

# A Hydrazine Insertion Route to N'-Alkyl Benzohydrazides by an Unexpected Carbon–Carbon Bond Cleavage

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## **SUPPORTING INFORMATION**

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## General

The aldehydes used in the study were purchased from Sigma-Aldrich. The hydrazine derivatives were either purchased from Sigma-Aldrich or synthesised using a reported protocol.<sup>1</sup> Et<sub>3</sub>N was procured from local suppliers. Solvents were distilled prior to use. IBX was synthesised from 2-iodobenzoic acid using a literature protocol.<sup>2</sup> Silica gel (100-200 mesh) and other common reagents were procured from local suppliers. Proton and carbon nuclear magnetic resonance spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer. Elemental analysis was recorded on Thermo Finnigan FLASH EA 1112 & Thermo Scientific FLASH 2000 instrument. High resolution mass spectral analysis (HRMS) was performed on a XEVO G2-S QT instrument of Waters Corporation, USA. Melting points were recorded on Buchi, M-560 apparatus and are uncorrected. X-ray crystal data was recorded on a Bruker AXS, Apex II, Source (Mo K $\alpha$ ) instrument.

### Experimental Section:

#### General procedure for the synthesis of Morita-Baylis-Hillman (MBH) adducts:<sup>3</sup>

To a solution of the aldehyde (5 mmol) in dioxane:water (1:1, 0.5 mL) was added methyl acrylate (3 mmol) followed by DABCO (5 mmol) and the reaction mixture stirred at room temperature. Upon completion (TLC), the reaction was quenched with H<sub>2</sub>O (10 mL); the reaction mixture was extracted with EtOAc (3  $\times$  15 mL), the combined organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography using EtOAc:Petroleum ether (1:4) as an eluent to afford the desired MBH adducts.

#### General procedure for the synthesis of MBH Ketones:<sup>4</sup>

The MBH adduct (1.0 mmol) and IBX (1.5 equiv.) were dissolved in CH<sub>3</sub>CN (7 mL) in a 25 mL round-bottom flask and stirred at 70 °C. The reaction progress was monitored by TLC. After complete consumption of the starting material, the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The product was then extracted from the residue using EtOAc: Petroleum ether (1:1) and the organic layer was concentrated under reduced pressure. The crude MBH ketone obtained was used as such for the subsequent step without further purification.

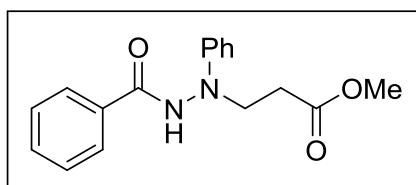
#### General procedure for the synthesis of the benzohydrazides:

**Method A:** The MBH ketone **1** (0.5 mmol) was dissolved in CH<sub>3</sub>CN (500  $\mu$ L). Phenylhydrazine (**2a**, 0.75 mmol) was then added to the solution followed by the addition of Et<sub>3</sub>N (0.25 mmol). The reaction mixture was further stirred at room temperature for the time mentioned in **Scheme 2** of the manuscript for the respective benzohydrazide derivatives. The reaction mixture was then diluted with H<sub>2</sub>O (5 mL) and extracted with EtOAc (3  $\times$  15 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography using EtOAc and petroleum ether as an eluent (*ratio defined for each derivative in the tabulation below*).

**Method B:** The MBH ketone **1** (0.5 mmol) was dissolved in CH<sub>3</sub>CN (500  $\mu$ L). The hydrazine hydrochloride derivative (0.75 mmol) was then added to the solution followed by H<sub>2</sub>O (50  $\mu$ L) and Et<sub>3</sub>N (1.75 mmol). The reaction mixture then stirred at room temperature for the time mentioned in **Schemes 2 & 3** of the manuscript for the respective benzohydrazide derivatives. The reaction mixture was then diluted with H<sub>2</sub>O (5 mL) and extracted with EtOAc (3  $\times$  8 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography using EtOAc and petroleum ether as an eluent (*ratio defined for each derivative in the tabulation below*).

### Representative example:

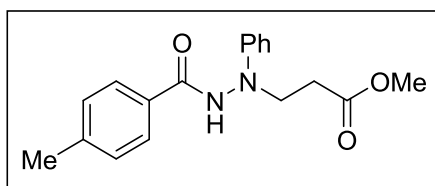
#### Synthesis of Methyl 3-(2-benzoyl-1-phenylhydrazinyl)propanoate (**3a**):



The MBH ketone **1a** (190 mg, 1.0 mmol) was dissolved in CH<sub>3</sub>CN (1 mL). Phenylhydrazine (147.5  $\mu$ L, 1.5 mmol) was then added to the solution followed by the addition of Et<sub>3</sub>N (70  $\mu$ L, 0.5 mmol). The reaction mixture was further stirred at room temperature for 15 h. The reaction mixture was then diluted with H<sub>2</sub>O (8 mL) and extracted with EtOAc (3  $\times$  15 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The crude residue was purified by silica gel column chromatography (EtOAc: petroleum ether, 2:8) to obtain the benzohydrazide **3a** as a light yellow solid. Yield: 216 mg (73%); Light yellow solid; mp 106-108  $^{\circ}$ C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  2.78 (t, *J* = 6.5 Hz, 2H), 3.65 (s, 3H), 3.97 (t, *J* = 6.5 Hz, 2H), 6.88 (masked t, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 8.43 (bs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  31.93, 48.01, 51.97, 113.08, 119.88, 127.30, 128.81, 129.36, 132.19, 132.58, 147.62, 166.63, 173.42; HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Na: 321.1210; found: 321.1210.

### Tabulated Data of the synthesized products:

#### Methyl 3-(2-(4-methylbenzoyl)-1-phenylhydrazinyl)propanoate (**3b**):

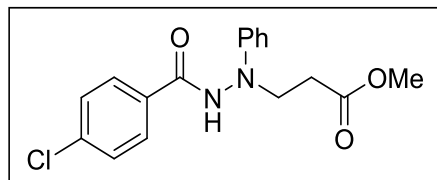


Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 136 mg (87%); Off white solid; mp 145-147  $^{\circ}$ C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  2.44 (s, 3H), 2.78 (t, *J* = 6.5 Hz, 2H), 3.65 (s, 3H), 3.97 (t, *J* = 6.5 Hz, 2H), 6.86 (masked t, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 8.0

Hz, 2H), 7.26 (t,  $J = 8.0$  Hz, 2H), 7.29 (d,  $J = 8.0$  Hz, 2H), 7.79 (d,  $J = 8.0$  Hz, 2H), 8.27 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.54, 32.00, 48.05, 51.91, 113.07, 119.83, 127.26, 129.33, 129.45, 129.76, 142.73, 147.77, 166.51, 173.35; Anal. calculated for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3$ : C, 69.21; H, 6.45; N, 8.97; found C, 69.32; H, 6.42; N, 8.89.

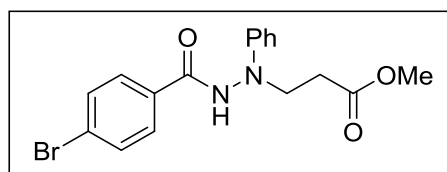
**Methyl 3-(2-(4-chlorobenzoyl)-1-phenylhydrazinyl)propanoate (3c):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 131 mg (79%); Off white solid; mp 163-165 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.76 (t,  $J = 6.5$  Hz, 2H), 3.65 (s, 3H), 3.93 (t,  $J = 6.0$  Hz, 2H), 6.85 (d,  $J = 8.0$  Hz, 2H), 6.88 (masked t,  $J = 7.0$  Hz, 1H), 7.26 (t,  $J = 8.0$  Hz, 2H), 7.44 (d,  $J = 8.5$  Hz, 2H), 7.83 (d,  $J = 8.5$  Hz, 2H), 8.57 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.89, 48.04, 52.03, 113.10, 120.03, 128.73, 129.08, 129.40, 130.97, 138.48, 147.38, 165.56, 173.56; Anal. calculated for  $\text{C}_{17}\text{H}_{17}\text{ClN}_2\text{O}_3$ : C, 61.36; H, 5.15; N, 8.42; found C, 61.45; H, 5.12; N, 8.49.

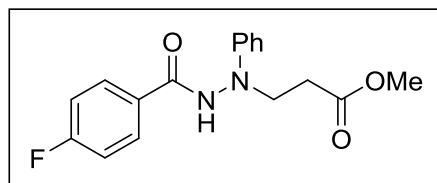
**Methyl 3-(2-(4-bromobenzoyl)-1-phenylhydrazinyl)propanoate (3d):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 157 mg (83%); Orange solid; mp 157-160 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.78 (t,  $J = 6.5$  Hz, 2H), 3.67 (s, 3H), 3.96 (t,  $J = 6.5$  Hz, 2H), 6.87 (d,  $J = 9.0$  Hz, 2H), 6.90 (masked t,  $J = 7.5$  Hz, 1H), 7.28 (t,  $J = 7.5$  Hz, 2H), 7.63 (d,  $J = 8.5$  Hz, 2H), 7.79 (d,  $J = 8.5$  Hz, 2H), 8.64 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.89, 48.03, 52.07, 113.11, 120.06, 126.99, 128.89, 129.42, 131.40, 132.07, 147.34, 165.70, 173.63; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{17}\text{H}_{17}\text{BrN}_2\text{O}_3\text{Na}$ : 399.0315; found: 399.0327.

**Methyl 3-(2-(4-fluorobenzoyl)-1-phenylhydrazinyl)propanoate (3e):**

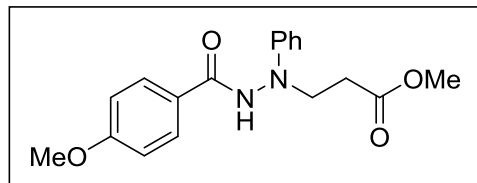


Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 3:7)

Yield: 155 mg (98%); Off white solid; mp 112-115 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.76 (t,  $J = 6.5$  Hz, 2H), 3.64 (s, 3H), 3.93 (t,  $J = 6.0$  Hz, 2H), 6.85 (d,  $J = 8.5$  Hz, 2H), 6.87 (masked t,  $J = 7.5$  Hz, 1H), 7.14 (t,  $J = 8.5$  Hz, 2H), 7.26 (t,  $J = 8.0$  Hz, 2H), 7.91 (dd,  $J = 5.5$  & 8.5 Hz, 2H), 8.61 (bs, 1H);  $^{13}\text{C}$  NMR

(125 MHz, CDCl<sub>3</sub>):  $\delta$  31.90, 48.02, 52.04, 113.06, 115.91 (d,  $J_{\text{C-F}} = 22$  Hz), 119.98, 128.73 (d,  $J_{\text{C-F}} = 3.0$  Hz), 129.40, 129.73 (d,  $J_{\text{C-F}} = 9.0$  Hz), 147.45, 165.14 (d,  $J_{\text{C-F}} = 252.0$  Hz), 165.60, 173.61; Anal. calculated for C<sub>17</sub>H<sub>17</sub>FN<sub>2</sub>O<sub>3</sub>: C, 64.55; H, 5.42; N, 8.86; found C, 65.10; H, 5.76; N, 8.45.

