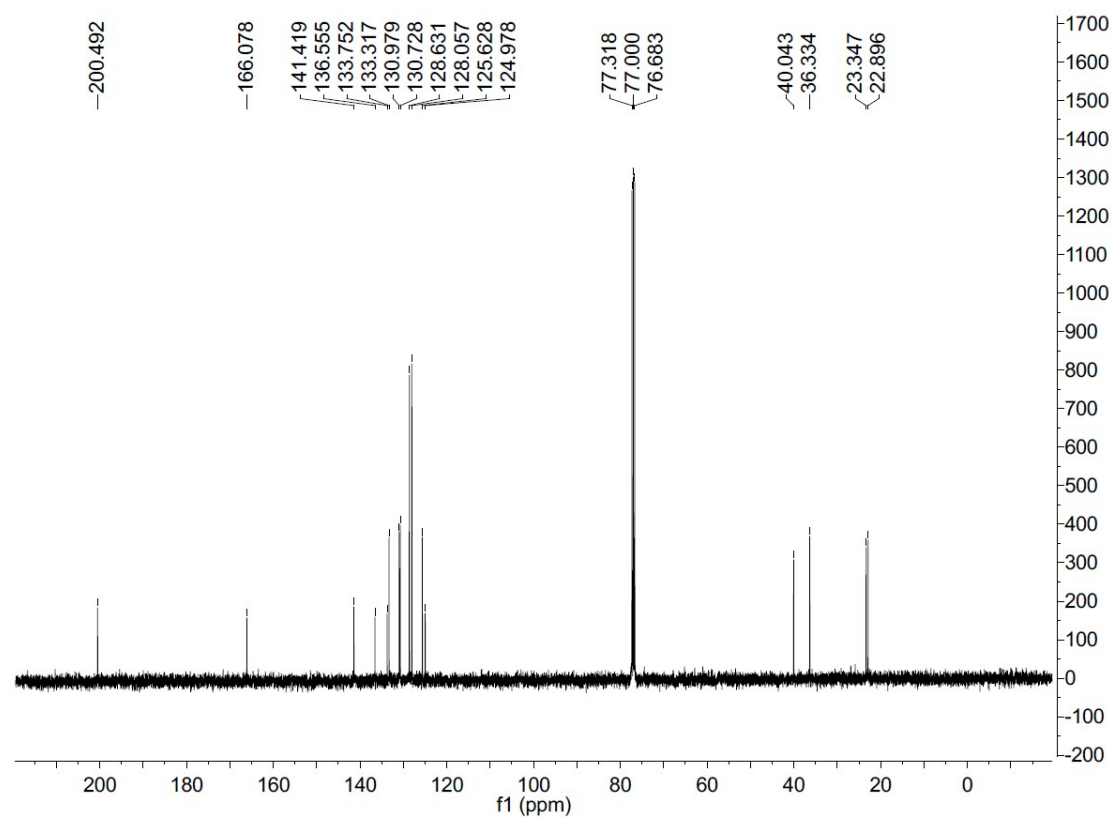
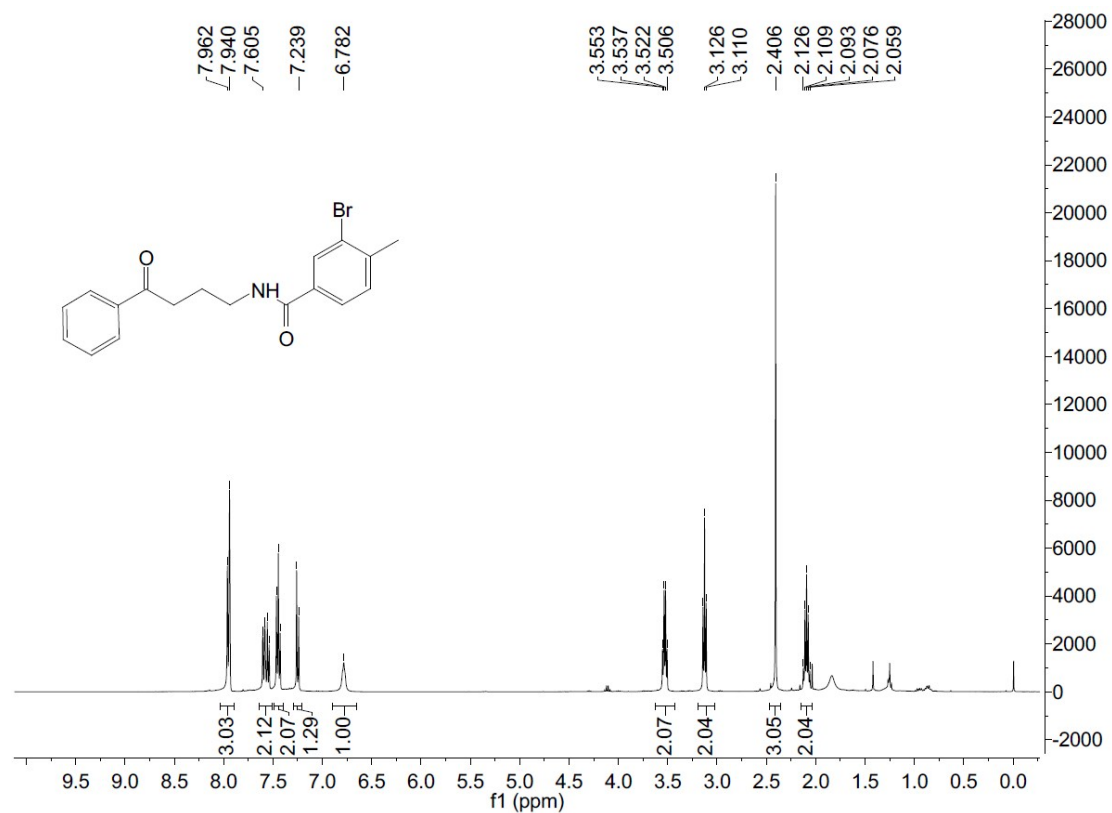
4ac



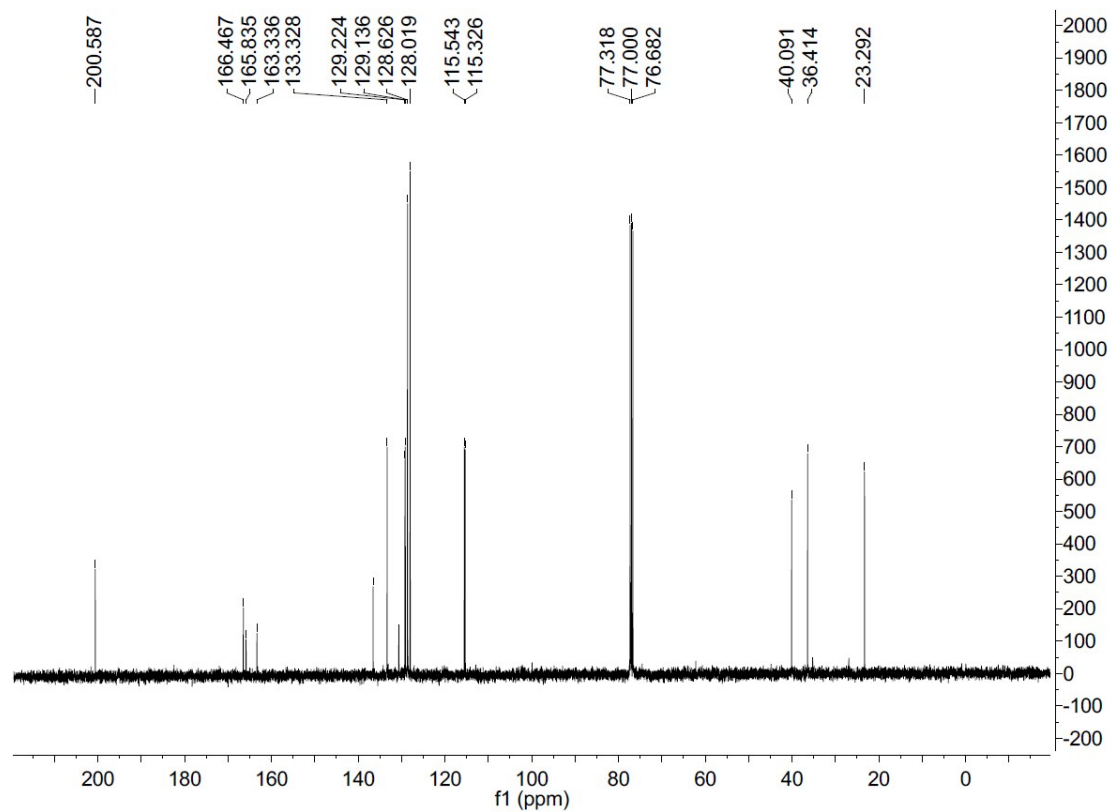
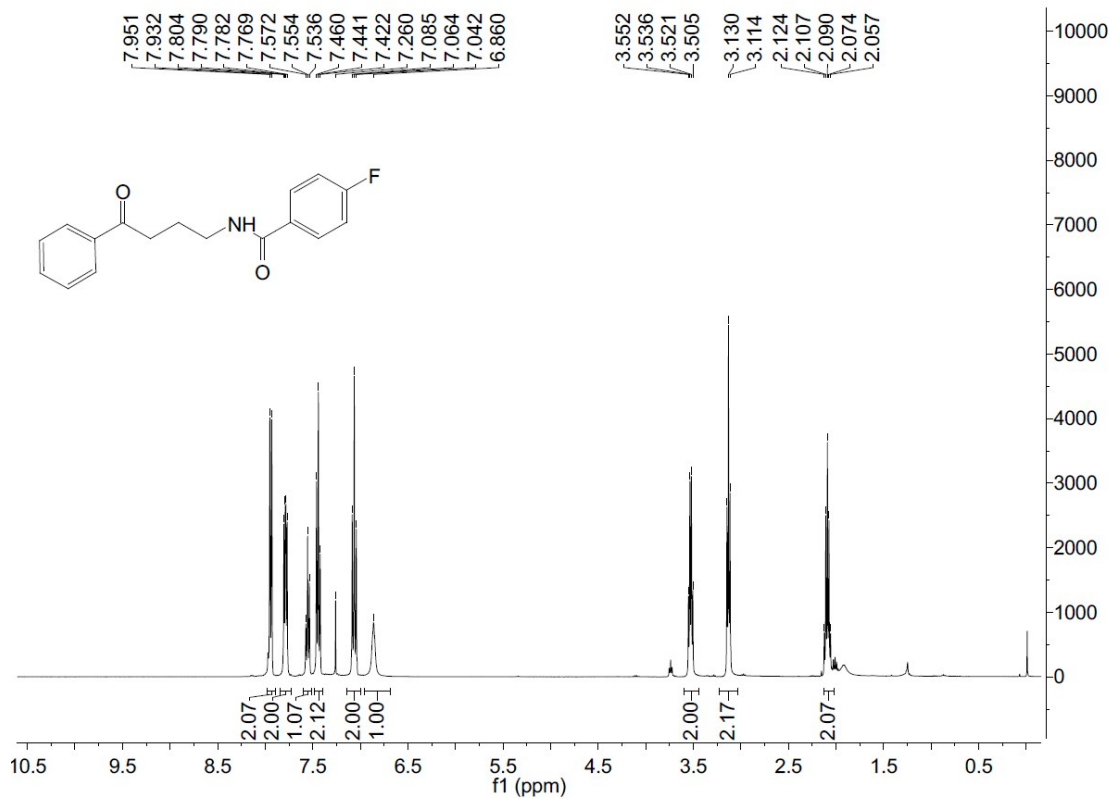
**4ad**



4ae

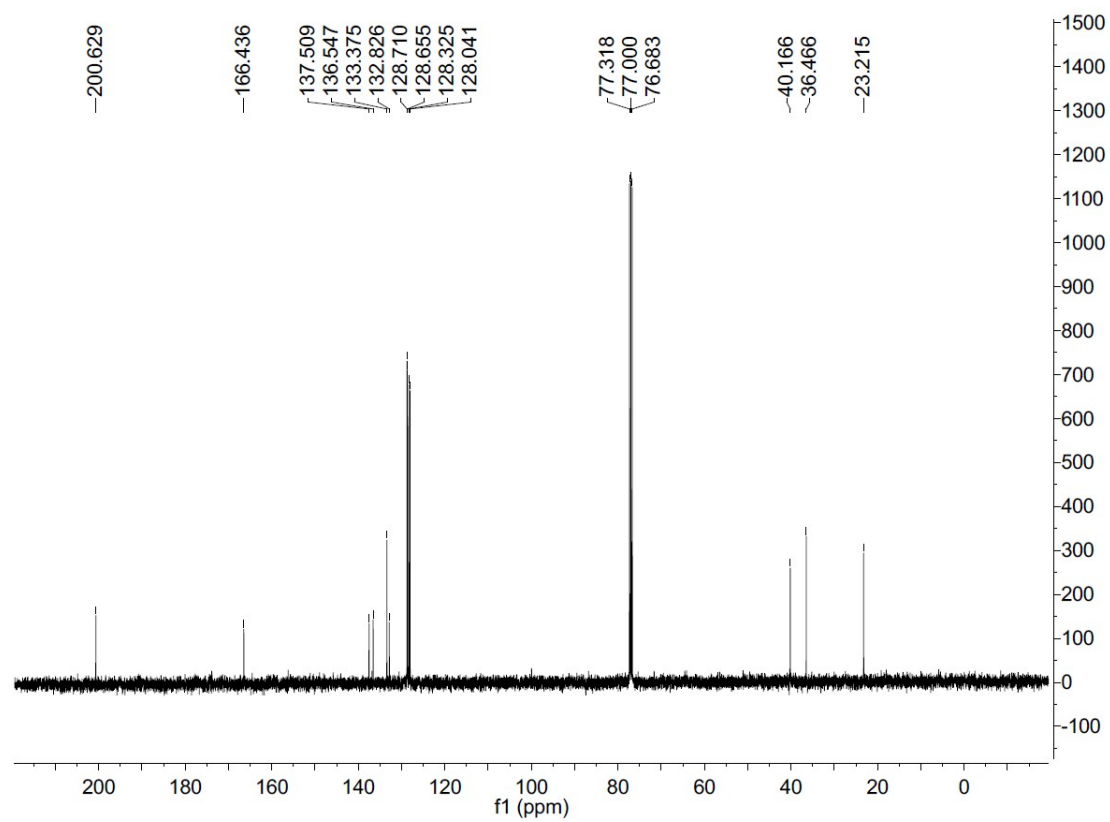
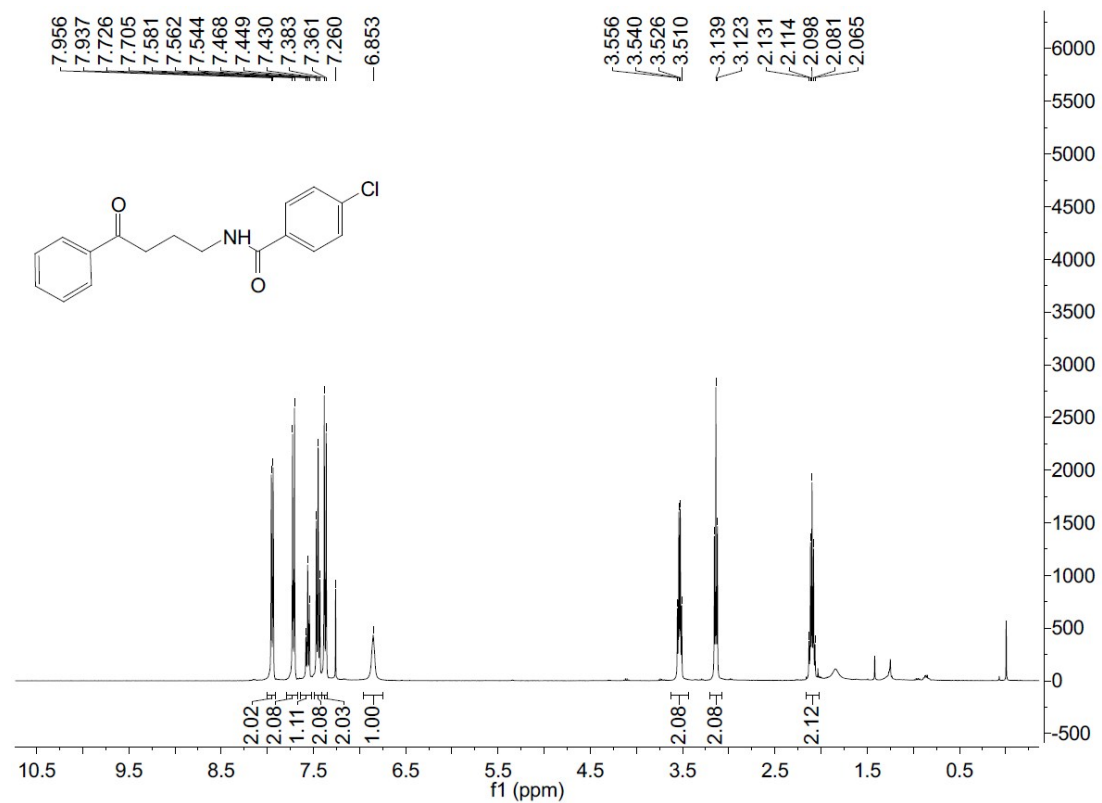


4af

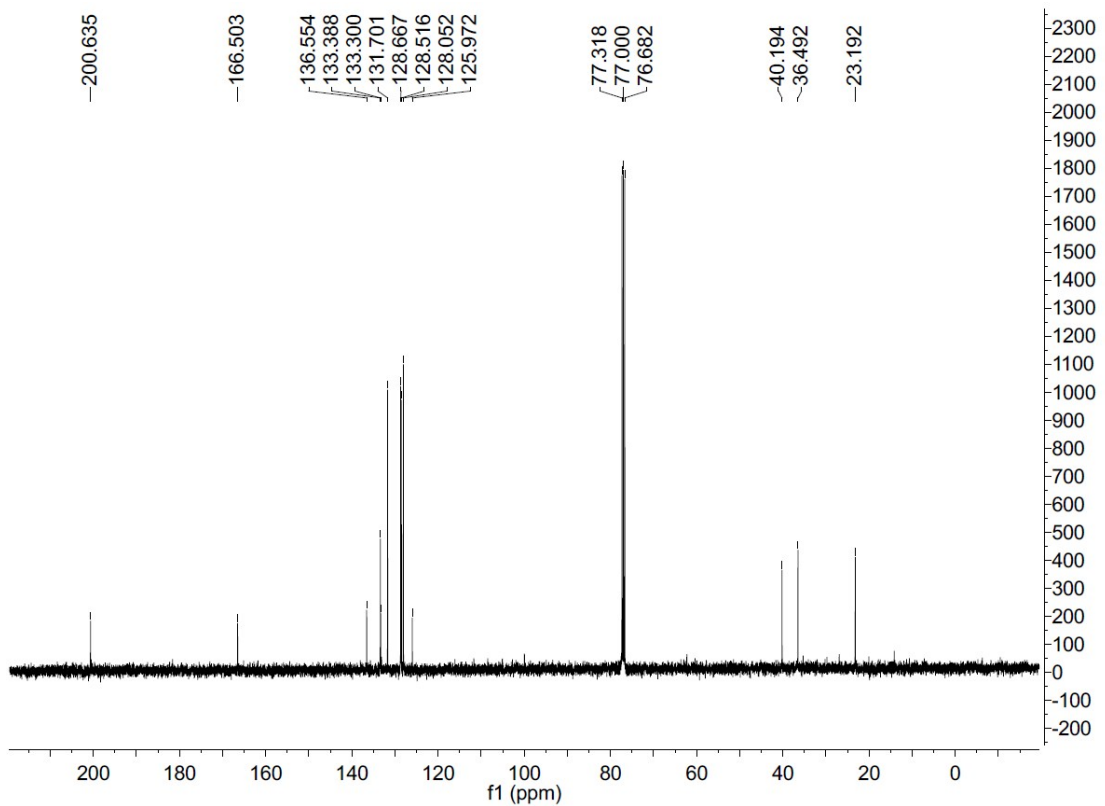
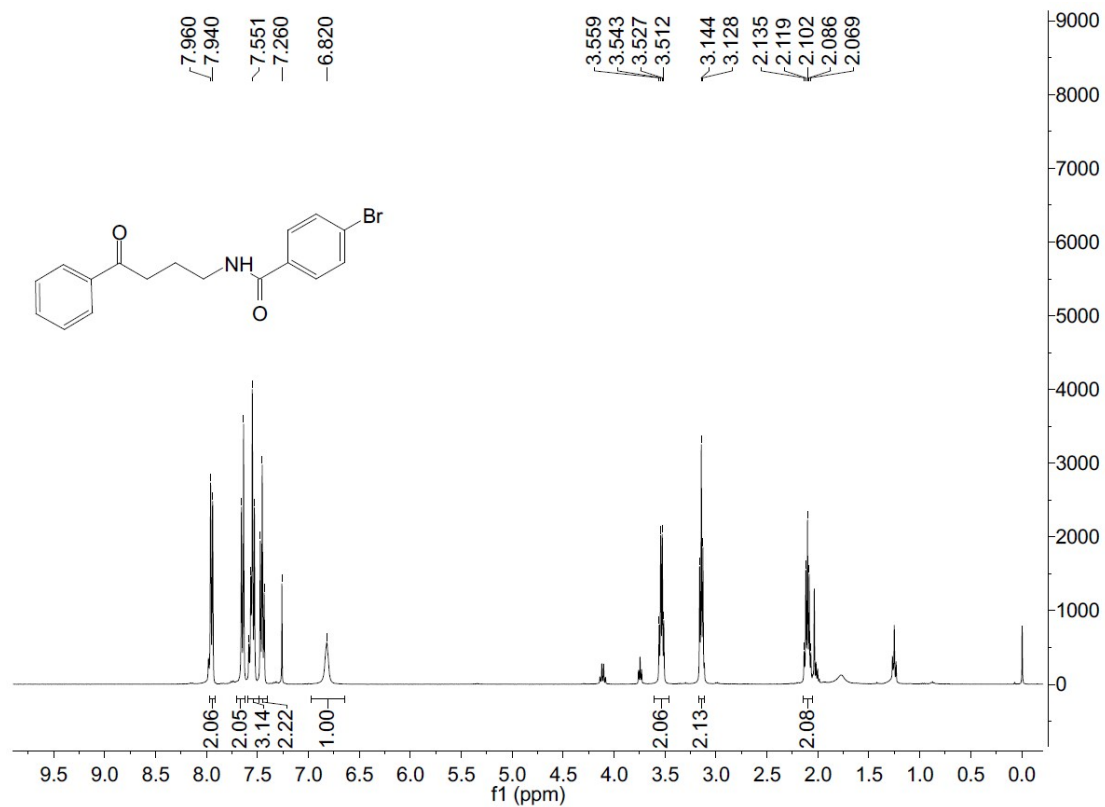




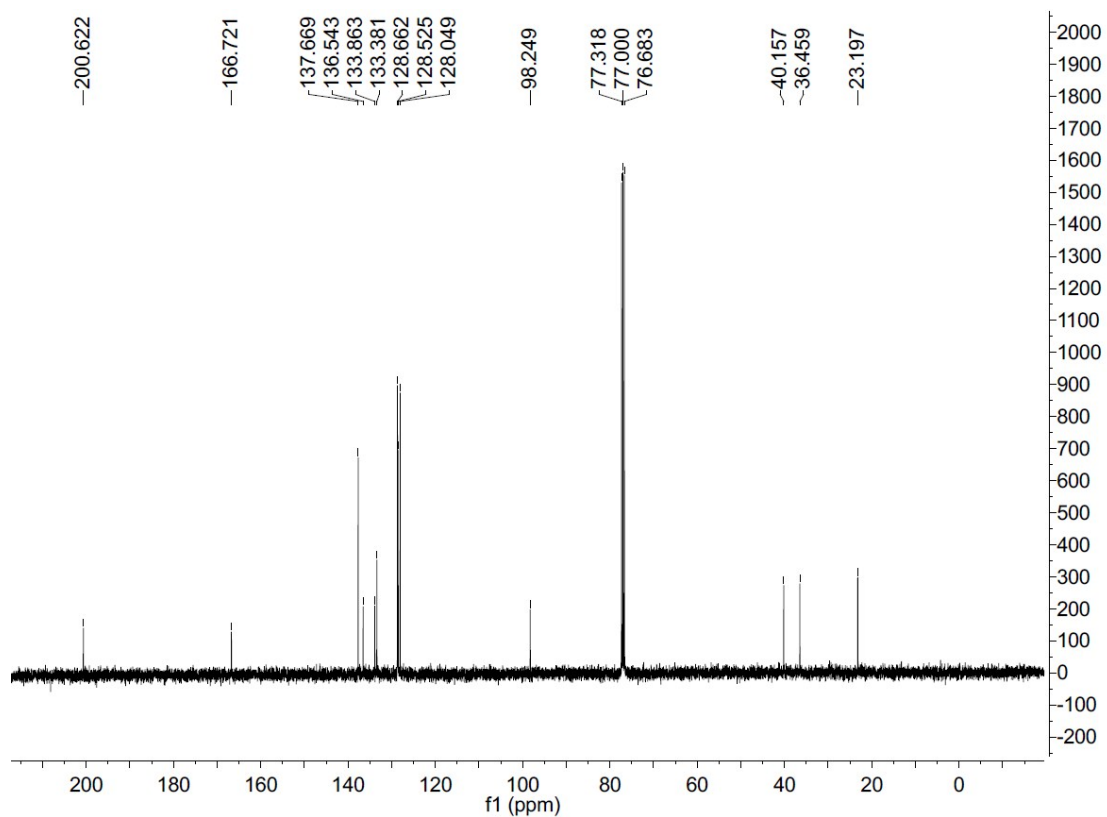
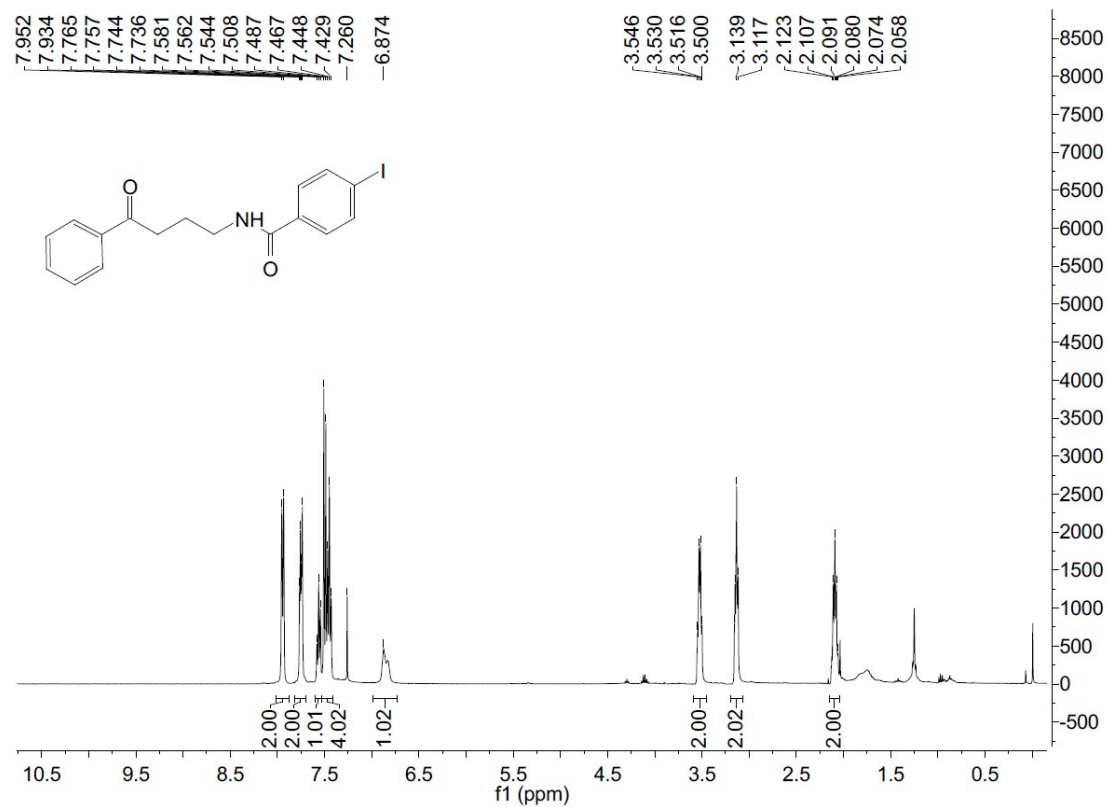
**4ag**



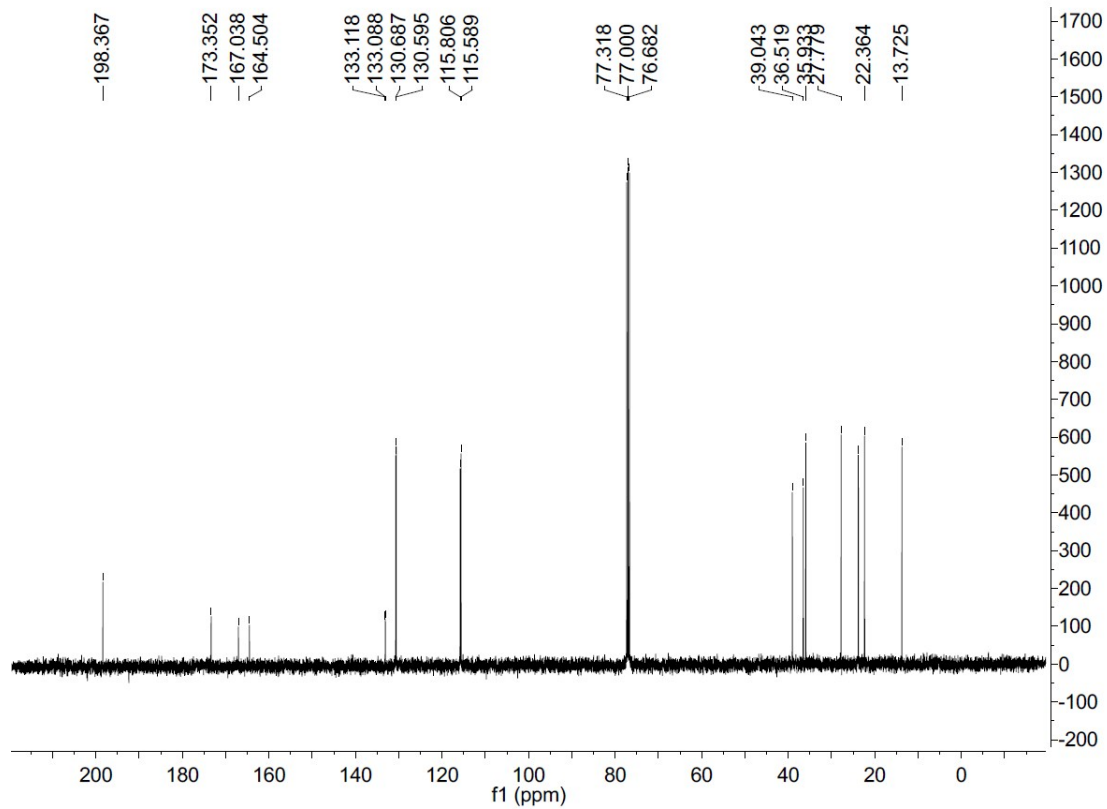
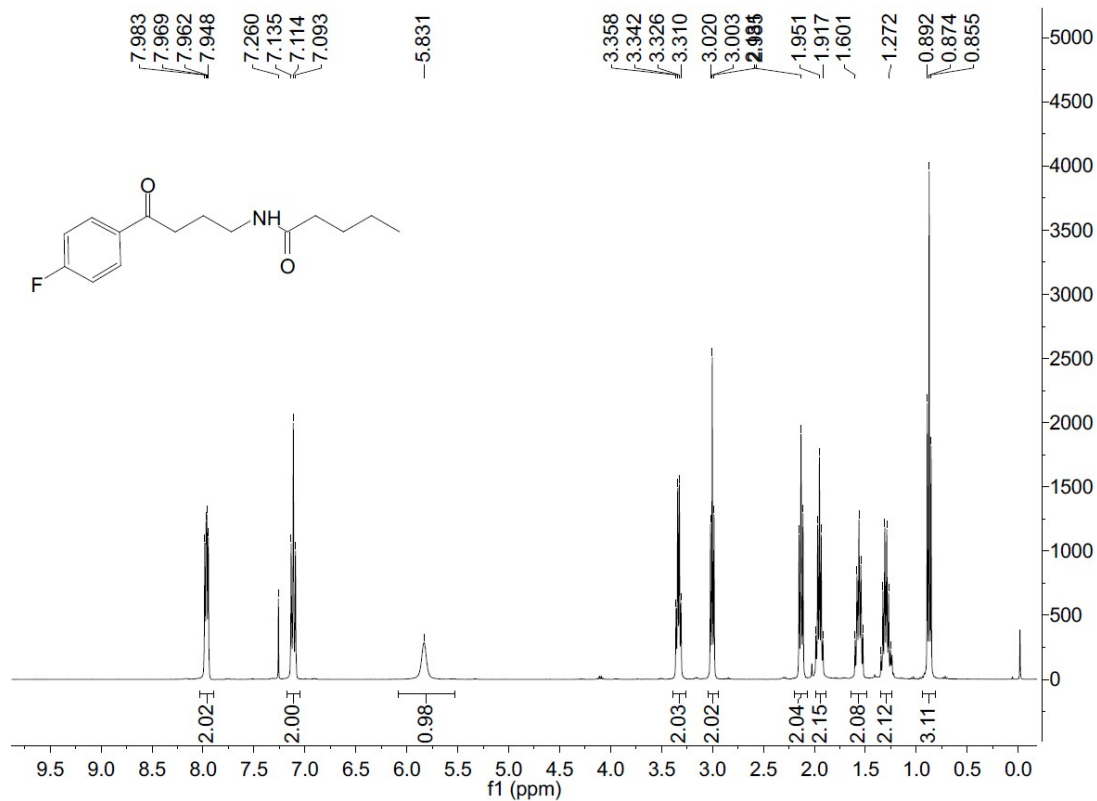
4ah