**Methyl 3-(2-(4-methoxybenzoyl)-1-phenylhydrazinyl)propanoate (3f):<sup>#</sup>**

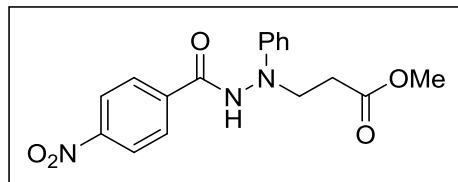


Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 103 mg (63%); Yellow solid; mp 157-160 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  2.80 (t,  $J = 6.5$  Hz, 2H), 3.68 (s, 3H), 3.91 (s, 3H), 3.99 (t,  $J = 6.5$  Hz, 2H), 6.89 (masked t,  $J = 7.0$  Hz, 1H), 6.91 (d,  $J = 8.0$  Hz, 2H), 7.00 (d,  $J = 8.5$  Hz, 2H), 7.29 (t,  $J = 7.5$  Hz, 2H), 7.89 (d,  $J = 9.0$  Hz, 2H), 8.33 (bs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  32.04, 48.07, 51.90, 55.46, 113.05, 114.04, 119.80, 124.84, 129.11, 129.32, 147.83, 162.77, 166.08, 173.40; HRMS (ESI-TOF):  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>: 329.1496; found: 329.1495.

<sup>#</sup>Corresponding pyrazole obtained as the minor product; see end of this section for structure, yield and tabulated data.

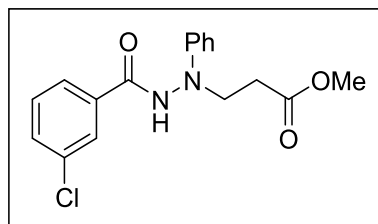
**Methyl 3-(2-(4-nitrobenzoyl)-1-phenylhydrazinyl)propanoate (3g):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 120 mg (70%); Light orange solid; mp 129-132 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  2.78 (t,  $J = 6.0$  Hz, 2H), 3.66 (s, 3H), 3.95 (t,  $J = 6.0$  Hz, 2H), 6.84 (d,  $J = 8.0$  Hz, 2H), 6.89 (t,  $J = 7.5$  Hz, 1H), 7.27 (t,  $J = 7.5$  Hz, 2H), 8.05 (d,  $J = 8.5$  Hz, 2H), 8.29 (d,  $J = 8.5$  Hz, 2H), 9.02 (bs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  31.78, 48.12, 52.17, 113.21, 120.34, 123.97, 128.58, 129.51, 138.19, 146.88, 149.96, 164.60, 173.84; Anal. calculated for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub>: C, 59.47; H, 4.99; N, 12.24; found C, 59.70; H, 5.08; N, 11.60.

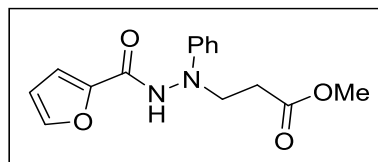
**Methyl 3-(2-(3-chlorobenzoyl)-1-phenylhydrazinyl)propanoate (3h):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 125 mg (75%); Brown semi-solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.78 (t,  $J$  = 6.5 Hz, 2H), 3.66 (s, 3H), 3.95 (t,  $J$  = 6.0 Hz, 2H), 6.86 (d,  $J$  = 8.0 Hz, 2H), 6.88 (masked t,  $J$  = 7.0 Hz, 1H), 7.27 (t,  $J$  = 7.5 Hz, 2H), 7.43 (t,  $J$  = 7.0 Hz, 1H), 7.55 (d,  $J$  = 8.0 Hz, 1H), 7.76 (d,  $J$  = 7.5 Hz, 1H), 7.90 (s, 1H), 8.47 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.88, 48.05, 52.04, 113.16, 120.09, 125.30, 127.71, 129.40, 130.13, 132.21, 134.40, 135.02, 147.33, 165.38, 173.52; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{17}\text{H}_{18}\text{ClN}_2\text{O}_3$ : 333.1000; found: 333.1002.

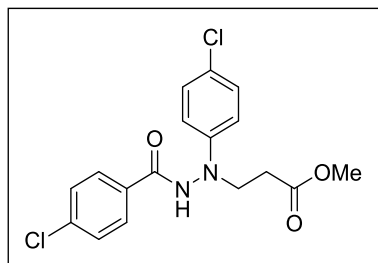
**Methyl 3-(2-(furan-2-carbonyl)-1-phenylhydrazinyl)propanoate (3i):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 114 mg (79%); Orange solid; mp 105-108  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.76 (t,  $J$  = 6.5 Hz, 2H), 3.64 (s, 3H), 3.93 (t,  $J$  = 6.5 Hz, 2H), 6.53-6.58 (m, 1H), 6.87 (masked t,  $J$  = 7.0 Hz, 1H), 6.89 (d,  $J$  = 8.0 Hz, 2H), 7.21-7.28 (m, 3H), 7.50-7.54 (unresolved m, 1H), 8.32 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.86, 48.36, 51.93, 112.31, 113.30, 115.98, 120.18, 129.36, 144.63, 146.56, 147.64, 157.61, 173.03; Anal. calculated for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_4$ : C, 62.49; H, 5.59; N, 9.72; found C, 62.37; H, 5.53; N, 9.78.

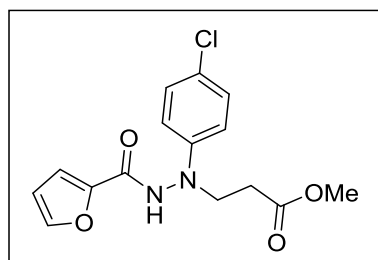
**Methyl 3-(2-(4-chlorobenzoyl)-1-(4-chlorophenyl)hydrazinyl)propanoate (3j):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 110 mg (60%); White solid; mp 163-168  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.74 (t,  $J$  = 6.0 Hz, 2H), 3.66 (s, 3H), 3.91 (t,  $J$  = 6.0 Hz, 2H), 6.76 (d,  $J$  = 8.5 Hz, 2H), 7.19 (d,  $J$  = 9.0 Hz, 2H), 7.46 (d,  $J$  = 8.0 Hz, 2H), 7.83 (d,  $J$  = 8.0 Hz, 2H), 8.66 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.83, 48.13, 52.14, 114.27, 124.91, 128.72, 129.14, 129.25, 130.68, 138.70, 146.07, 165.49, 173.49; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{17}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_3\text{Na}$ : 389.0430; found: 389.0432.

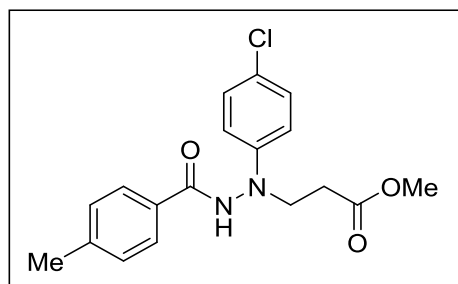
**Methyl 3-(1-(4-chlorophenyl)-2-(furan-2-carbonyl)hydrazinyl)propanoate (3k):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 113 mg (70%); Mustard solid; mp 83-85 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.74 (t,  $J$  = 6.5 Hz, 2H), 3.66 (s, 3H), 3.91 (t,  $J$  = 6.5 Hz, 2H), 6.55-6.60 (m, 1H), 6.81 (d,  $J$  = 8.5 Hz, 2H), 7.19 (d,  $J$  = 9.0 Hz, 2H), 7.23 (d,  $J$  = 3.5 Hz, 1H), 7.53 (s, 1H), 8.36 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.87, 48.47, 51.92, 112.33, 114.50, 116.09, 116.12, 125.06, 129.18, 144.69, 146.43, 157.46, 172.80; Anal. calculated for  $\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{O}_4$ : C, 55.82; H, 4.68; N, 8.68; found C, 55.73; H, 4.62; N, 8.75.

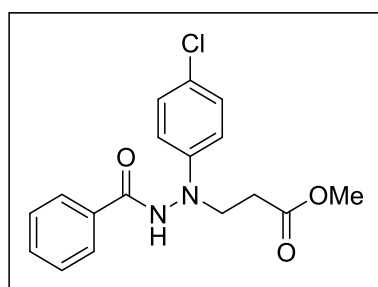
**Methyl 3-(1-(4-chlorophenyl)-2-(4-methylbenzoyl)hydrazinyl)propanoate (3l):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 116 (67%); White solid; mp 179-182 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.43 (s, 3H), 2.74 (t,  $J$  = 6.5 Hz, 2H), 3.65 (s, 3H), 3.91 (t,  $J$  = 6.5 Hz, 2H), 6.77 (d,  $J$  = 9.0 Hz, 2H), 7.18 (d,  $J$  = 9.0 Hz, 2H), 7.27 (d,  $J$  = 9.0 Hz, 2H), 7.77 (d,  $J$  = 8.0 Hz, 2H), 8.49 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.58, 31.91, 48.09, 52.04, 114.23, 124.66, 127.26, 129.17, 129.40, 129.50, 142.97, 146.46, 166.49, 173.27; Anal. calculated for  $\text{C}_{18}\text{H}_{19}\text{ClN}_2\text{O}_3$ : C, 62.34; H, 5.52; N, 8.08; found C, 62.74; H, 5.73; N, 7.75.

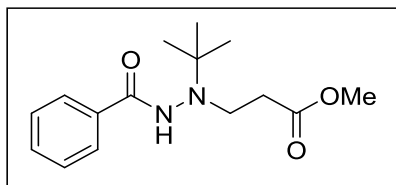
**Methyl 3-(2-benzoyl-1-(4-chlorophenyl)hydrazinyl)propanoate (3m):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 126 mg (76%); White solid; mp 135-137 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.75 (t,  $J$  = 6.5 Hz, 2H), 3.66 (s, 3H), 3.93 (t,  $J$  = 6.0 Hz, 2H), 6.79 (d,  $J$  = 9.0 Hz, 2H), 7.19 (d,  $J$  = 9.0 Hz, 2H), 7.49 (t,  $J$  = 2H), 7.58 (t,  $J$  = 6.5 Hz, 1H), 7.88 (d,  $J$  = 7.5 Hz, 2H), 8.50 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.87, 48.09, 52.04, 114.24, 124.68, 127.29, 128.83, 129.17, 132.29, 132.35, 146.36, 166.60, 173.24; Anal. calculated for  $\text{C}_{17}\text{H}_{17}\text{ClN}_2\text{O}_3$ : C, 61.36; H, 5.15; N, 8.42; found C, 61.93; H, 5.39; N, 8.23.

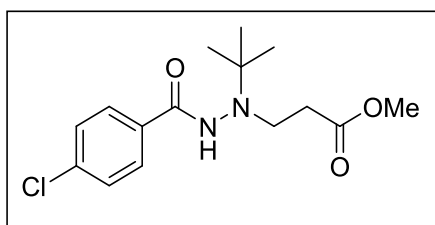
**Methyl 3-(2-benzoyl-1-(tert-butyl)hydrazinyl)propanoate (3n):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 84 mg (60%); White solid; mp 123-125 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.17 (s, 9H), 2.56 (t, *J* = 6.5 Hz, 2H), 3.08 (bs, 2H), 3.48 (s, 3H), 6.66 (bs, 1H), 7.35-7.42 (m, 2H), 7.43-7.50 (m, 1H), 7.70 (d, *J* = 7.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 25.44, 32.94, 45.88, 51.58, 58.69, 126.98, 128.60, 131.55, 133.84, 167.01, 173.71; HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calculated for C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>Na: 301.1523; found: 301.1521.

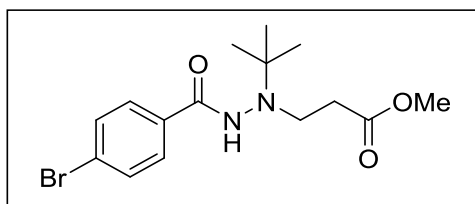
**Methyl 3-(1-(tert-butyl)-2-(4-chlorobenzoyl)hydrazinyl)propanoate (3o):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 108 mg (69%); White solid; mp 114-116 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.17 (s, 9H), 2.57 (t, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 6.5 Hz, 2H), 3.50 (s, 3H), 6.64 (bs, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 25.45, 32.95, 45.79, 51.62, 58.74, 128.44, 128.85, 132.17, 137.81, 165.95, 173.74; Anal. calculated for C<sub>15</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>3</sub>: C, 57.60; H, 6.77; N, 8.96; found C, 57.68; H, 6.72; N, 8.91.

**Methyl 3-(2-(4-bromobenzoyl)-1-(tert-butyl)hydrazinyl)propanoate (3p):**

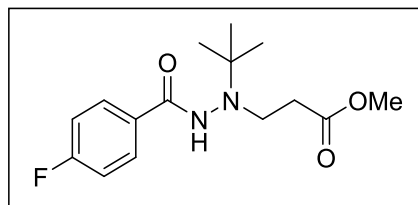


Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 134 mg (75%); White solid; mp 108-112 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.18 (s, 9H), 2.58 (t, *J* = 6.5 Hz, 2H), 3.10 (bs, 2H), 3.51 (s, 3H), 6.64 (bs, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 25.44, 32.93, 45.79, 51.67, 58.78, 126.27, 128.61, 131.87, 132.58, 166.08, 173.81; HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calculated for C<sub>15</sub>H<sub>21</sub>BrN<sub>2</sub>O<sub>3</sub>Na: 379.0628; found: 379.0627.



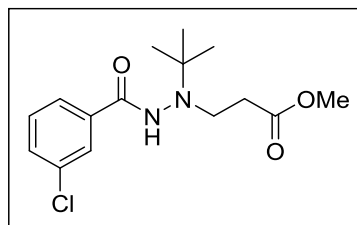
**Methyl 3-(1-(tert-butyl)-2-(4-fluorobenzoyl)hydrazinyl)propanoate (3q):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 101 mg (68%); White solid; mp 117-120 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.19 (s, 9H), 2.59 (t,  $J$  = 7.0 Hz, 2H), 3.11 (bs, 2H), 3.51 (s, 3H), 6.58 (bs, 1H), 7.11 (t,  $J$  = 9.0 Hz, 2H), 7.75 (dd,  $J$  = 5.5 & 9.0 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.42, 32.90, 45.81, 51.69, 58.78, 115.73 (d,  $J_{\text{C-F}}$  = 22.0 Hz), 129.33 (d,  $J_{\text{C-F}}$  = 9.0 Hz), 129.86 (d,  $J_{\text{C-F}}$  = 3.0 Hz), 164.78 (d,  $J_{\text{C-F}}$  = 251.0 Hz), 166.00, 173.92; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{15}\text{H}_{21}\text{FN}_2\text{O}_3\text{Na}$ : 319.1428; found: 319.1429.

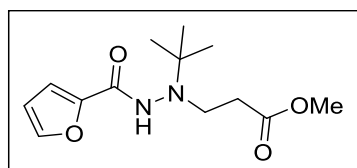
**Methyl 3-(1-(tert-butyl)-2-(3-chlorobenzoyl)hydrazinyl)propanoate (3r):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 97 mg (62%); White solid; mp 121-123 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.20 (s, 9H), 2.59 (t,  $J$  = 6.5 Hz, 2H), 3.12 (t,  $J$  = 6.0 Hz, 2H), 3.54 (s, 3H), 6.59 (bs, 1H), 7.37 (t,  $J$  = 8.0 Hz, 1H), 7.48 (d,  $J$  = 8.0 Hz, 1H), 7.59 (d,  $J$  = 8.0 Hz, 1H), 7.70-7.75 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.45, 32.92, 45.82, 51.67, 58.80, 124.96, 127.40, 129.97, 131.65, 134.89, 135.62, 165.76, 173.76. Anal. calculated for  $\text{C}_{15}\text{H}_{21}\text{ClN}_2\text{O}_3$ : C, 57.60; H, 6.77; N, 8.96; found C, 57.68; H, 6.72; N, 8.87.

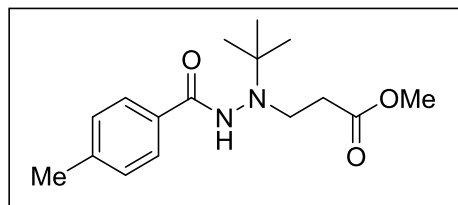
**Methyl 3-(1-(tert-butyl)-2-(furan-2-carbonyl)hydrazinyl)propanoate (3s):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 54 mg (40%); Light yellow solid; mp 113-115 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.18 (s, 9H), 2.57 (t,  $J$  = 6.5 Hz, 2H), 3.10 (t,  $J$  = 6.5 Hz, 2H), 3.54 (s, 3H), 6.49-6.53 (m, 1H), 6.84 (bs, 1H), 7.16 (d,  $J$  = 3.0 Hz, 1H), 7.45 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.34, 32.97, 46.22, 51.57, 58.70, 112.15, 115.19, 144.01, 147.00, 157.86, 173.48; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_4\text{Na}$ : 291.1315; found: 291.1317.

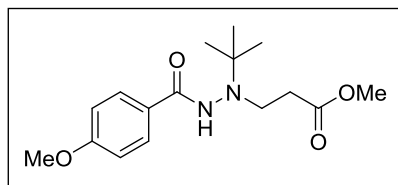
**Methyl 3-(1-(tert-butyl)-2-(4-methylbenzoyl)hydrazinyl)propanoate (3t):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 61 mg (42%); White solid; mp 114-116 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.19 (s, 9H), 2.39 (s, 3H), 2.59 (t,  $J = 7.0$  Hz, 2H), 3.07-3.13 (m, 2H), 3.50 (s, 3H), 6.57 (bs, 1H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.63 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.43, 25.43, 32.95, 45.93, 51.58, 58.70, 126.97, 129.26, 130.93, 142.00, 166.89, 173.80; Anal. calculated for  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_3$ : C, 65.73; H, 8.27; N, 9.58; found C, 65.78; H, 8.23; N, 9.65.

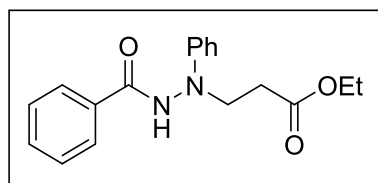
**Methyl 3-(1-(tert-butyl)-2-(4-methoxybenzoyl)hydrazinyl)propanoate (3u):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 73 mg (47%); White solid; mp 124-126 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.18 (s, 9H), 2.58 (t,  $J = 6.5$  Hz, 2H), 3.10 (bs, 2H), 3.49 (s, 3H), 3.84 (s, 3H), 6.55 (bs, 1H), 6.91 (d,  $J = 9.0$  Hz, 2H), 7.70 (d,  $J = 8.5$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.42, 32.92, 45.91, 51.64, 55.43, 58.71, 113.82, 125.89, 128.79, 162.27, 166.49, 173.93; Anal. calculated for  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_4$ : C, 62.32; H, 7.84; N, 9.08; found C, 62.48; H, 7.93; N, 8.85.

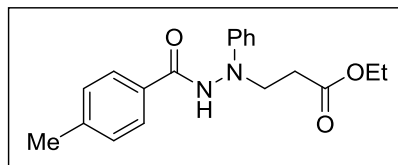
**Ethyl 3-(2-benzoyl-1-phenylhydrazinyl)propanoate (5a):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 120 mg (77%); Off white solid; mp 117-119 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.21 (t,  $J = 7.5$  Hz, 3H), 2.76 (t,  $J = 6.5$  Hz, 2H), 3.96 (t,  $J = 6.5$  Hz, 2H), 4.09 (q,  $J = 7.5$  Hz, 2H), 6.87 (masked t,  $J = 7.5$  Hz, 1H), 6.88 (d,  $J = 8.0$  Hz, 2H), 7.26 (t,  $J = 7.5$  Hz, 2H), 7.48 (t,  $J = 7.5$  Hz, 2H), 7.57 (t,  $J = 7.5$  Hz, 1H), 7.89 (d,  $J = 7.5$  Hz, 2H), 8.45 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.10, 32.21, 48.02, 60.90, 113.09, 119.85, 127.27, 128.79, 129.34, 132.15, 132.68, 147.68, 166.52, 172.97; HRMS (ESI-TOF):  $m/z$  [ $\text{M} + \text{Na}$ ] $^+$  calculated for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3\text{Na}$ : 335.1366; found: 335.1362.

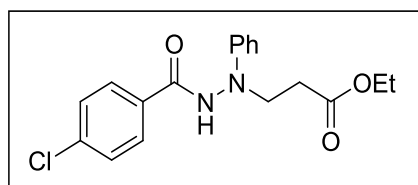
**Ethyl 3-(2-(4-methylbenzoyl)-1-phenylhydrazinyl)propanoate (5b):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 98 mg (60%); Light orange solid; mp 123-126 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.21 (t, *J* = 7.0 Hz, 3H), 2.43 (s, 3H), 2.75 (t, *J* = 6.5 Hz, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 6.85 (masked t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 7.21-7.31 (m, 4H), 7.79 (d, *J* = 8.0 Hz, 2H), 8.44 (bs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.12, 21.57, 32.20, 47.97, 60.92, 113.06, 119.78, 127.28, 129.33, 129.45, 129.72, 142.74, 147.76, 166.55, 173.02; Anal. calculated for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>: C, 69.92; H, 6.79; N, 8.58; found C, 70.27; H, 6.37; N, 8.21.

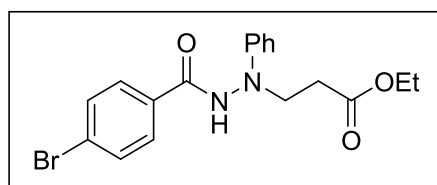
**Ethyl 3-(2-(4-chlorobenzoyl)-1-phenylhydrazinyl)propanoate (5c):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 156 mg (90%); Light orange solid; mp 117-119 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.21 (t, *J* = 7.0 Hz, 3H), 2.73 (t, *J* = 6.5 Hz, 2H), 3.91 (t, *J* = 6.5 Hz, 2H), 4.09 (q, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.87 (masked t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 8.70 (bs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.11, 32.13, 48.00, 61.00, 113.10, 119.95, 128.76, 129.03, 129.37, 130.98, 138.44, 147.44, 165.59, 173.13; Anal. calculated for C<sub>18</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>3</sub>: C, 62.34; H, 5.52; N, 8.08; found C, 62.88; H, 5.75; N, 7.50.