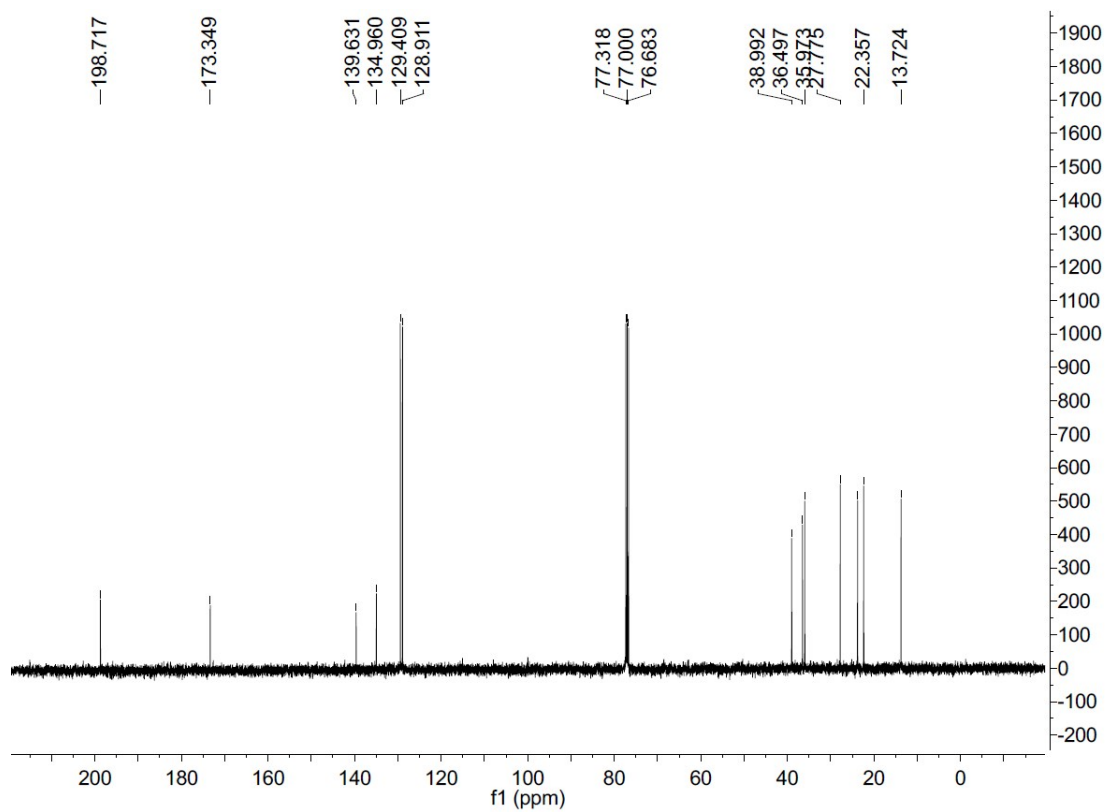
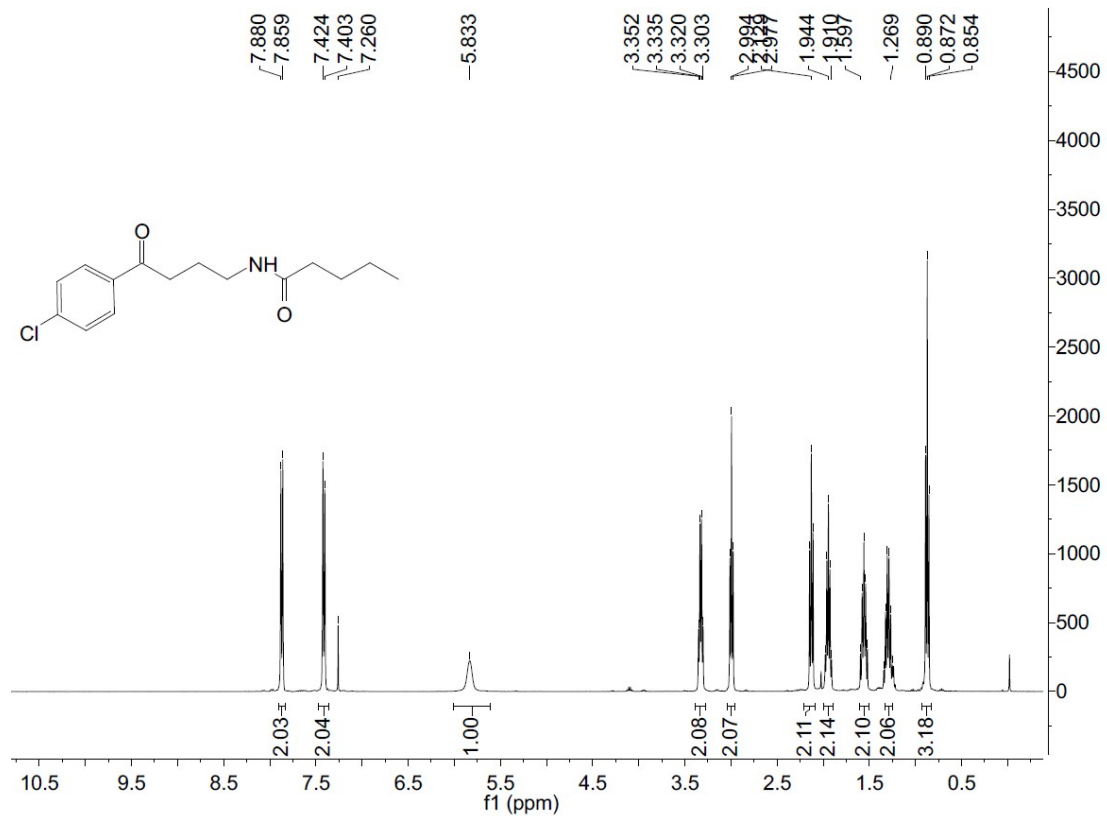
4ai



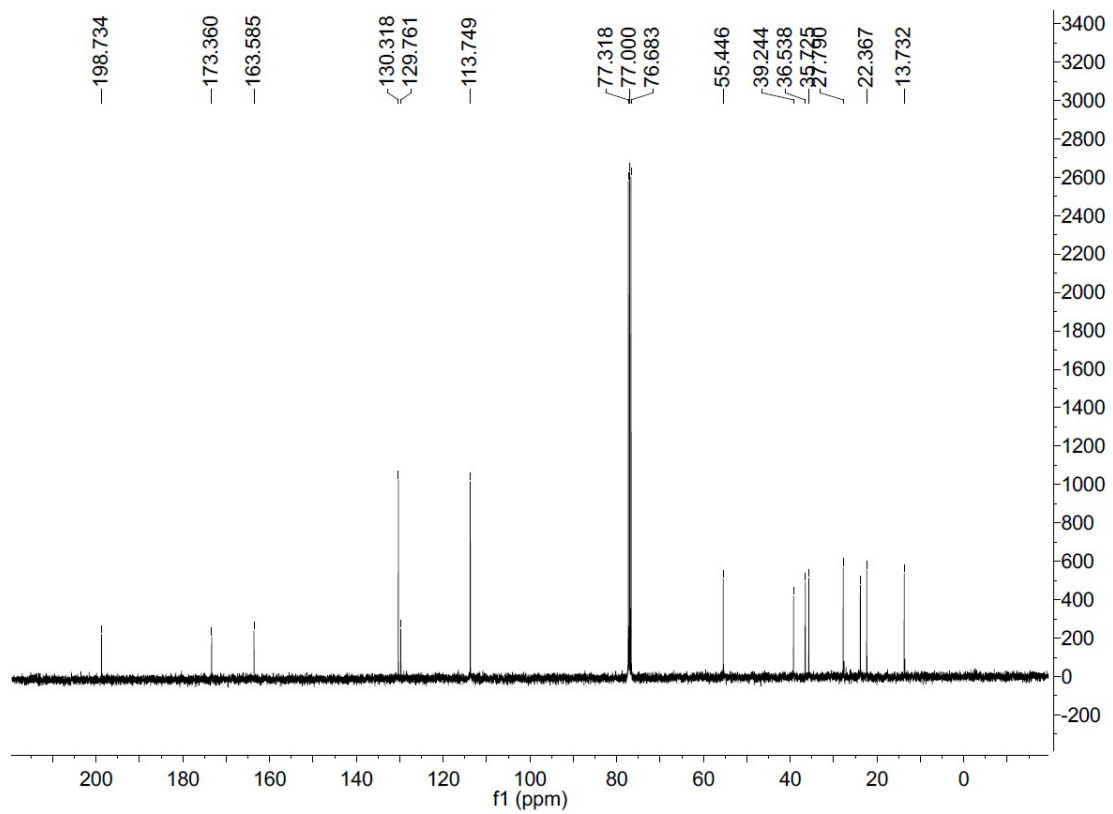
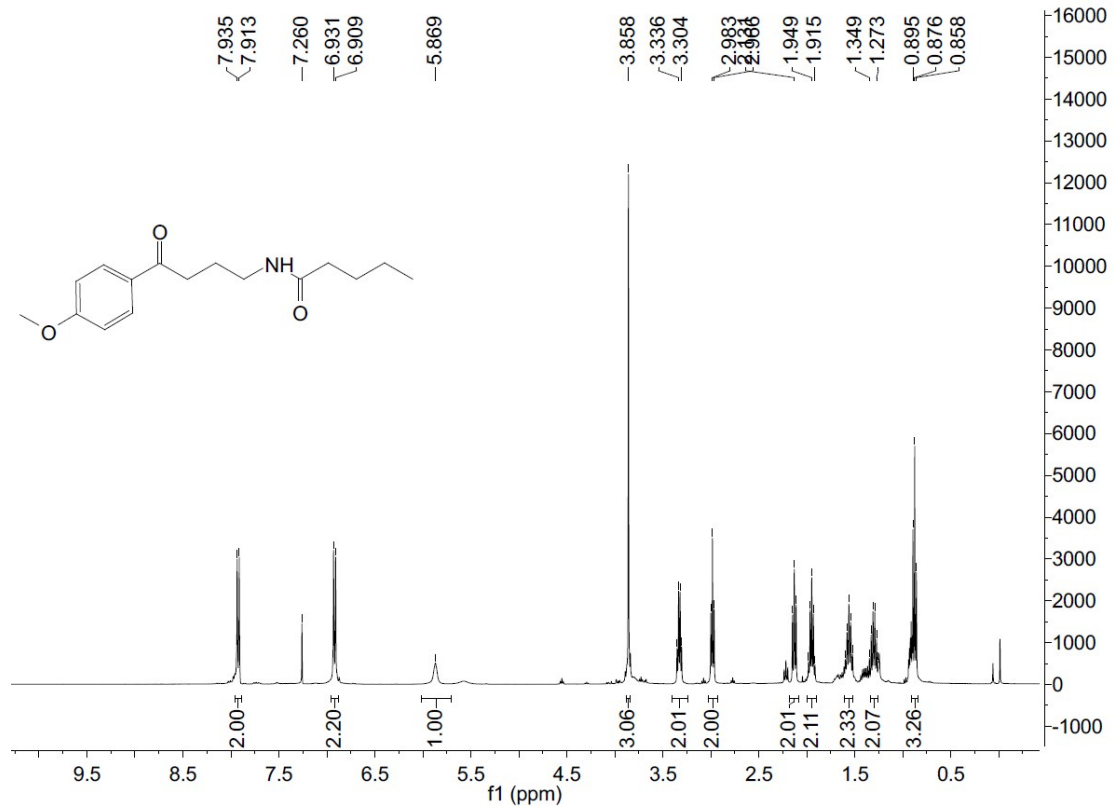
4bj



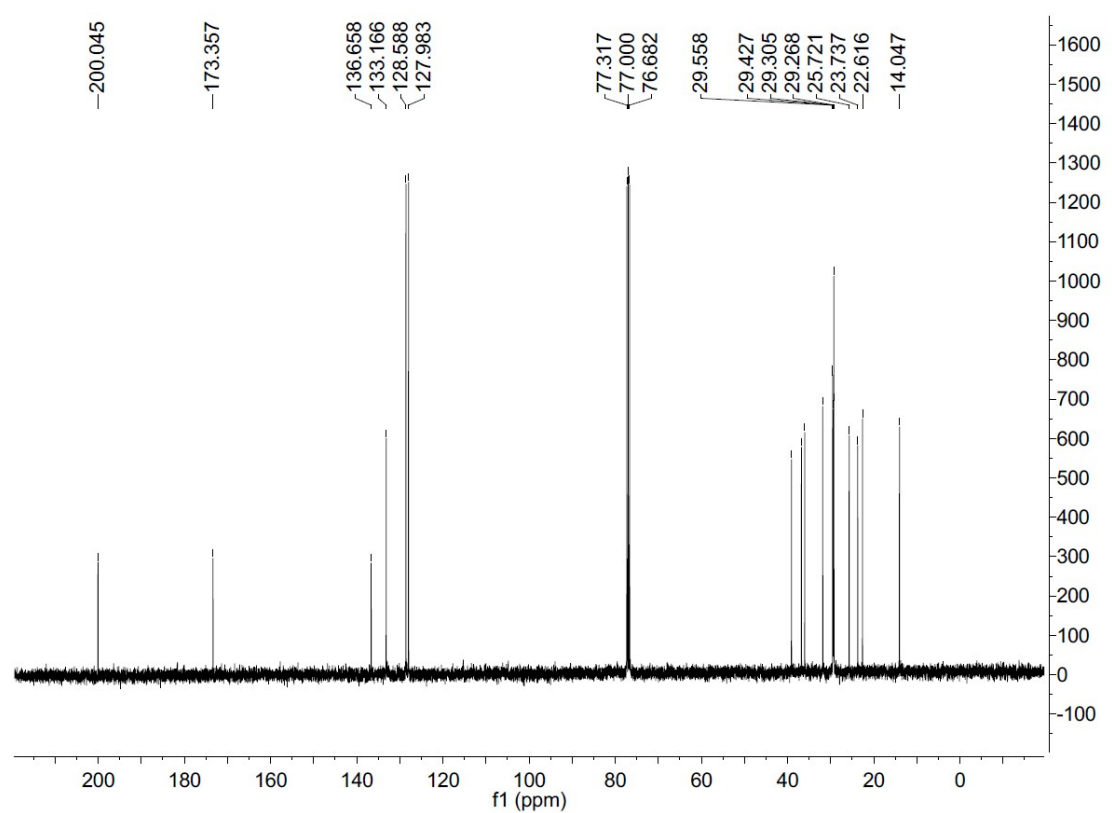
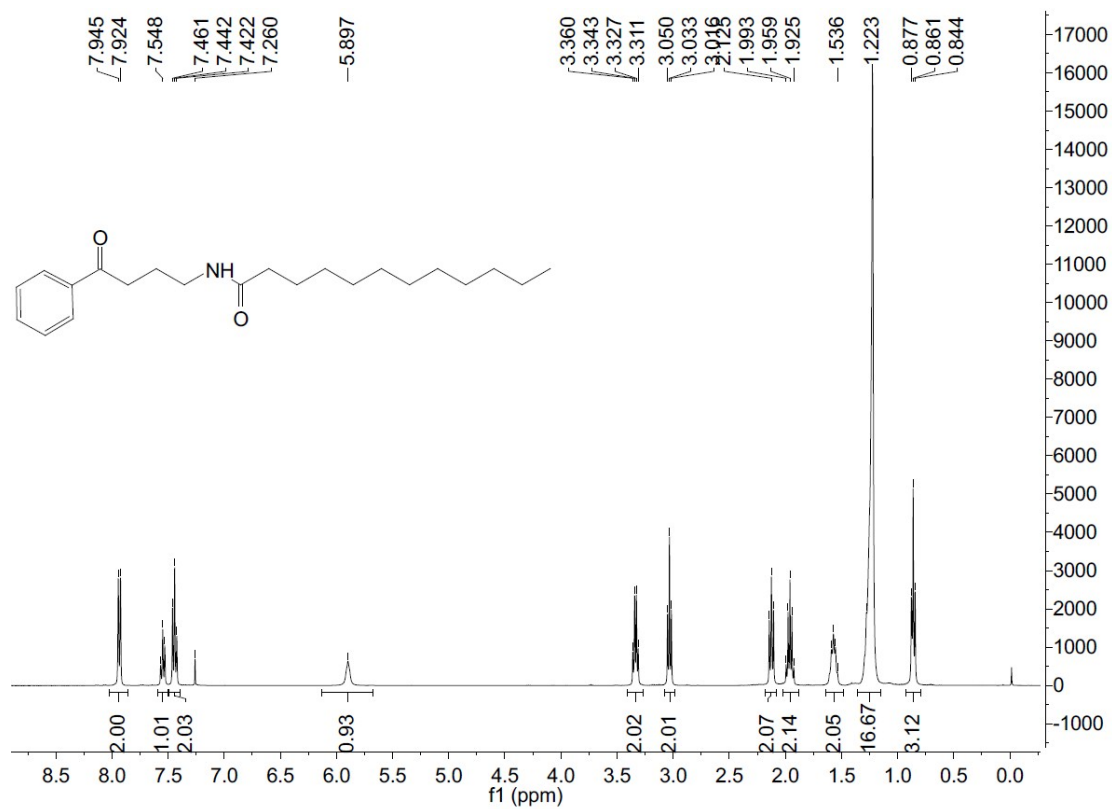
4cj



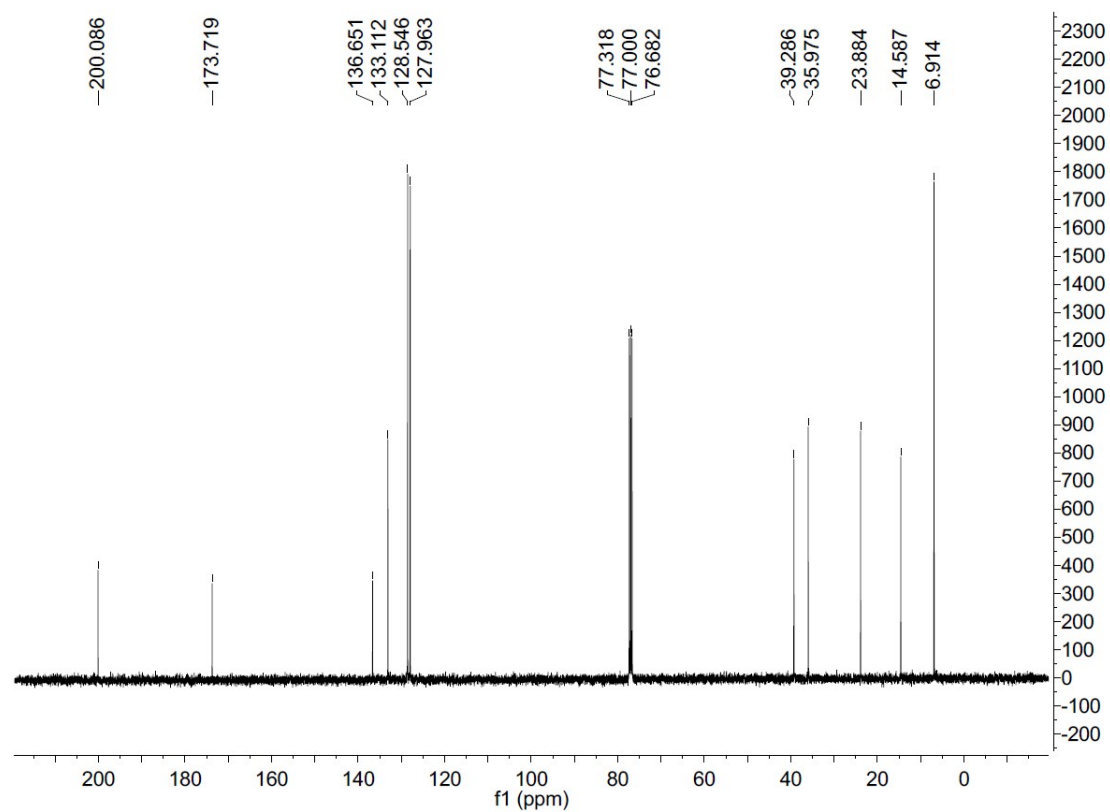
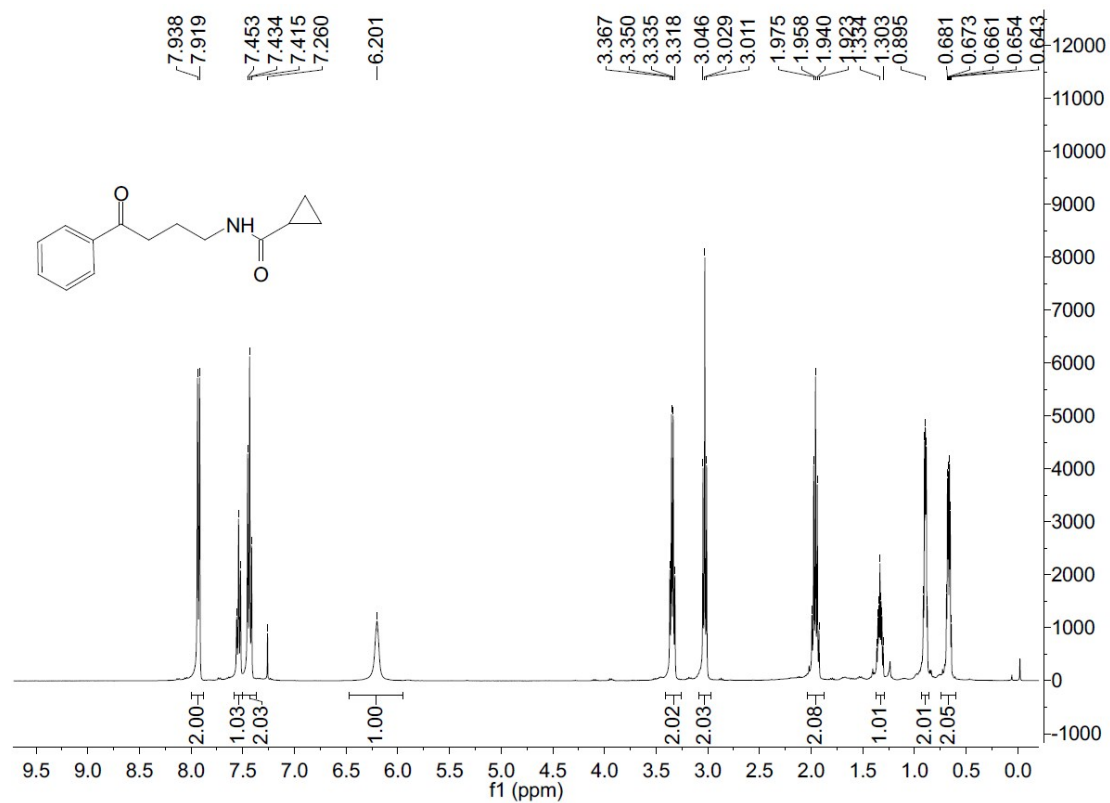
4dj



**4ak**

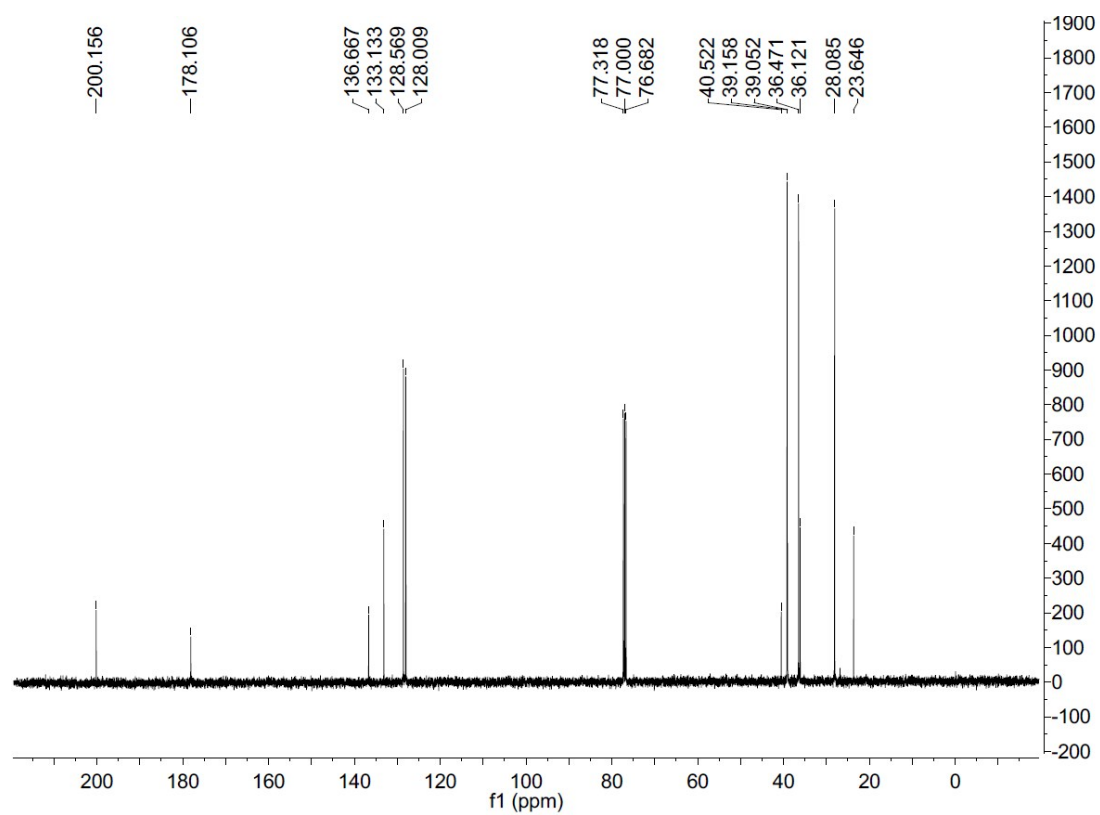
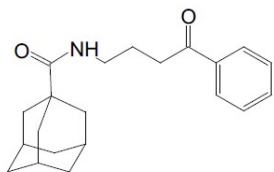
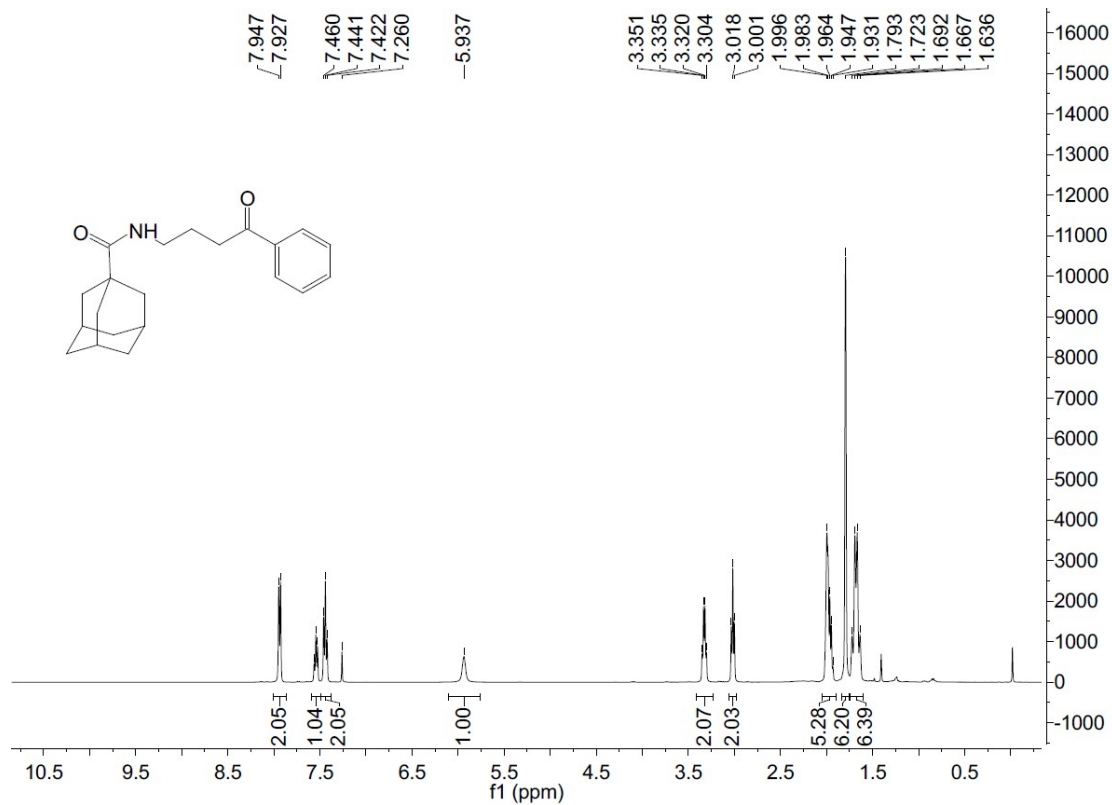