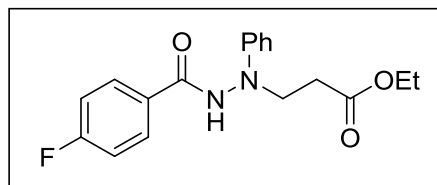
**Ethyl 3-(2-(4-bromobenzoyl)-1-phenylhydrazinyl)propanoate (5d):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 150 mg (77%); Yellow solid; mp 132-136 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.22 (t, *J* = 7.0 Hz, 3H), 2.75 (t, *J* = 6.0 Hz, 2H), 3.94 (t, *J* = 6.0 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.87 (masked t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 8.60 (bs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.10, 32.14, 48.02, 61.28, 113.11, 120.00, 126.95, 128.88, 129.39, 131.47, 132.05, 147.38, 165.62, 173.20; HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calculated for C<sub>18</sub>H<sub>20</sub>BrN<sub>2</sub>O<sub>3</sub>: 391.0652; found: 391.0654.

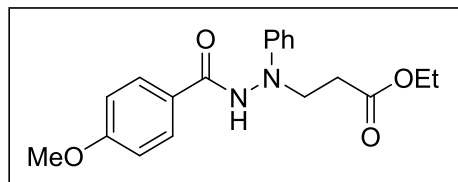
**Ethyl 3-(2-(4-fluorobenzoyl)-1-phenylhydrazinyl)propanoate (5e):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 149 mg (90%); White solid; mp 90-93 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.21 (t,  $J = 7.0$  Hz, 3H), 2.74 (t,  $J = 6.0$  Hz, 2H), 3.93 (t,  $J = 6.0$  Hz, 2H), 4.09 (q,  $J = 6.0$  Hz, 2H), 6.85 (d,  $J = 9.0$  Hz, 2H), 6.87 (masked t,  $J = 8.0$  Hz, 1H), 7.13 (t,  $J = 8.5$  Hz, 2H), 7.26 (t,  $J = 8.5$  Hz, 2H), 7.87-7.95 (m, 2H), 8.62 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.11, 32.13, 47.99, 60.99, 113.07, 115.87 (d,  $J_{\text{C-F}} = 22$  Hz), 119.90, 128.79 (d,  $J_{\text{C-F}} = 3.0$  Hz), 129.37, 129.73 (d,  $J_{\text{C-F}} = 9.0$  Hz), 147.49, 165.12 (d,  $J_{\text{C-F}} = 251.0$  Hz), 165.53, 173.16; Anal. calculated for  $\text{C}_{18}\text{H}_{19}\text{FN}_2\text{O}_3$ : C, 65.44; H, 5.80; N, 8.48; found C, 65.79; H, 6.05; N, 8.08

**Ethyl 3-(2-(4-methoxybenzoyl)-1-phenylhydrazinyl)propanoate (5f):<sup>#</sup>**

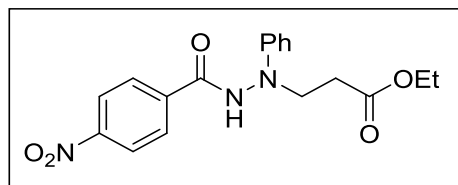


Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 103 mg (60%); Light yellow solid; mp 120-124 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.21 (t,  $J = 7.5$  Hz, 3H), 2.75 (t,  $J = 6.5$  Hz, 2H), 3.87 (s, 3H), 3.94 (t,  $J = 6.5$  Hz, 2H), 4.09 (q,  $J = 7.0$  Hz, 2H), 6.85 (masked t,  $J = 7.0$  Hz, 1H), 6.87 (d,  $J = 8.0$  Hz, 2H), 6.95 (d,  $J = 8.5$  Hz, 2H), 7.25 (t,  $J = 8.0$  Hz, 2H), 7.86 (d,  $J = 8.5$  Hz, 2H), 8.39 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.12, 32.21, 47.97, 55.48, 60.90, 113.03, 113.99, 119.70, 124.81, 129.16, 129.31, 147.84, 162.72, 166.10, 173.04; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4\text{Na}$ : 365.1472; found: 365.1473.

<sup>#</sup>Corresponding regioisomeric pyrazoles obtained as the minor products; see end of this section for structures, yields and tabulated data.

**Ethyl 3-(2-(4-nitrobenzoyl)-1-phenylhydrazinyl)propanoate (5g):**

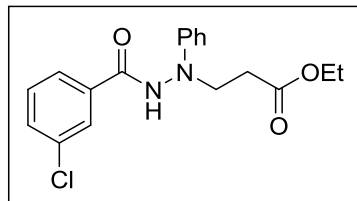


Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 125 mg (70%); Yellow solid; mp 129-131 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.24 (t,  $J = 7.0$  Hz, 3H), 2.78 (t,  $J = 6.0$  Hz, 2H), 3.96 (t,  $J = 6.0$  Hz, 2H), 4.12 (q,  $J = 7.5$  Hz, 2H), 6.86 (d,  $J = 8$  Hz, 2H), 6.91 (t,  $J = 7.5$  Hz, 1H), 7.29 (t,  $J = 8$  Hz, 2H), 8.08 (d,  $J = 8.5$  Hz, 2H), 8.30 (d,  $J = 8.5$  Hz, 2H), 9.09 (bs,

1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.11, 32.03, 48.09, 61.22, 113.23, 120.29, 123.97, 128.58, 129.49, 138.24, 146.89, 149.95, 164.54, 173.51; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_5\text{Na}$ : 380.1217; found: 380.1216.

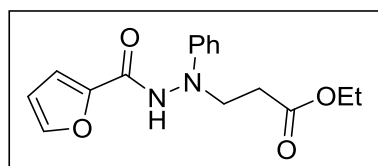
**Ethyl 3-(2-(3-chlorobenzoyl)-1-phenylhydrazinyl)propanoate (5h):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 113 mg (65%); Orange red gum;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.21 (t,  $J = 7.5$  Hz, 3H), 2.72 (t,  $J = 6.5$  Hz, 2H), 3.89 (t,  $J = 6.5$  Hz, 2H), 4.09 (q,  $J = 7.0$  Hz, 2H), 6.83 (d,  $J = 8.0$  Hz, 2H), 6.86 (masked t,  $J = 7.5$  Hz, 1H), 7.24 (t,  $J = 8.5$  Hz, 2H), 7.38 (t,  $J = 8.0$  Hz, 1H), 7.52 (d,  $J = 8.0$  Hz, 1H), 7.74 (d,  $J = 7.5$  Hz, 1H), 7.85-7.91 (m, 1H), 8.71 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.11, 32.11, 47.96, 61.01, 113.16, 120.01, 125.35, 127.72, 129.36, 130.09, 132.16, 134.42, 134.95, 147.41, 165.41, 173.08; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{18}\text{H}_{20}\text{ClN}_2\text{O}_3$ : 347.1157; found: 347.1152.

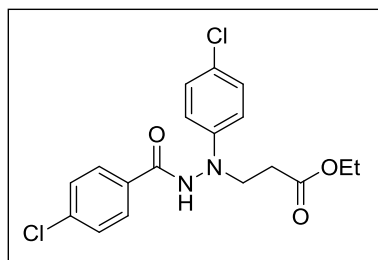
**Ethyl 3-(2-(furan-2-carbonyl)-1-phenylhydrazinyl)propanoate (5i):**



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 95 mg (63%); Orange solid; mp 100-103  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.20 (t,  $J = 7.0$  Hz, 3H), 2.75 (t,  $J = 6.5$  Hz, 2H), 3.93 (t,  $J = 6.5$  Hz, 2H), 4.09 (q,  $J = 7.0$  Hz, 2H), 6.53-6.59 (m, 1H), 6.87 (masked t,  $J = 7.0$  Hz, 1H), 6.89 (d,  $J = 8.0$  Hz, 2H), 7.22-7.29 (m, 3H), 7.51 (s, 1H), 8.34 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.10, 32.07, 48.28, 60.89, 112.31, 113.29, 115.95, 120.13, 129.34, 144.62, 146.58, 147.67, 157.61, 172.64; Anal. calculated for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4$ : C, 63.56; H, 6.00; N, 9.27; found C, 63.45; H, 6.08; N, 9.23.

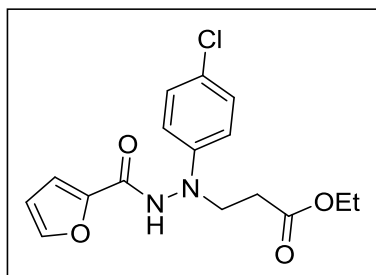
**Ethyl 3-(2-(4-chlorobenzoyl)-1-(4-chlorophenyl)hydrazinyl)propanoate (5j):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 116 mg (61%); Yellow solid; mp 110-112 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22 (t,  $J$  = 7.0 Hz, 3H), 2.71 (t,  $J$  = 6.0 Hz, 2H), 3.88 (t,  $J$  = 6.0 Hz, 2H), 4.10 (q,  $J$  = 7.0 Hz, 2H), 6.75 (d,  $J$  = 8.5 Hz, 2H), 7.18 (d,  $J$  = 8.5 Hz, 2H), 7.43 (d,  $J$  = 8.5 Hz, 2H), 7.81 (d,  $J$  = 8.0 Hz, 2H), 8.78 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.11, 32.06, 48.08, 61.14, 114.27, 124.82, 128.74, 129.10, 129.22, 130.68, 138.66, 146.12, 165.54, 173.06; Anal. calculated for  $\text{C}_{18}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_3$ : C, 57.71; H, 4.76; N, 7.35; found C, 57.03; H, 4.91; N, 7.42.

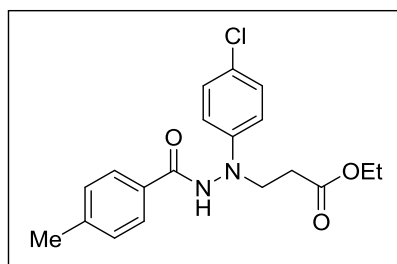
**Ethyl 3-(1-(4-chlorophenyl)-2-(furan-2-carbonyl)hydrazinyl)propanoate (5k):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 106 mg (63%); Orange solid; mp 78-81 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.21 (t,  $J$  = 7.0 Hz, 3H), 2.72 (t,  $J$  = 6.5 Hz, 2H), 3.90 (t,  $J$  = 6.5 Hz, 2H), 4.10 (q,  $J$  = 7.0 Hz, 2H), 6.50-6.59 (m, 1H), 6.81 (d,  $J$  = 9.0 Hz, 2H), 7.19 (d,  $J$  = 9.0 Hz, 2H), 7.23 (d,  $J$  = 3.0 Hz, 1H), 7.52 (s, 1H), 8.44 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.10, 32.04, 48.36, 60.97, 112.35, 114.47, 116.13, 124.95, 129.16, 144.75, 146.39, 146.41, 157.53, 172.49; Anal. calculated for  $\text{C}_{16}\text{H}_{17}\text{ClN}_2\text{O}_4$ : C, 57.06; H, 5.09; N, 8.32; found C, 57.12; H, 5.15; N, 8.26.