4al

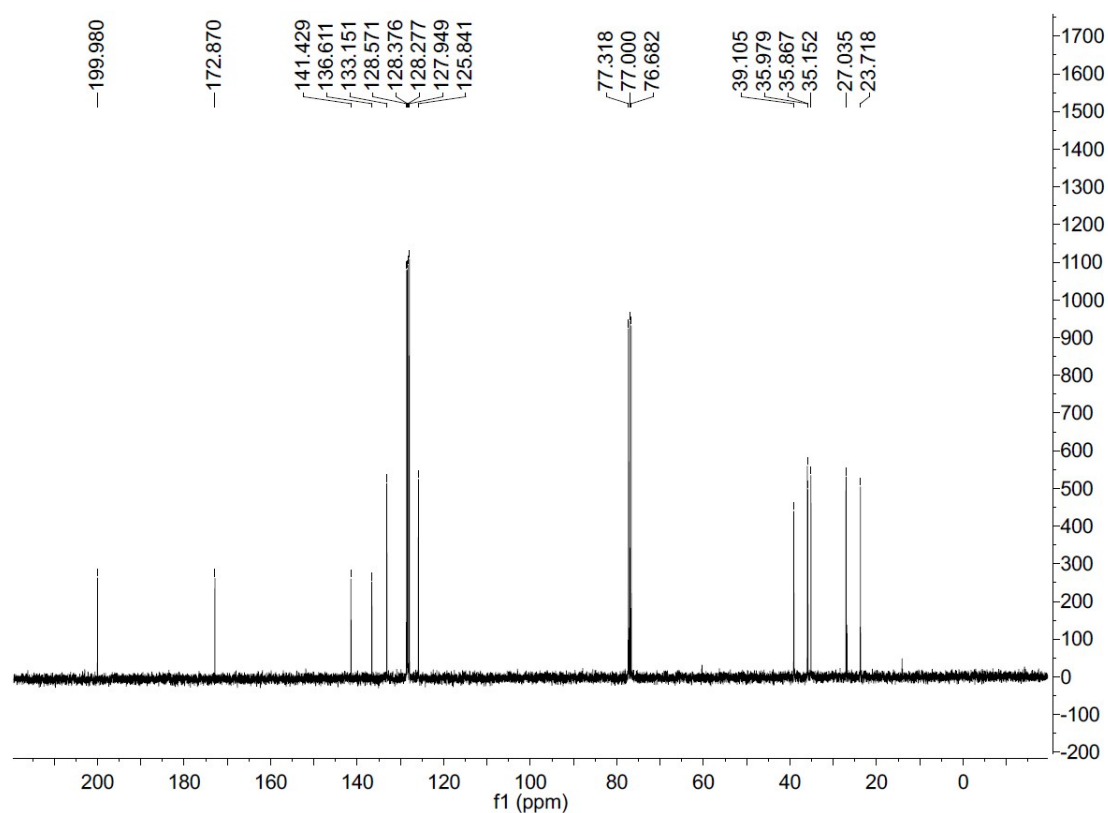
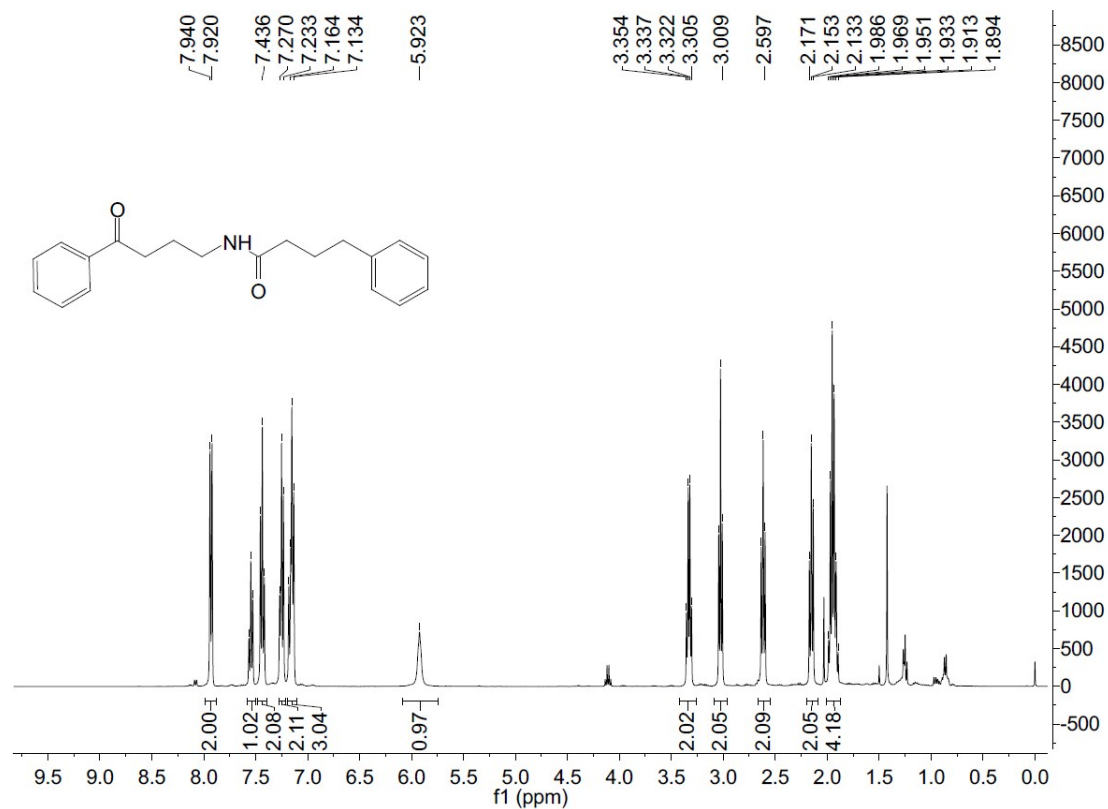




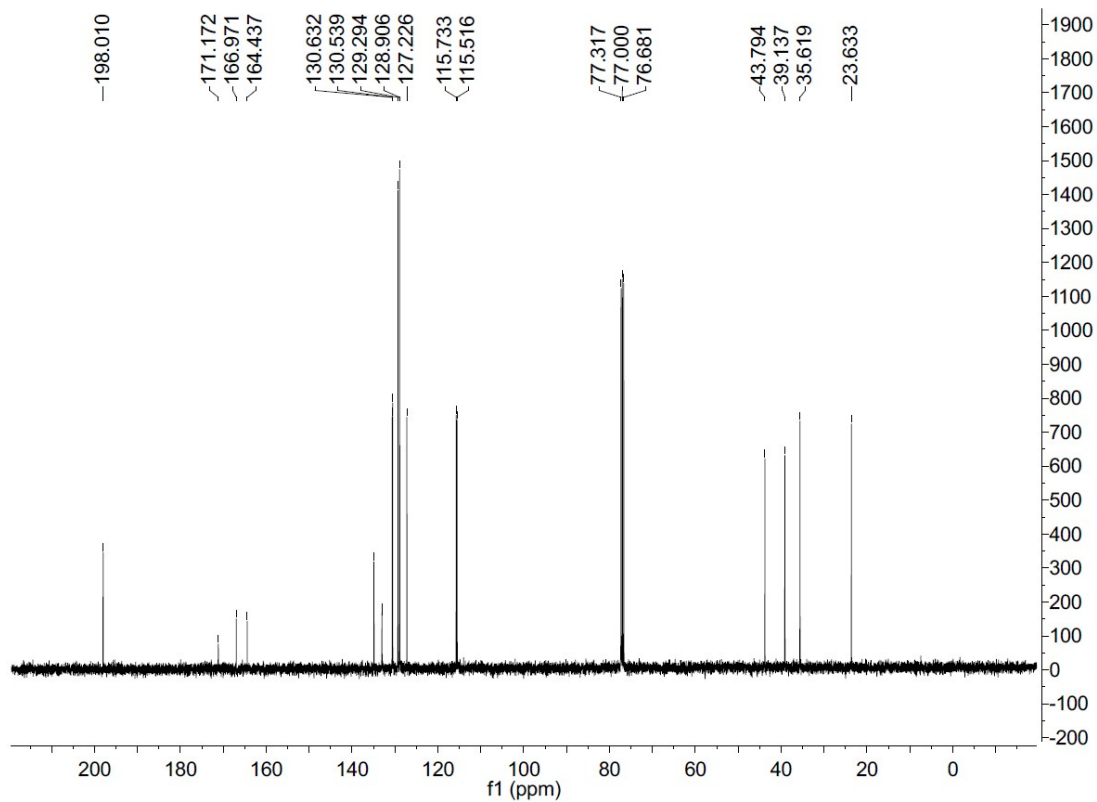
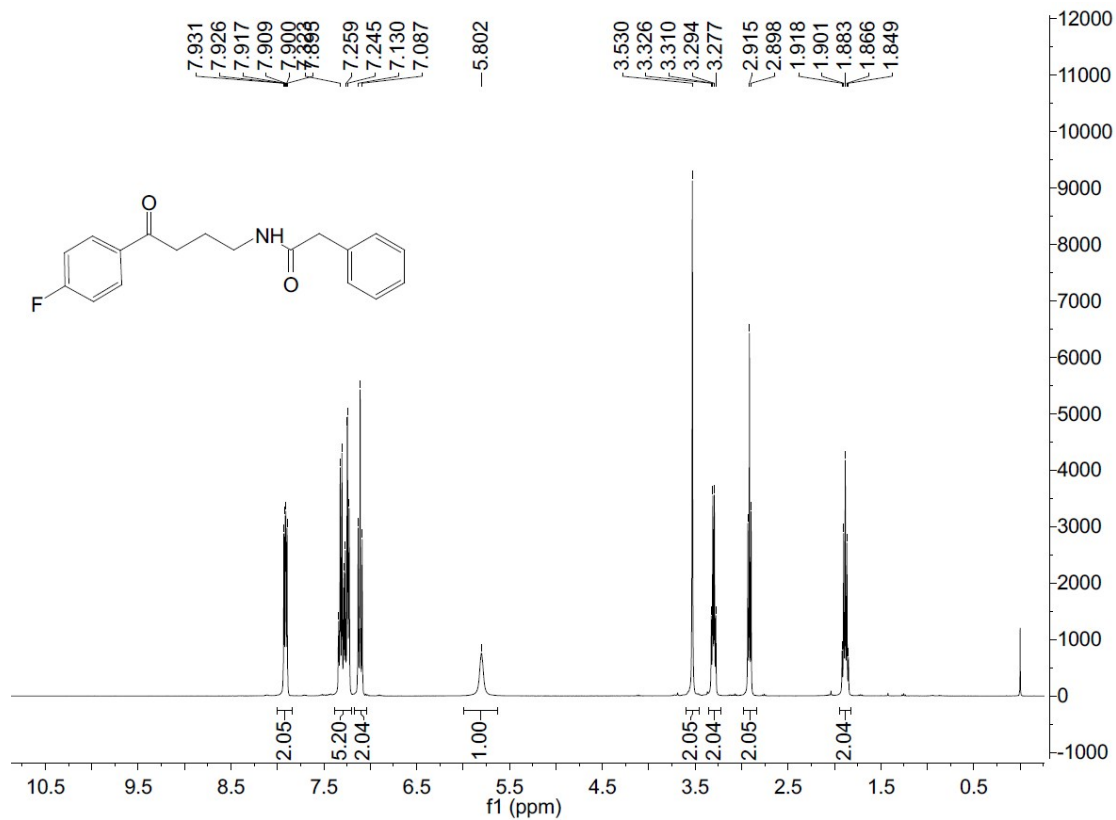
**4am**



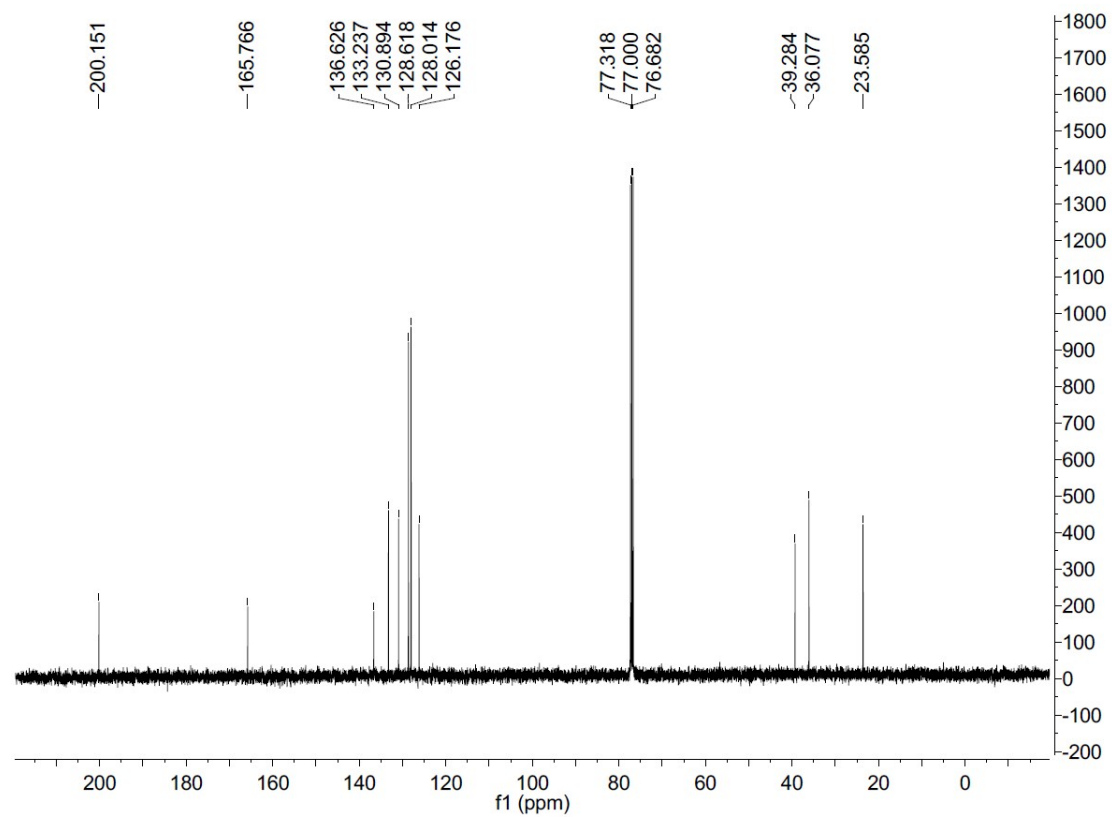
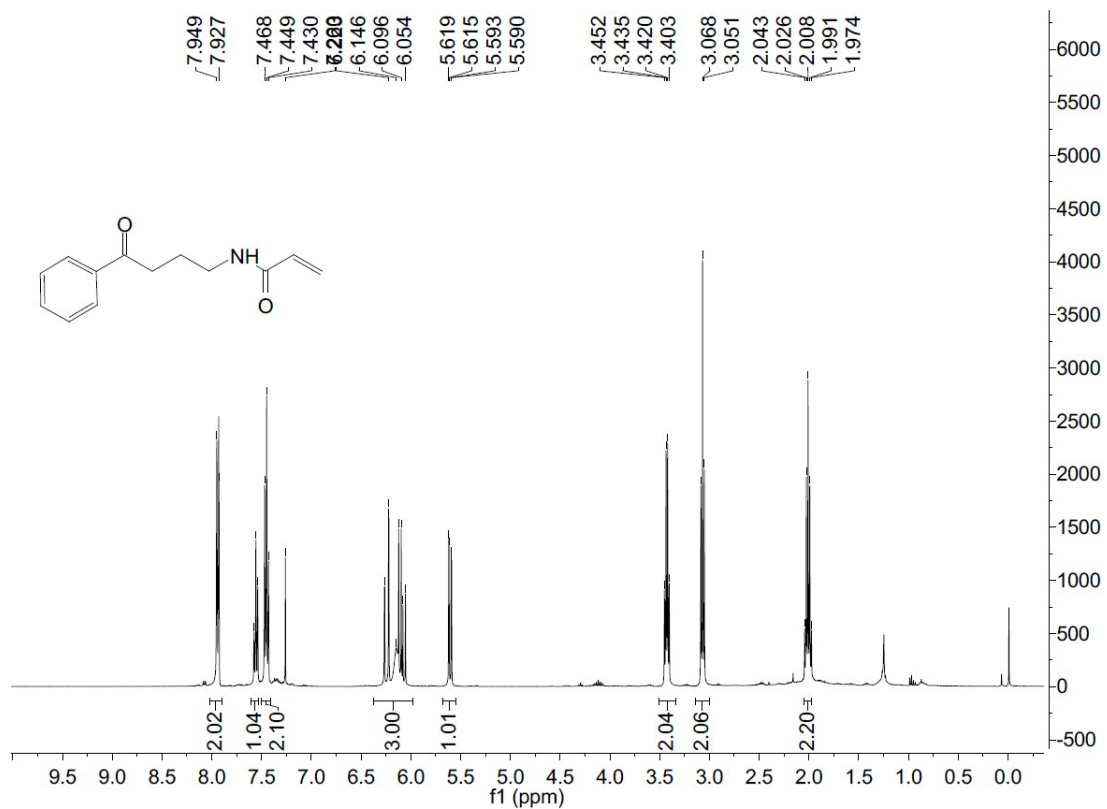
**4an**