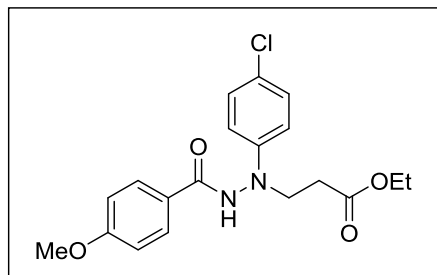
**Ethyl 3-(1-(4-chlorophenyl)-2-(4-methylbenzoyl)hydrazinyl)propanoate (5l):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 122 mg (67%); Light yellow solid; mp 154-157 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22 (t,  $J$  = 7.0 Hz, 3H), 2.43 (s, 3H), 2.73 (t,  $J$  = 6.0 Hz, 2H), 3.91 (t,  $J$  = 6.0 Hz, 2H), 4.10 (q,  $J$  = 7.0 Hz, 2H), 6.78 (d,  $J$  = 8.5 Hz, 2H), 7.18 (d,  $J$  = 9.0 Hz, 2H), 7.27 (d,  $J$  = 9.0 Hz, 2H), 7.77 (d,  $J$  = 8.0 Hz, 2H), 8.47 (bs, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.12, 21.58, 32.15, 48.07, 61.01, 114.22, 124.62, 127.25, 129.16, 129.45, 129.50, 142.94, 146.47, 166.42, 172.87; Anal. calculated for  $\text{C}_{19}\text{H}_{21}\text{ClN}_2\text{O}_3$ : C, 63.24; H, 5.87; N, 7.76; found C, 63.79; H, 5.96; N, 7.35.

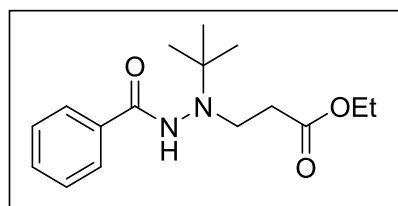
**Ethyl 3-(1-(4-chlorophenyl)-2-(4-methoxybenzoyl)hydrazinyl)propanoate (5m):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 126 mg (67%); White solid; mp 143-145 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.22 (t, *J* = 6.0 Hz, 3H), 2.73 (t, *J* = 6.0 Hz, 2H), 3.88 (s, 3H), 3.91 (t, *J* = 6.5 Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 8.42 (bs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.11, 32.19, 48.09, 55.48, 60.98, 114.05, 114.20, 124.55, 124.57, 129.14 (2 C's), 146.58, 162.86, 165.99, 172.88; Anal. calculated for C<sub>19</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>4</sub>: C, 60.56; H, 5.62; N, 7.43; found C, 60.61; H, 5.67; N, 7.24.

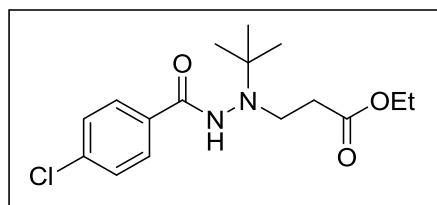
**Ethyl 3-(2-benzoyl-1-(tert-butyl)hydrazinyl)propanoate (5n):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 105 mg (72%); Light yellow solid; mp 105-108 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.13 (t, *J* = 7 Hz, 3H), 1.20 (s, 9H), 2.59 (t, *J* = 6.5 Hz, 2H), 3.11 (t, *J* = 6.5 Hz, 2H), 3.96 (q, *J* = 7.0 Hz, 2H), 6.63 (bs, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.03, 25.46, 33.14, 45.79, 58.73, 60.51, 126.97, 128.61, 131.55, 133.91, 166.93, 173.33; Anal. calculated for C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>: C, 65.73; H, 8.27; N, 9.58; found C, 65.63; H, 8.31; N, 9.52.

**Ethyl 3-(1-(tert-butyl)-2-(4-chlorobenzoyl)hydrazinyl)propanoate (5o):**

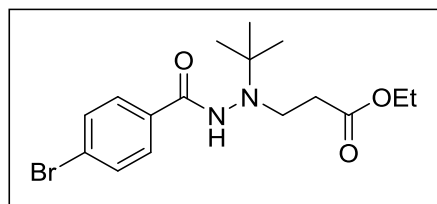


Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 123 mg (75% ); White solid; mp 115-117 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.13 (t, *J* = 7.0 Hz, 3H), 1.19 (s, 9H), 2.57 (t, *J* = 6.0 Hz, 2H), 3.11 (bs, 2H), 3.96 (q, *J* = 7.0 Hz, 2H ), 6.62 (d, *J* = 5.0 Hz, 1H), 7.40 (dd, *J* = 9.0 & 2.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.06,

25.44, 33.09, 45.64, 58.80, 60.61, 128.44, 128.88, 132.16, 137.86, 165.92, 173.44; Anal. calculated for  $C_{16}H_{23}ClN_2O_3$ : C, 58.80; H, 7.09; N, 8.57; found C, 58.85; H, 7.18; N, 8.40.

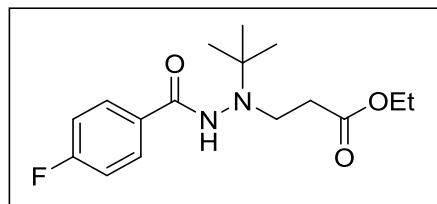
**Ethyl 3-(2-(4-bromobenzoyl)-1-(tert-butyl)hydrazinyl)propanoate (5p):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 111 mg (60% ); Light green solid; mp 112-115 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  1.13 (t,  $J$  = 7.0 Hz, 3H), 1.19 (s, 9H), 2.57 (t,  $J$  = 6.5 Hz, 2H), 3.11 (t,  $J$  = 6.0 Hz, 2H), 3.97 (q,  $J$  = 7.0 Hz, 2H), 6.64 (bs, 1H), 7.56 (d,  $J$  = 8.0 Hz, 2H), 7.61 (d,  $J$  = 8.0 Hz, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  14.07, 25.44, 33.07, 45.61, 58.81, 60.64, 126.28, 128.64, 131.85, 132.56, 166.08, 173.45; HRMS (ESI-TOF):  $m/z$   $[M + Na]^+$  calculated for  $C_{16}H_{23}BrN_2O_3Na$ : 393.0784; found: 393.0784.

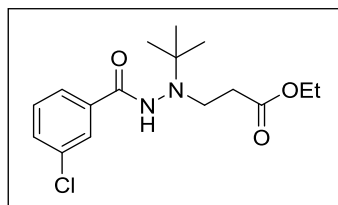
**Ethyl 3-(1-(tert-butyl)-2-(4-fluorobenzoyl)hydrazinyl)propanoate (5q):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 90 mg (58% ); White solid; mp 68-71 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  1.12 (t,  $J$  = 7.0 Hz, 3H), 1.18 (s, 9H), 2.57 (t,  $J$  = 6.5 Hz, 2H), 3.10 (bs, 2H), 3.94 (q,  $J$  = 7.0 Hz, 2H), 6.64 (bs, 1H), 7.09 (t,  $J$  = 8.5 Hz, 2H), 7.75 (dd,  $J$  = 8.0 & 5.5 Hz, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  14.05, 25.43, 33.07, 45.63, 58.78, 60.61, 115.68 (d,  $J_{C-F}$  = 22.0 Hz), 129.33 (d,  $J_{C-F}$  = 9.0 Hz), 129.90 (d,  $J_{C-F}$  = 3.0 Hz), 164.77 (d,  $J_{C-F}$  = 251.0 Hz), 165.96, 173.48; Anal. calculated for  $C_{16}H_{23}FN_2O_3$ : C, 61.92; H, 7.47; N, 9.03; found C, 61.85; H, 7.41; N, 9.08.

**Ethyl 3-(1-(tert-butyl)-2-(3-chlorobenzoyl)hydrazinyl)propanoate(5r):**



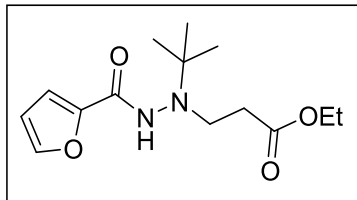
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 88 mg (54% ); White solid; mp 100-103 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  1.13 (t,  $J$  = 7.0 Hz, 3H), 1.18 (s, 9H), 2.56 (t,  $J$  = 6.5 Hz, 2H), 3.1 (bs, 2H), 3.96 (q,  $J$  = 7.0 Hz, 2H), 6.70 (bs, 1H), 7.35 (t,  $J$  = 8.0 Hz, 1H), 7.45 (d,  $J$  = 7.5 Hz, 1H), 7.58 (d,  $J$  = 8.0 Hz, 1H), 7.71 (s, 1H);  $^{13}C$  NMR (125 MHz,



CDCl<sub>3</sub>):  $\delta$  14.06, 25.44, 33.05, 45.61, 58.82, 60.67, 124.99, 127.41, 129.96, 131.65, 134.81, 135.56, 165.83, 173.41; Anal. calculated for C<sub>16</sub>H<sub>23</sub>ClN<sub>2</sub>O<sub>3</sub>: C, 58.80; H, 7.09; N, 8.57; found C, 59.39; H, 7.30; N, 8.22.

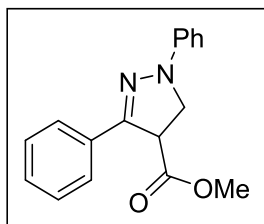
**Ethyl 3-(1-(tert-butyl)-2-(furan-2-carbonyl)hydrazinyl)propanoate (5s):**



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 47 mg (33% ); Red gum; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.13 (t,  $J$  = 7.0 Hz, 3H), 1.18 (s, 9H), 2.55 (t,  $J$  = 7.0 Hz, 2H), 3.09 (t,  $J$  = 6.5 Hz, 2H), 3.98 (q,  $J$  = 7.5 Hz, 2H ), 6.48-6.52 (m, 1H), 6.80 (bs, 1H), 7.14 (d,  $J$  = 3.0 Hz, 1H), 7.44 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  14.01, 25.32, 33.11, 46.03, 58.71, 60.51, 112.16, 115.21, 144.03, 146.95, 157.90, 173.10; HRMS (ESI-TOF):  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub>: 283.1652; found: 283.1654

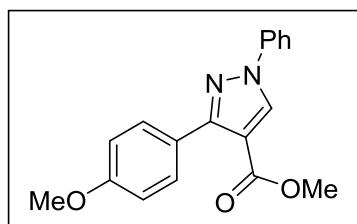
**Methyl 1,3-diphenyl-4,5-dihydro-1H-pyrazole-4-carboxylate (4):**



Purified by silica gel chromatography (EtOAc: petroleum ether, 1:9)

Yield: 70 mg (50%); Mustard solid; mp 96-99 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  3.72 (s, 3H), 4.04-4.12 (m, 1H), 4.35 (dd,  $J$  = 10.0 Hz & 6.0 Hz, 1H), 4.49 (dd,  $J$  = 12.5 Hz & 6.0 Hz, 1H), 6.91 (t,  $J$  = 7.5 Hz, 1H), 7.17 (d,  $J$  = 7.5 Hz, 2H), 7.30-7.37 (m, 3H), 7.40 (t,  $J$  = 8.0 Hz, 2H), 7.80 (d,  $J$  = 7.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  50.36, 52.81, 53.11, 113.19, 119.85, 125.93, 128.57, 128.65, 129.17, 131.86, 144.87, 144.99, 171.18; HRMS (ESI-TOF):  $m/z$  [M + H]<sup>+</sup> calculated for C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>: 281.1285; found: 281.1286.

**Methyl 3-(4-methoxyphenyl)-1-phenyl-1H-pyrazole-4-carboxylate (6):<sup>#</sup>**

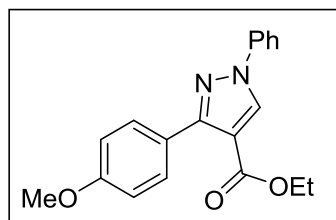


Purified by silica gel chromatography (EtOAc: petroleum ether, 1:9)

Yield: 20 mg (13%); Brown solid; mp 115-118 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.77 (s, 3H), 3.82 (s, 3H), 6.86 (d,  $J = 8.5$  Hz, 2H), 7.19-7.25 (m, 4H), 7.26-7.33 (m, 3H), 8.17 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  51.24, 55.22, 113.15, 113.59, 120.68, 125.37, 127.85, 128.87, 131.89, 139.38, 142.46, 145.53, 160.19, 163.51; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3$ : 309.1234; found: 309.1235.

<sup>#</sup>Formed alongside the benzohydrazide **3f**.

**Ethyl 3-(4-methoxyphenyl)-1-phenyl-1H-pyrazole-4-carboxylate (7a):<sup>#</sup>**

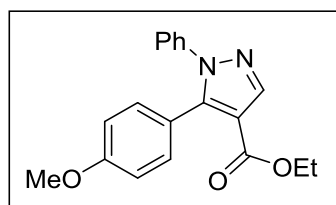


Purified by silica gel chromatography (EtOAc: petroleum ether, 1:9)

Yield: 19 mg (12%); Brown semi solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.27 (t,  $J = 7.0$  Hz, 3H), 3.81 (s, 3H), 4.24 (q,  $J = 7.0$  Hz, 2H), 6.86 (d,  $J = 9.0$  Hz, 2H), 7.19-7.25 (m, 4H), 7.25-7.33 (m, 3H), 8.17 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.26, 55.22, 60.04, 113.51, 113.54, 120.81, 125.36, 127.80, 128.86, 131.93, 139.41, 142.47, 145.38, 160.13, 163.10; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_3$ : 323.1390; found: 323.1389.

<sup>#</sup>Formed alongside the benzohydrazide **5f**.

**Ethyl 5-(4-methoxyphenyl)-1-phenyl-1H-pyrazole-4-carboxylate (7b):<sup>#</sup>**

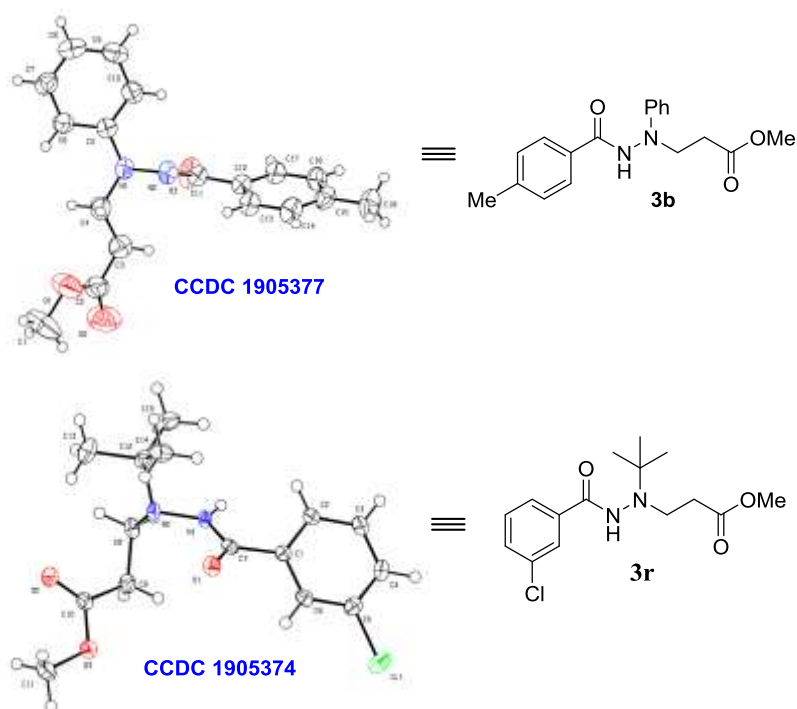


Purified by silica gel chromatography (EtOAc: petroleum ether, 1:9)

Yield: 24 mg (15%); Brown solid; mp 124-127 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.34 (t,  $J = 7.0$  Hz, 3H), 3.87 (s, 3H), 4.31 (q,  $J = 7.0$  Hz, 2H), 6.98 (d,  $J = 9.0$  Hz, 2H), 7.36 (t,  $J = 7.5$  Hz, 1H), 7.49 (t,  $J = 7.5$  Hz, 2H), 7.78 (d,  $J = 7.5$  Hz, 2H), 7.85 (d,  $J = 9.0$  Hz, 2H), 8.50 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.33, 55.31, 60.29, 113.36, 113.46, 119.49, 124.68, 127.37, 129.54, 130.73, 132.23, 139.34, 153.80, 160.09, 163.07; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_3$ : 323.1390; found: 323.1391.

<sup>#</sup>Formed alongside the benzohydrazide **5f**.

### X-ray crystal structures of 3b & 3r:



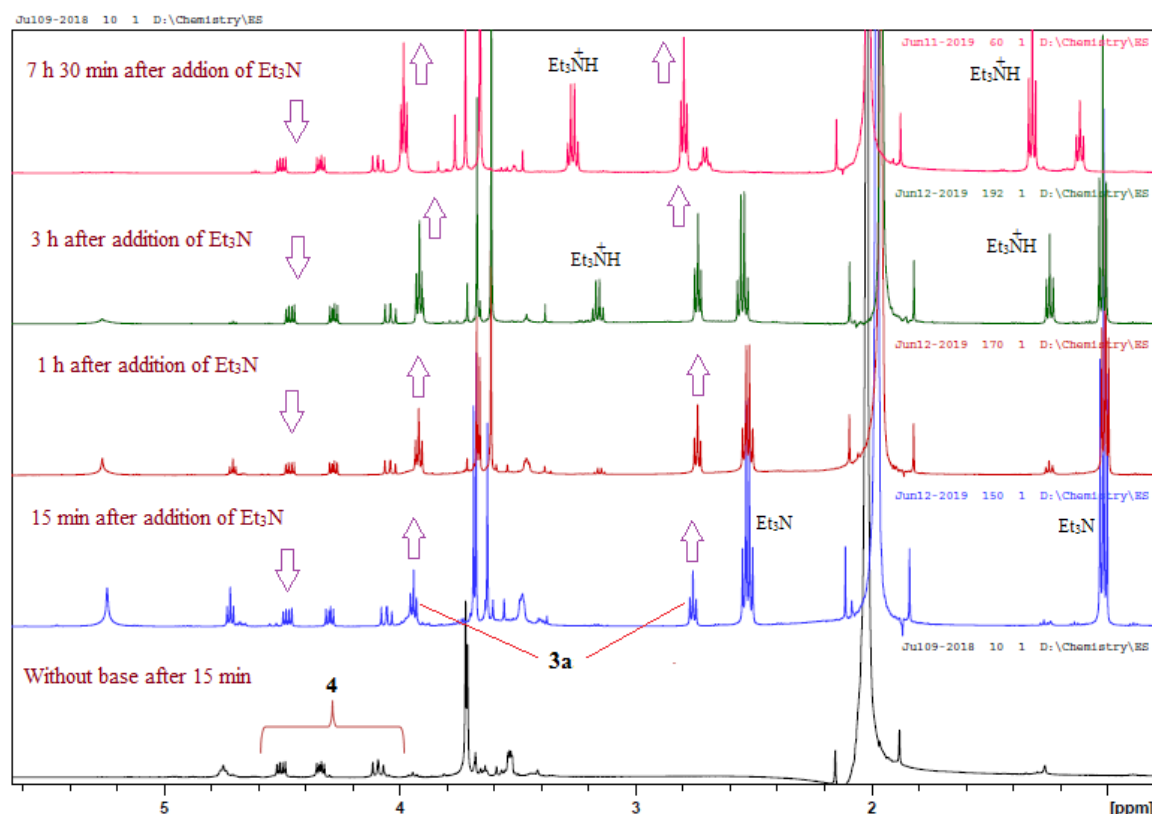
Crystal data and structure refinement for **3b** & **3r**

Compound	<b>3b</b>	<b>3r</b>
Identification code (CCDC Number)	1905377	1905374
Empirical formula	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	C <sub>15</sub> H <sub>21</sub> ClN <sub>2</sub> O <sub>3</sub>
Formula weight	312.36	312.79
Temperature/K	293.15	100
Crystal system	monoclinic	orthorhombic
Space group	P2 <sub>1</sub> /c	Pca21
a/Å	10.790(18)	15.994(12)
b/Å	17.43(3)	10.296(8)
c/Å	9.827(16)	9.623(7)
α/°	90	90
β/°	113.583(19)	90
γ/°	90	90
Volume/Å <sup>3</sup>	1694(5)	1585(2)
Z	4	4
ρ <sub>calc</sub> /mg/mm <sup>3</sup>	1.225	1.311
m/mm <sup>-1</sup>	0.084	0.252

F(000)	664	664
Crystal size/mm <sup>3</sup>	0.230 × 0.220 × 0.200	0.150 × 0.130 × 0.090
2θTheta range for data collection	4.118 to 49.994°	3.956 to 48.508°
Index ranges	-12 ≤ h ≤ 12, -20 ≤ k ≤ 20, -11 ≤ l ≤ 11	-18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -10 ≤ l ≤ 10
Reflections collected	26023	22252
Independent reflections	2980[R(int) = 0.0735]	2513[R(int) = 0.0707]
Data/restraints/parameters	2980/0/212	2513/1/194
Goodness-of-fit on F <sup>2</sup>	1.135	1.043
Final R indexes [I>2σ (I)]	R <sub>1</sub> = 0.0571, wR <sub>2</sub> = 0.1658	R <sub>1</sub> = 0.0275, wR <sub>2</sub> = 0.0675
Final R indexes [all data]	R <sub>1</sub> = 0.0775, wR <sub>2</sub> = 0.1781	R <sub>1</sub> = 0.0299, wR <sub>2</sub> = 0.0687
Largest diff. peak/hole / e Å <sup>-3</sup>	0.287/-0.315	0.120/-0.238

### Studies on the Reaction Mechanism:

<sup>1</sup>H NMR spectra recorded at various stages of the reaction of MBH ketone 1a with phenylhydrazine (2a)



### References:

1. Zhao, D.; Shi, Z.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, 52, 12426.
2. Frigerio, M.; Santagostina, M.; Sputore, S. *J. Org. Chem.* **1999**, 64, 4537.
3. Latorre, A.; Saez, J. A.; Rodríguez, S.; Gonzalez, V. F. *Tetrahedron Lett.* **2014**, 70, 97.
4. Santos, S. M.; Coelho, F. *RSC Adv.* **2012**, 2, 3237.