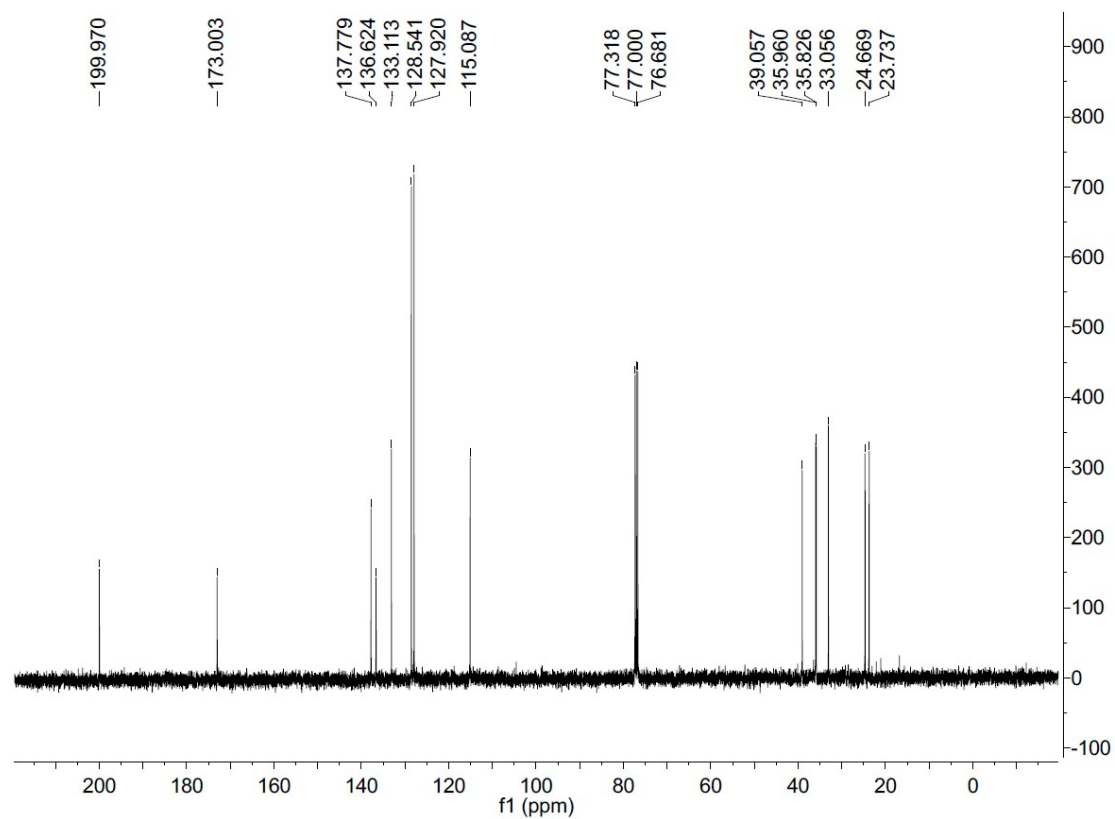
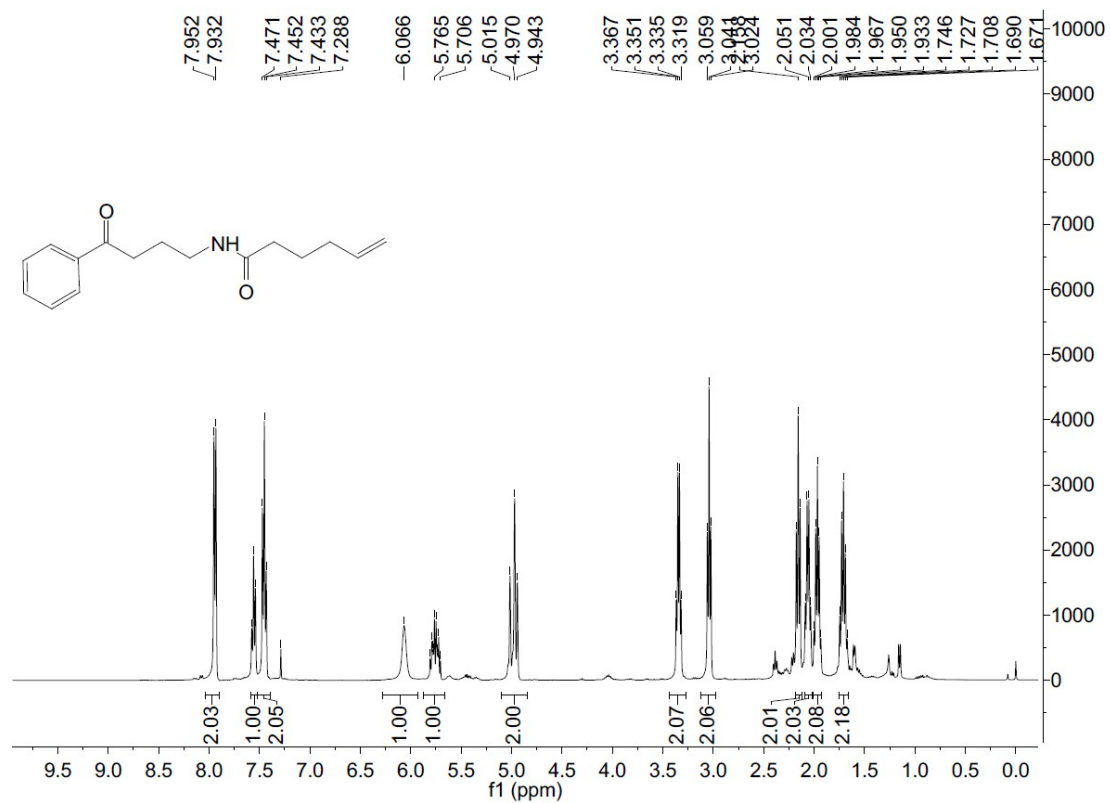
**4bo**



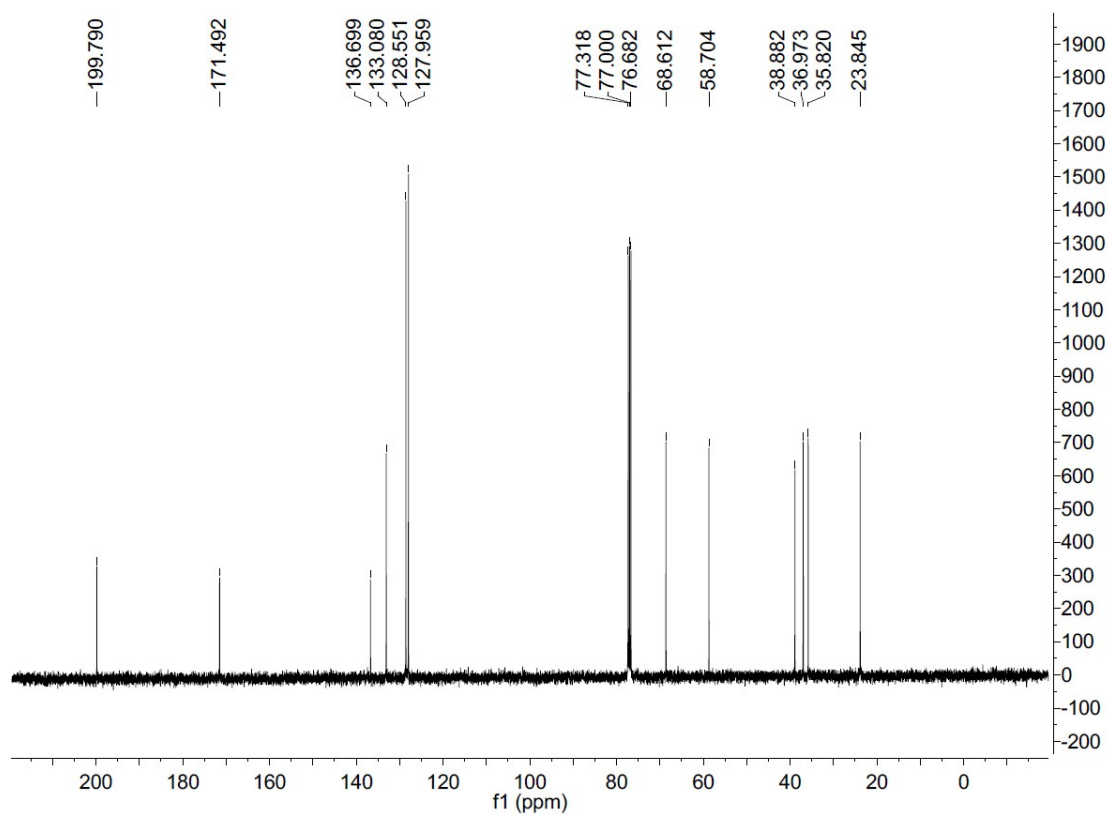
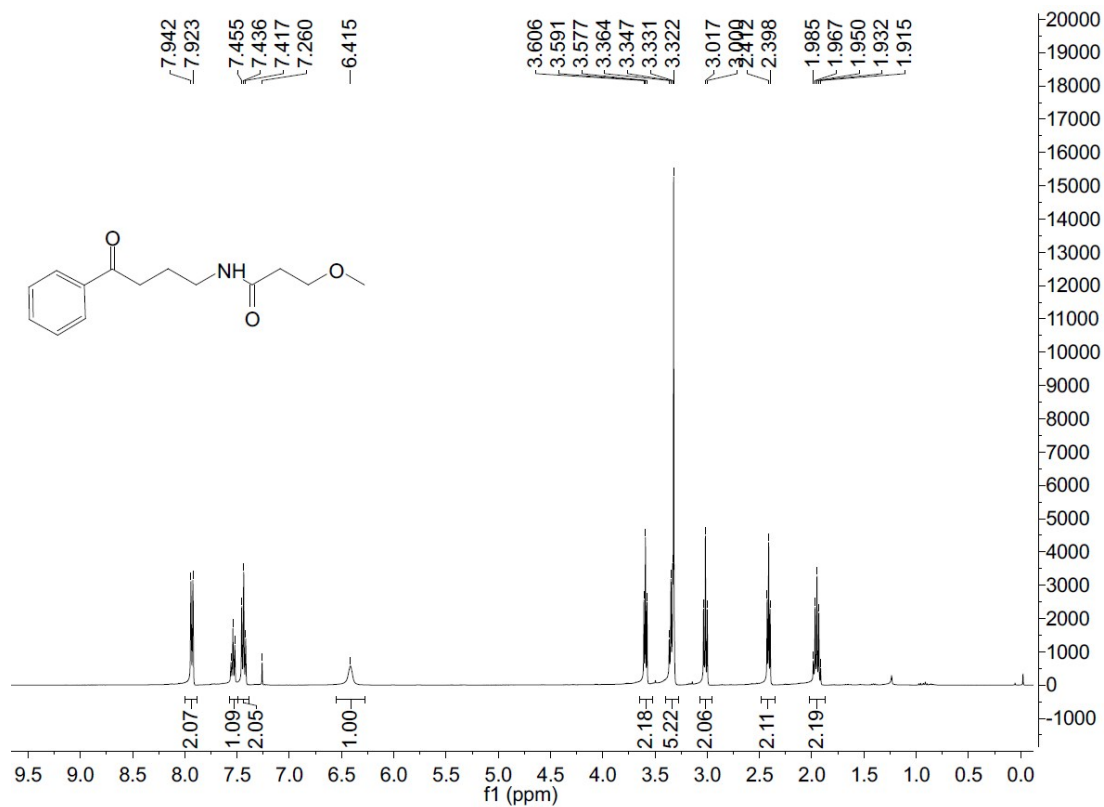
4ap



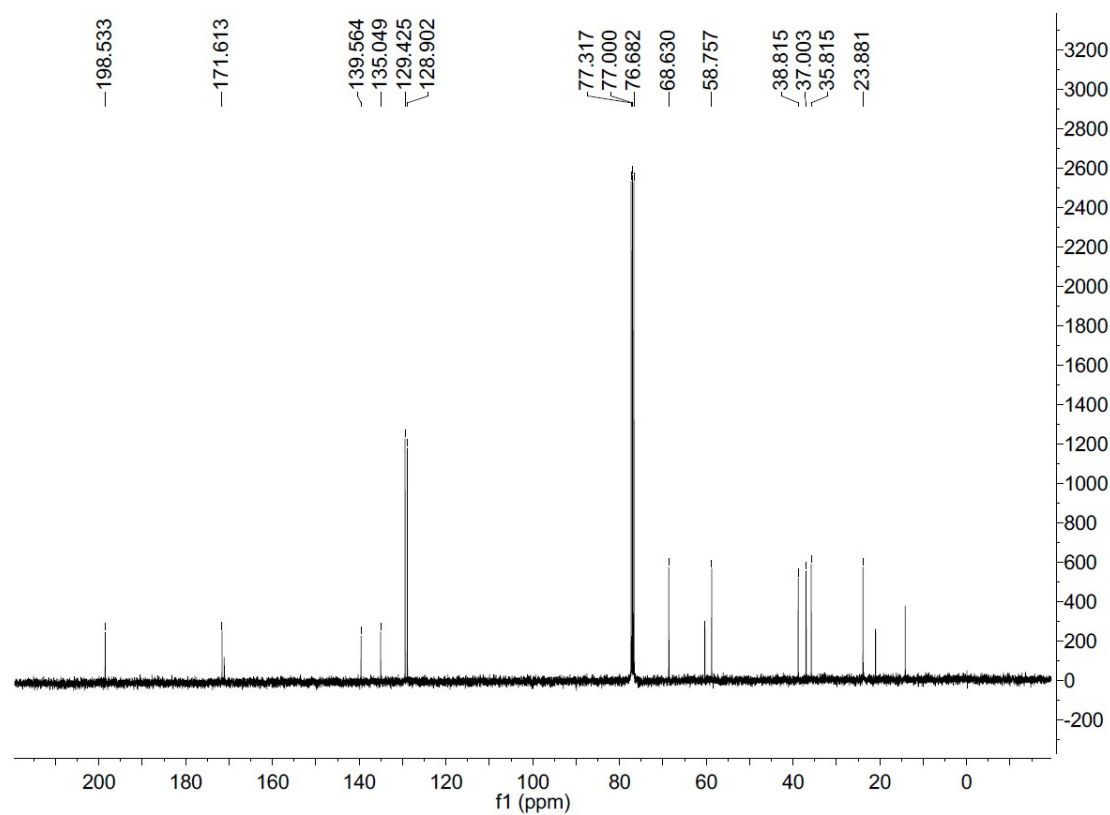
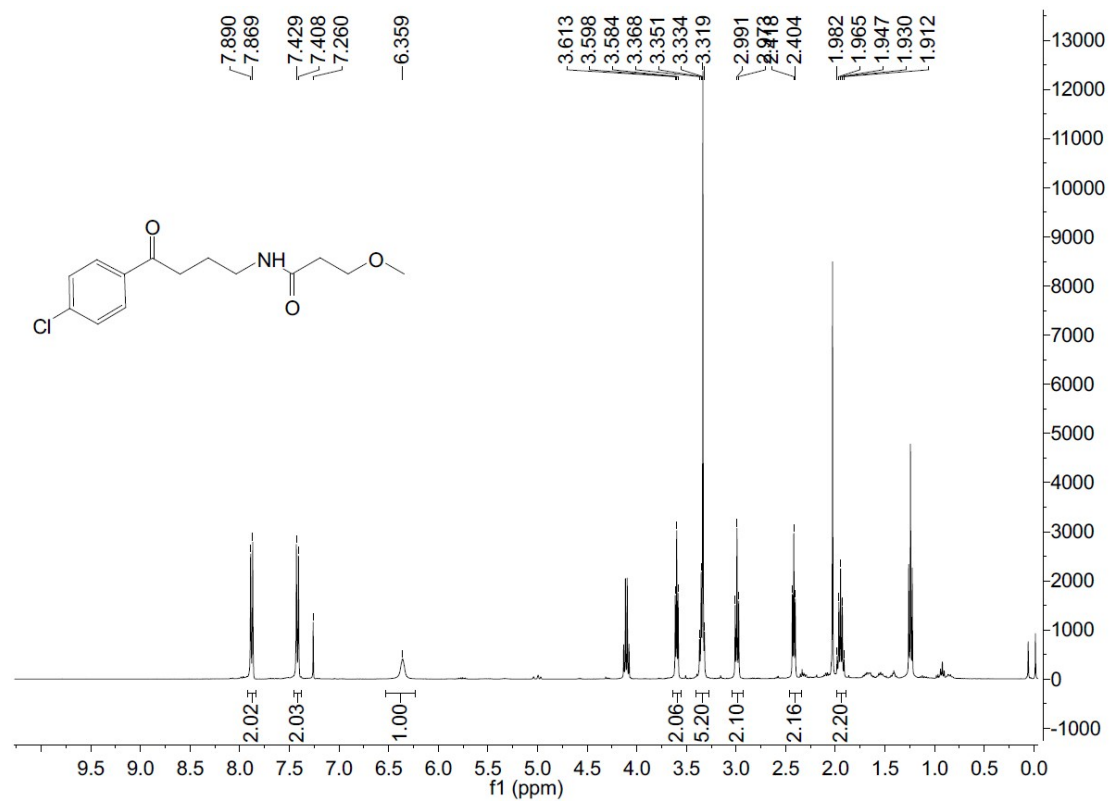
4aq