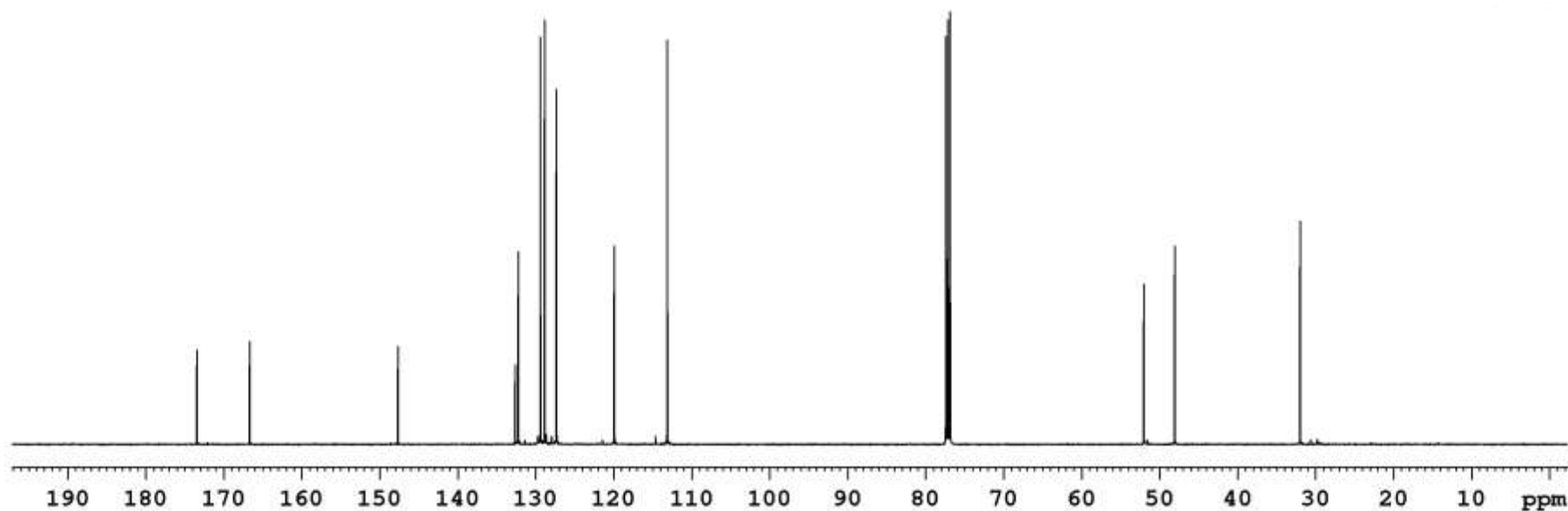
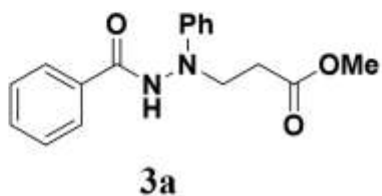
ES-AKJ-160, CDC13; 27 FEB 18

—173.415  
—166.625  
—147.623  
132.585  
132.192  
129.362  
128.806  
127.300  
—119.876  
—113.080

77.333  
77.078  
76.824

—51.970  
—48.014

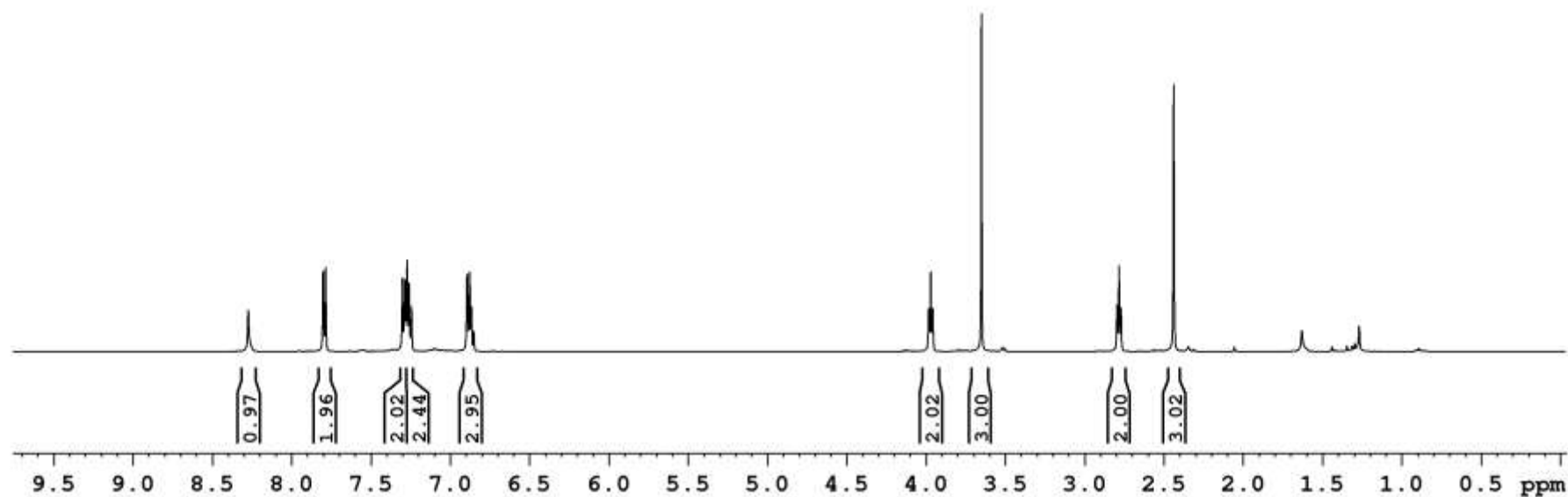
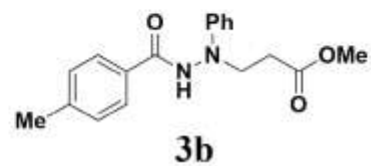
—31.930



=====

— 8.272  
7.800  
7.784  
7.299  
7.283  
7.274  
7.269  
7.258  
7.242  
6.892  
6.876  
6.864  
6.849

3.980  
3.967  
3.955  
3.647

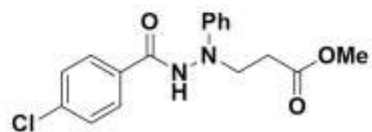
$$\begin{array}{r} 2.793 \\ 2.780 \\ 2.767 \\ \hline 2.435 \end{array}$$
[illegible]