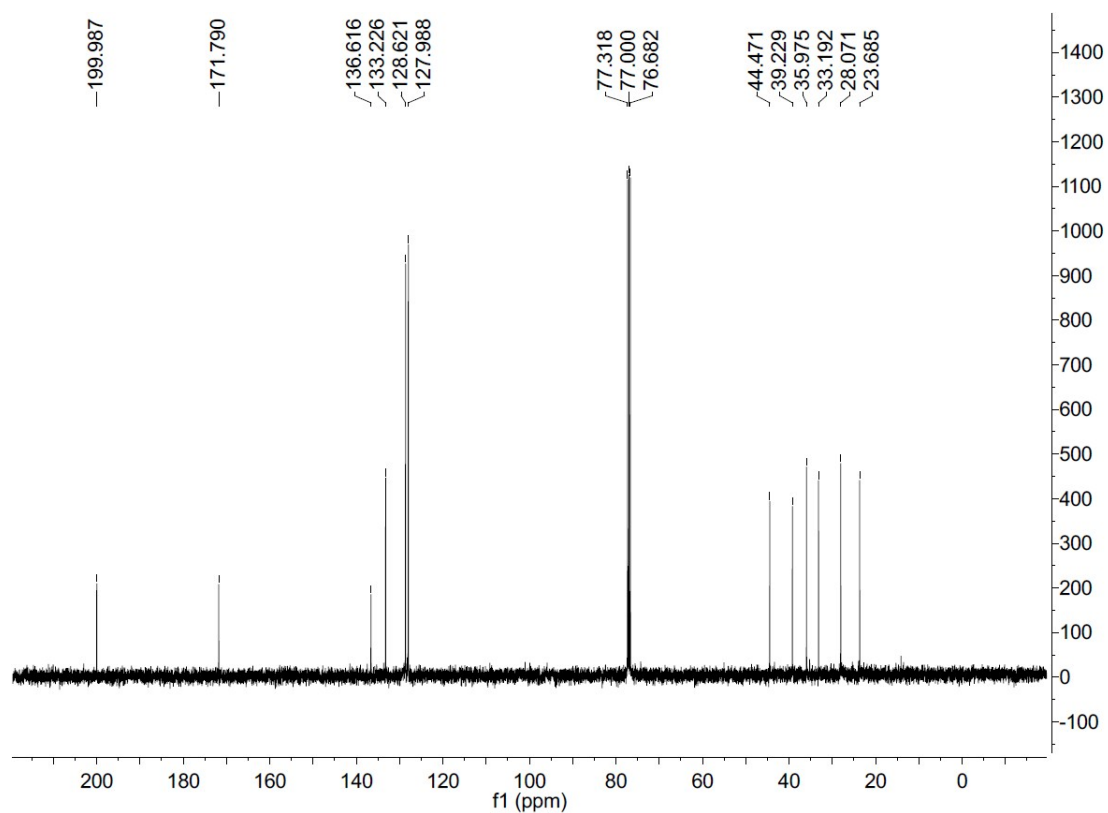
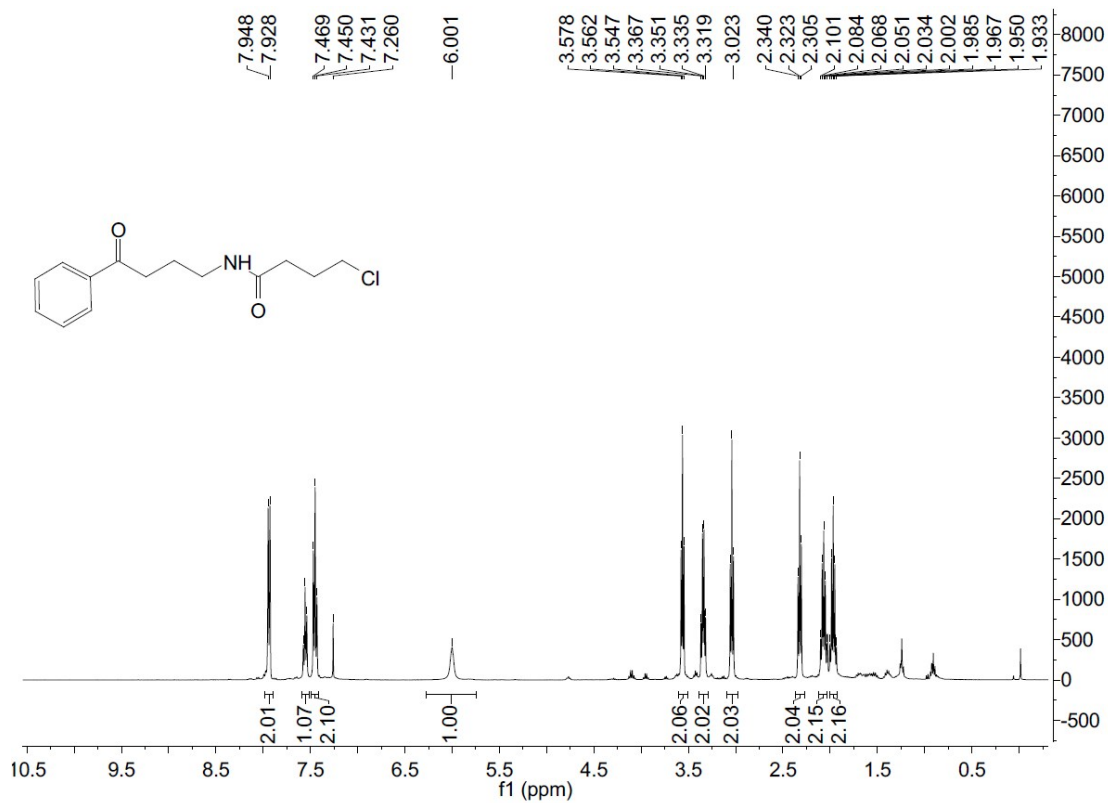
**4ar**



4cr

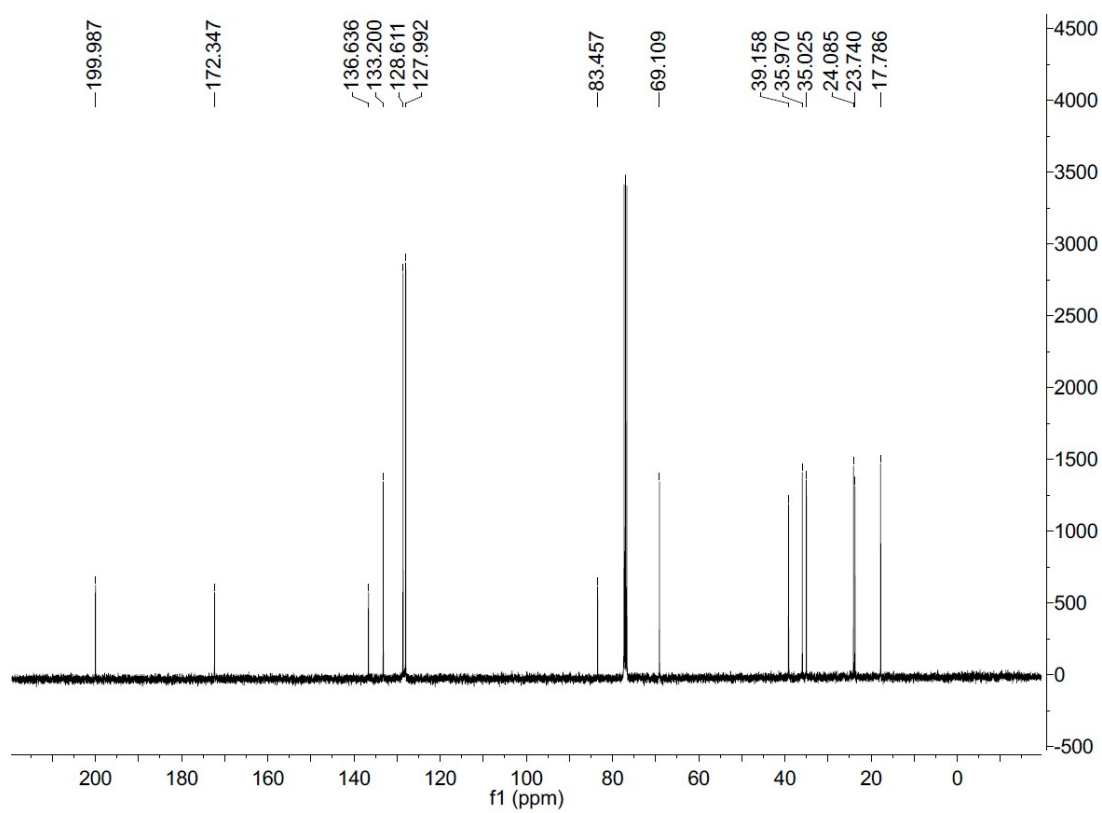
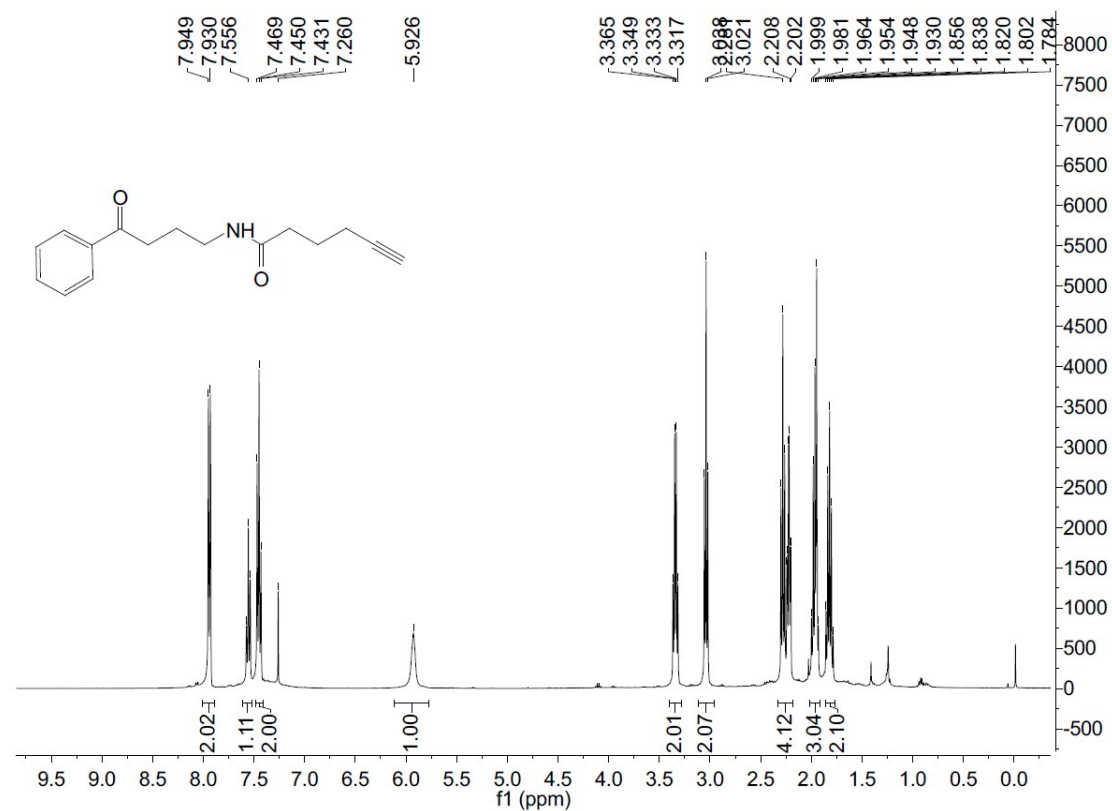


4as

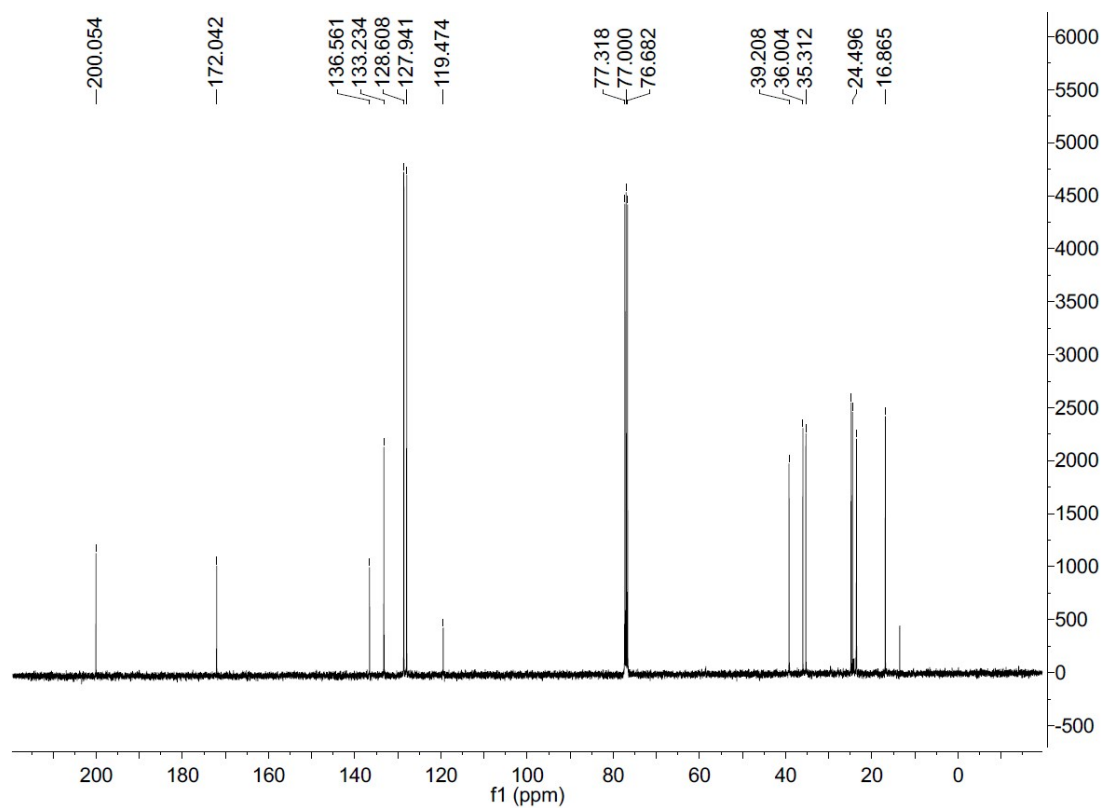
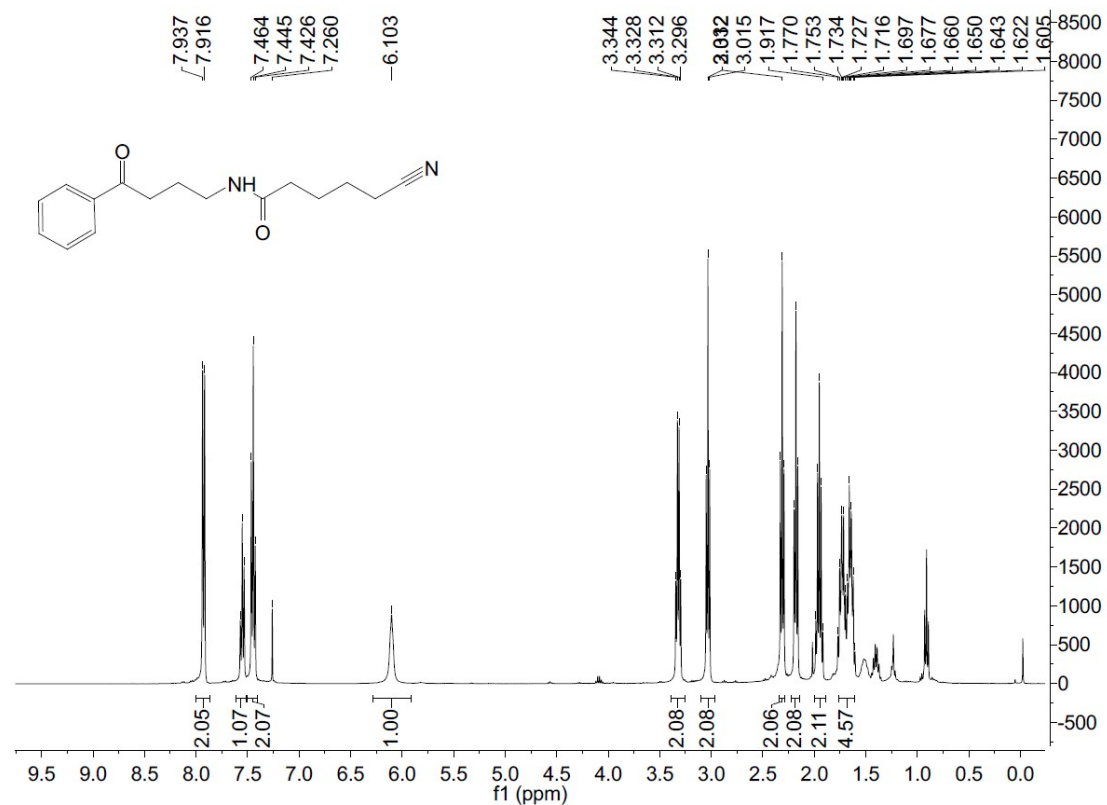




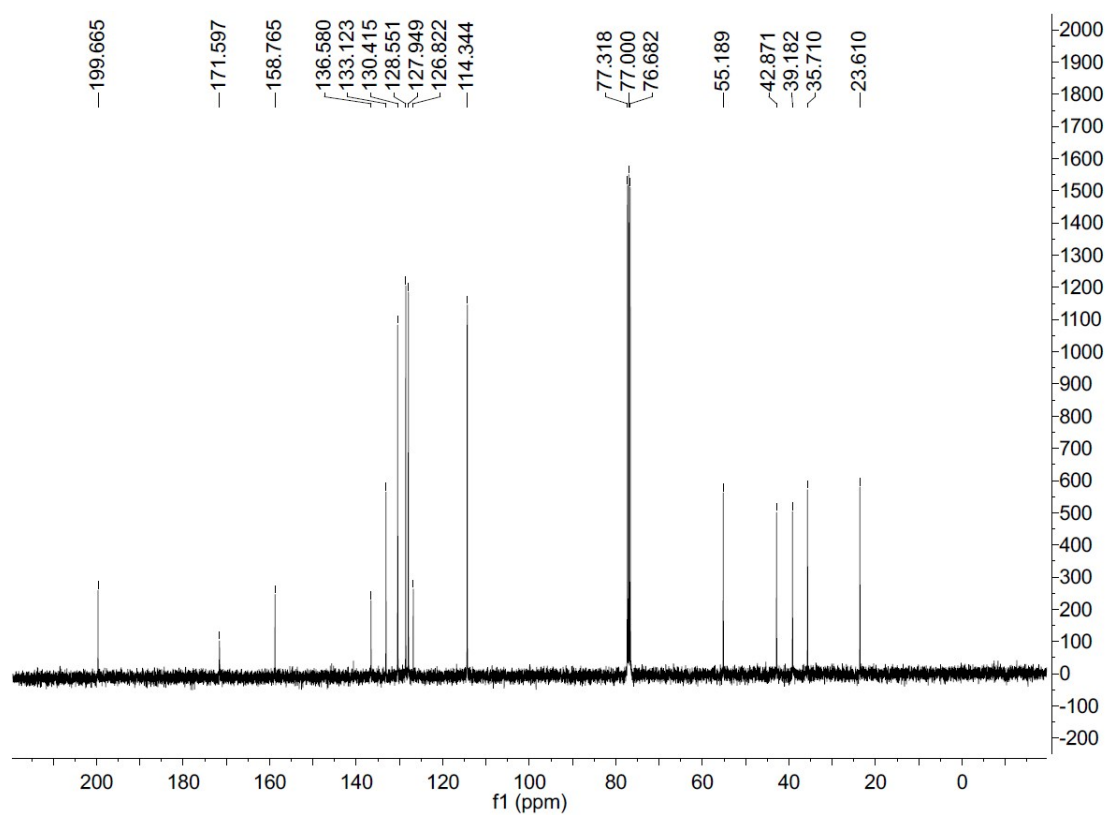
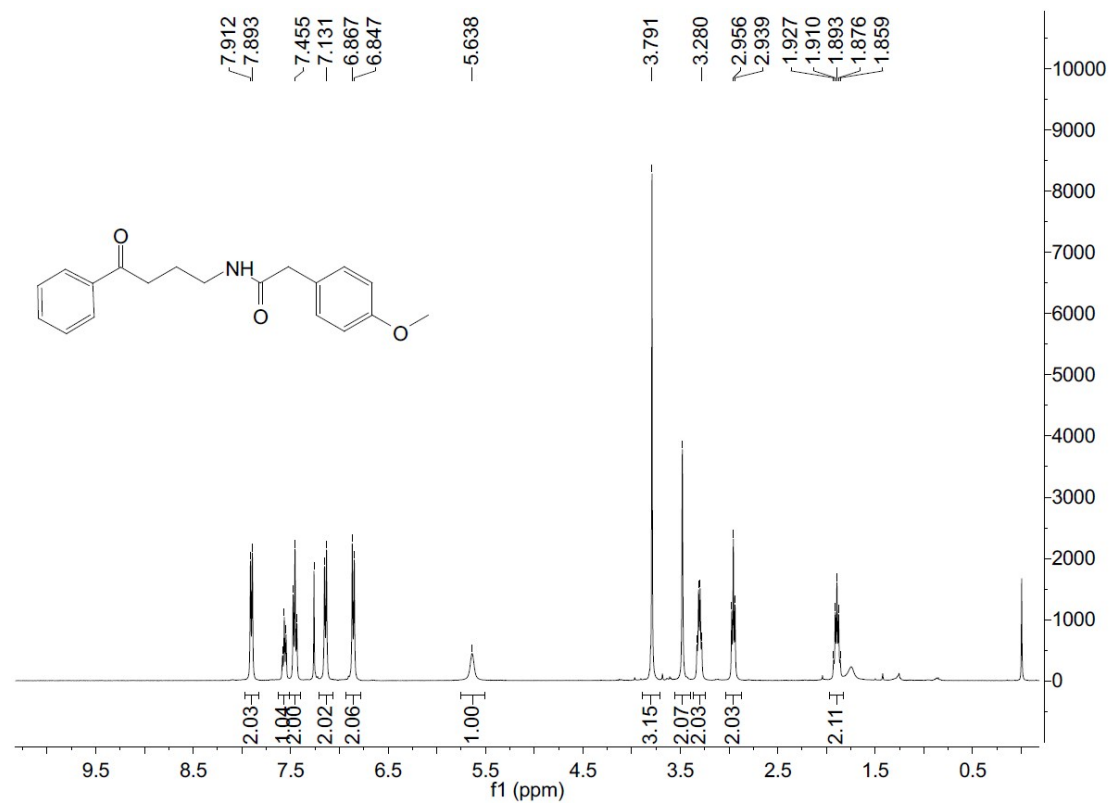
4at



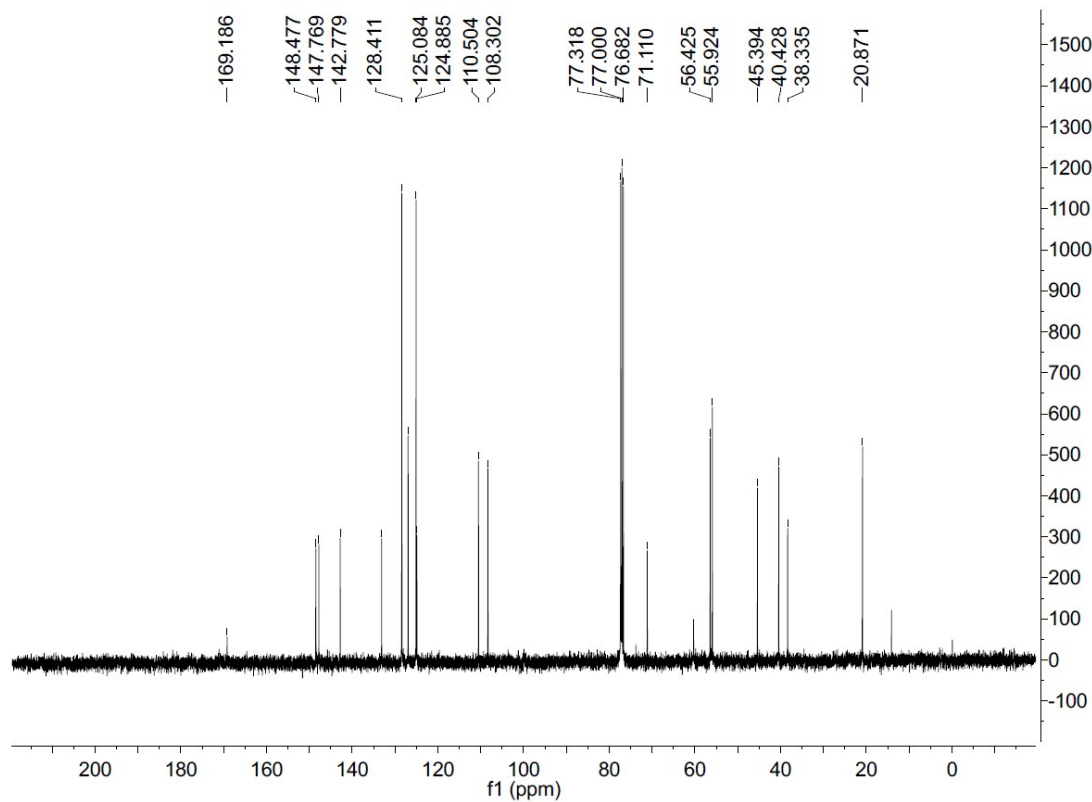
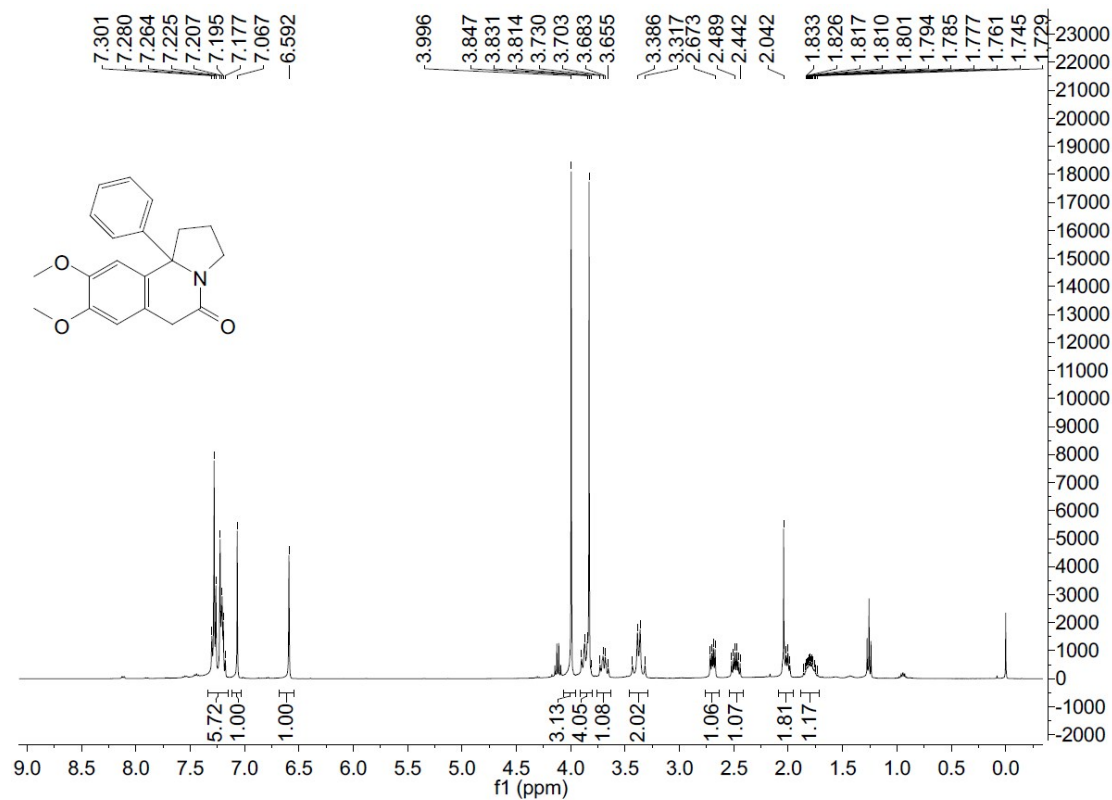
4au



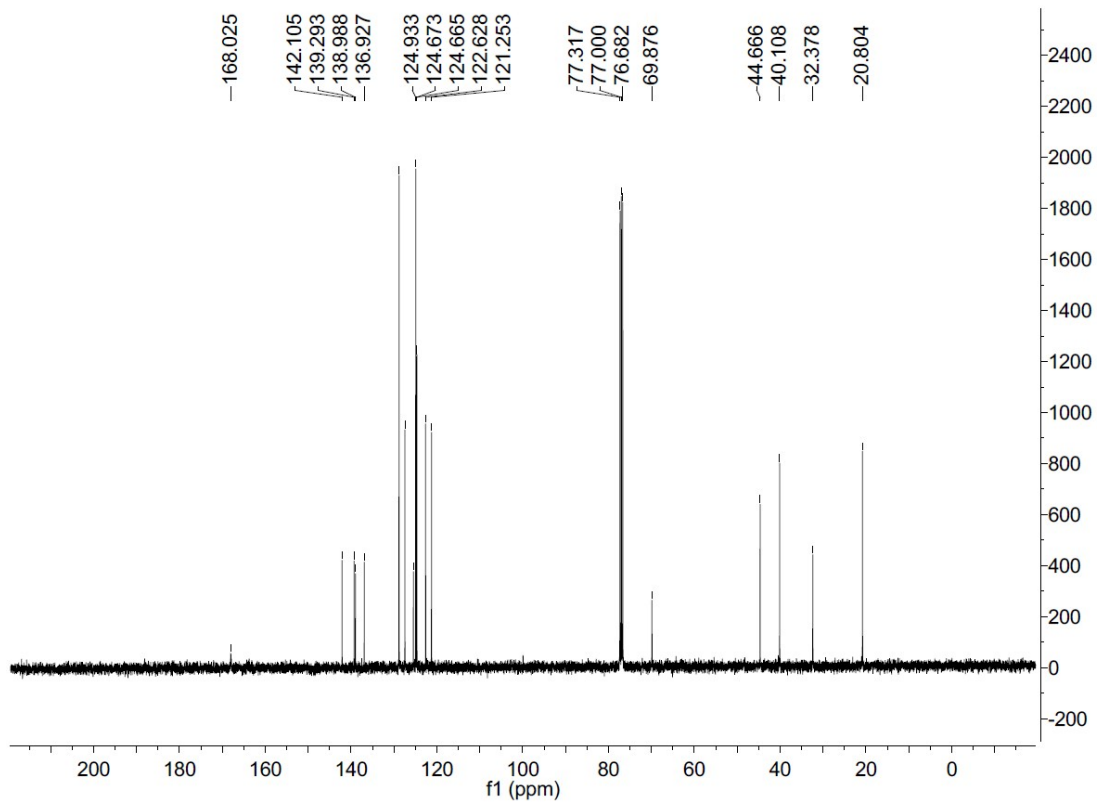
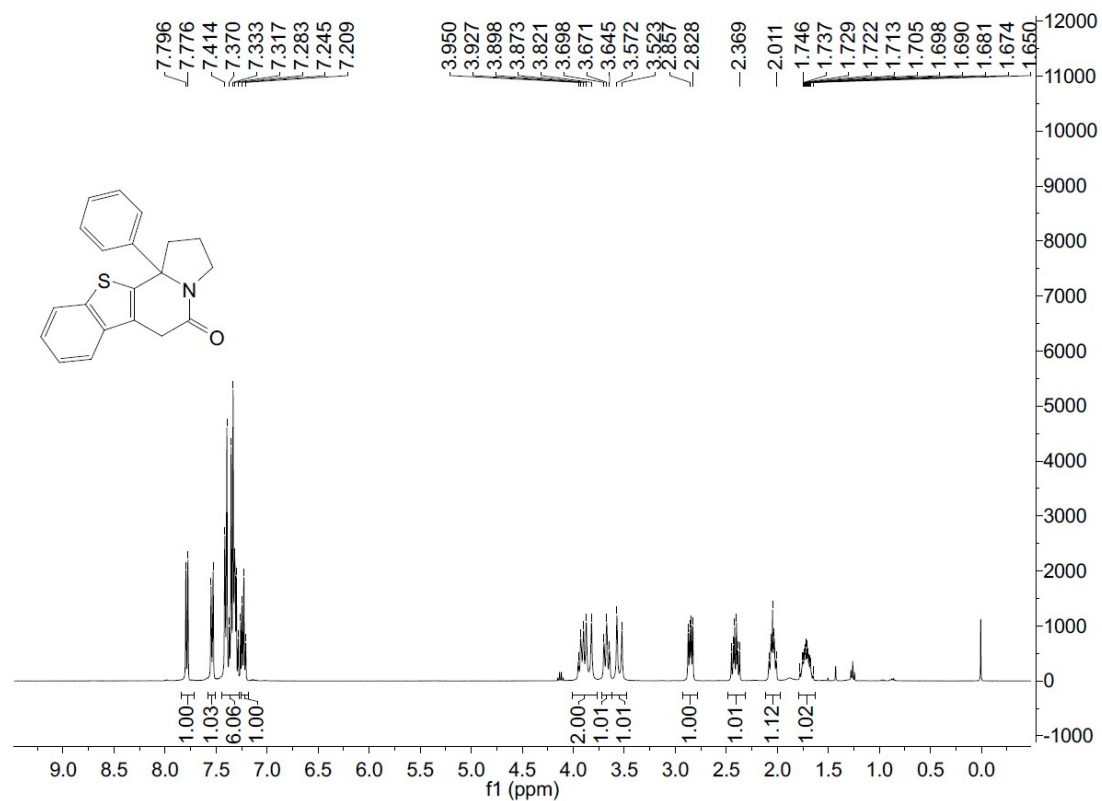
4av



4aw



**4ax**



5