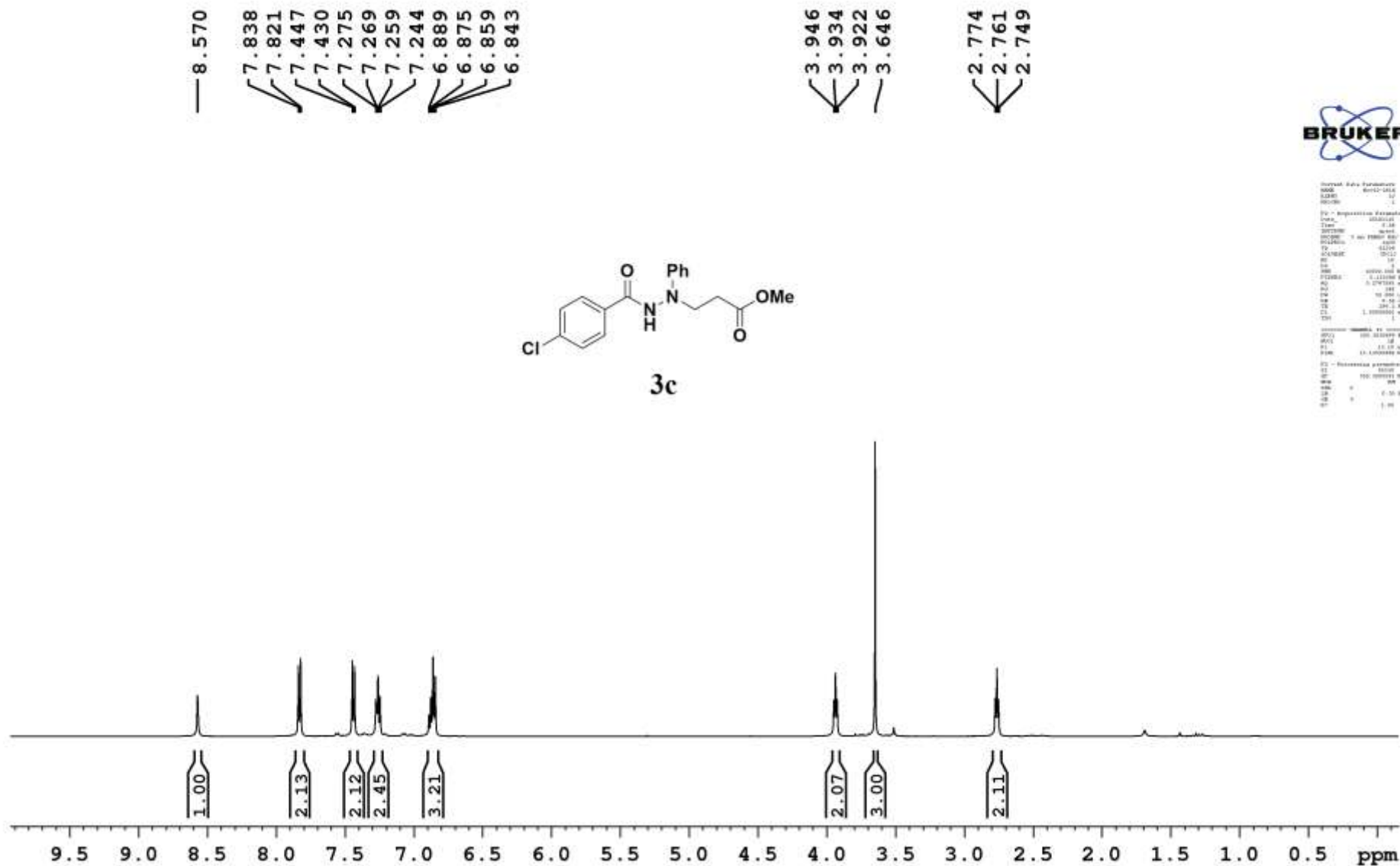




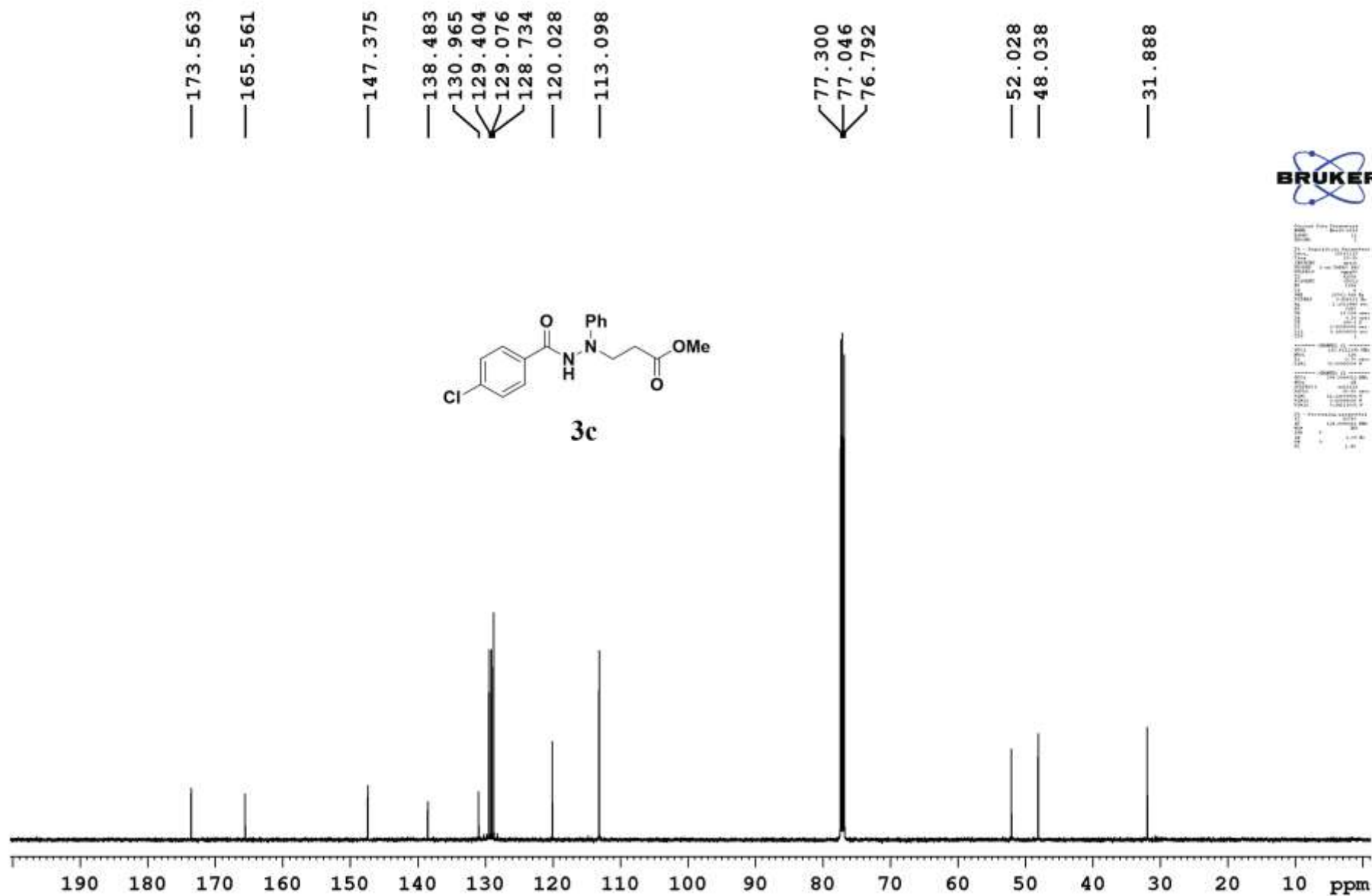
Current Data Parameters  
 NAME: 00112-1010  
 EXPNO: 1  
 F2 - Acquisition Parameters  
 Date\_ : 20181110  
 Time : 14.48  
 SFO500 : 500 MHz  
 PULPROG : zgpg30  
 TD : 65536  
 FIDRES : 0.10  
 AQ : 0.00010000  
 RG : 327.680  
 DQ : 0.00010000  
 PR : 1.00000000  
 DE : 1.00000000  
 TE : 300.2 K  
 D1 : 1.00000000  
 DELTA : 0.00000000  
 Acquisition Parameters  
 F1 : 500.136000 MHz  
 F2 : 125.760000 MHz  
 F3 : 125.760000 MHz  
 F4 : 125.760000 MHz  
 F5 : 125.760000 MHz  
 F6 : 125.760000 MHz  
 F7 : 125.760000 MHz  
 F8 : 125.760000 MHz  
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 F12 : 125.760000 MHz  
 F13 : 125.760000 MHz  
 F14 : 125.760000 MHz  
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 F98 : 125.760000 MHz  
 F99 : 125.760000 MHz  
 F100 : 125.760000 MHz



3c

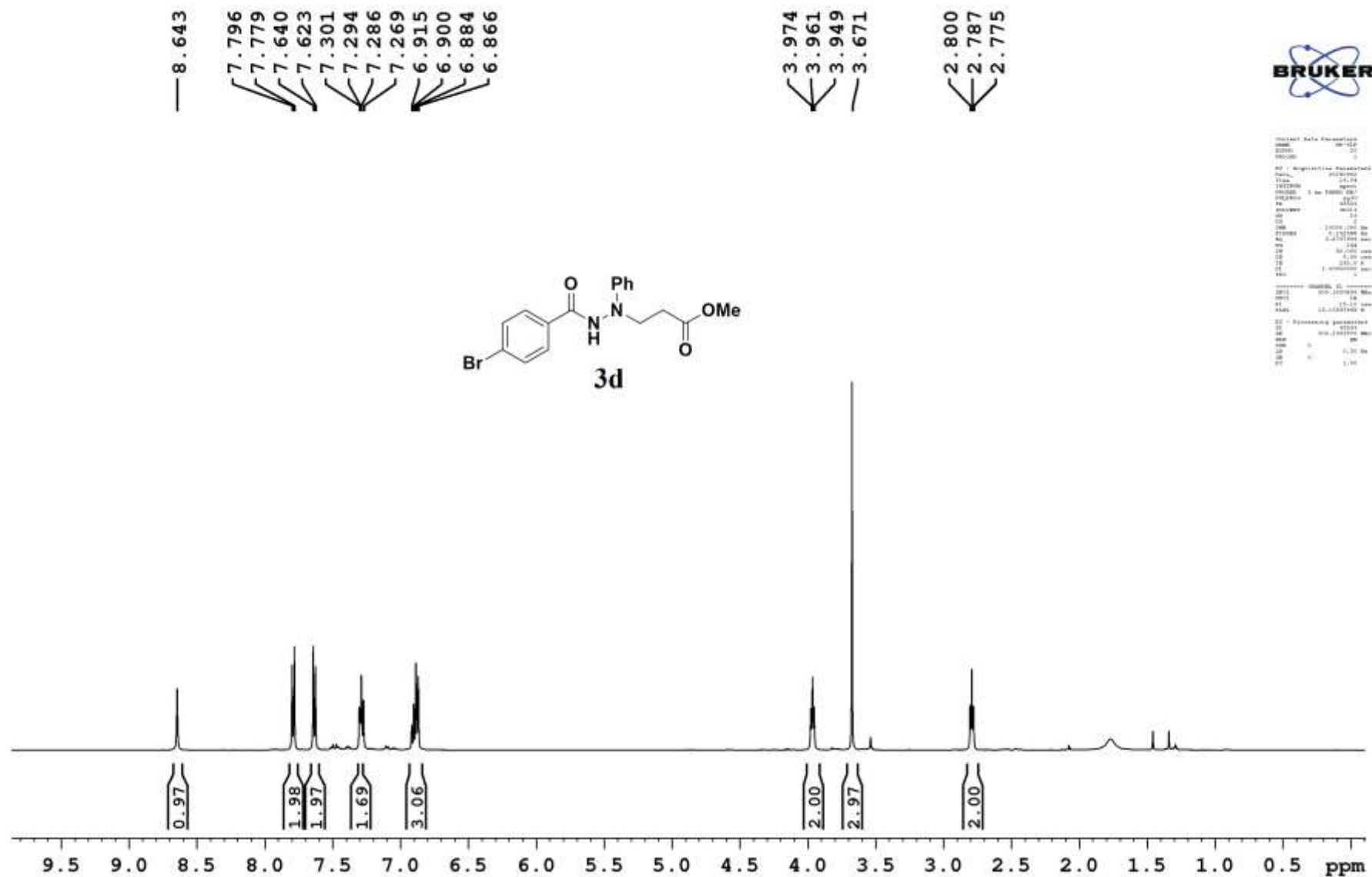


ES-AKJ-MC-50; 10/11/2018



Date: 10/11/2018  
 Time: 12:12:12  
 File: ES-AKJ-MC-50  
 Name: 3c  
 Solvent: CDCl3  
 Concentration: 100 mg/mL  
 Temperature: 25.00 °C  
 Frequency: 125.76 MHz  
 Acquisition: 1.00000000  
 Relaxation: 1.00000000  
 Decoupling: 1.00000000  
 Processing: 1.00000000  
 F2: 125.76 MHz  
 F1: 125.76 MHz  
 SFO: 125.76 MHz  
 AQ: 1.00000000  
 SI: 32768  
 SF: 125.76 MHz  
 AS: 32768  
 DS: 4  
 SC: 1.00000000  
 SD: 1.00000000  
 SN: 1.00000000  
 AR: 1.00000000  
 BR: 1.00000000  
 BU: 1.00000000  
 BV: 1.00000000  
 BW: 1.00000000  
 BX: 1.00000000  
 BY: 1.00000000  
 BZ: 1.00000000  
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 C2: 1.00000000  
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 C98: 1.00000000  
 C99: 1.00000000  
 C100: 1.00000000

ES-RK-EXP-61P, 1H, 02/09/18



Experiment: ES-RK-EXP-61P  
Date: 02/09/18  
Time: 14:14  
Operator: [Name]  
Sample: 3d  
Solvent: CDCl<sub>3</sub>  
Pulse: zgpg30  
Acq: 128  
F2: 400.136  
SFO: 100.628  
AQ: 1.00  
RG: 4096  
SD: 32768  
FID: 16384  
SI: 32768  
SF: 400.136  
WDW: EM  
SS: 0  
LB: 3.00  
GB: 0  
PC: 1.00  
SFO: 100.628  
AQ: 1.00  
RG: 4096  
SD: 32768  
FID: 16384  
SI: 32768  
SF: 400.136  
WDW: EM  
SS: 0  
LB: 3.00  
GB: 0  
PC: 1.00

ES-RK-EXP-61P, 13C, 02/09/18

—173.631

—165.700

—147.339

132.069

131.398

129.420

128.893

126.993

120.063

—113.109

77.307

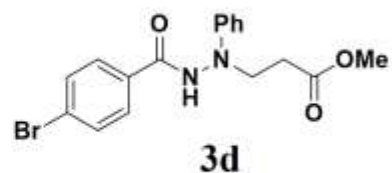
77.053

76.799

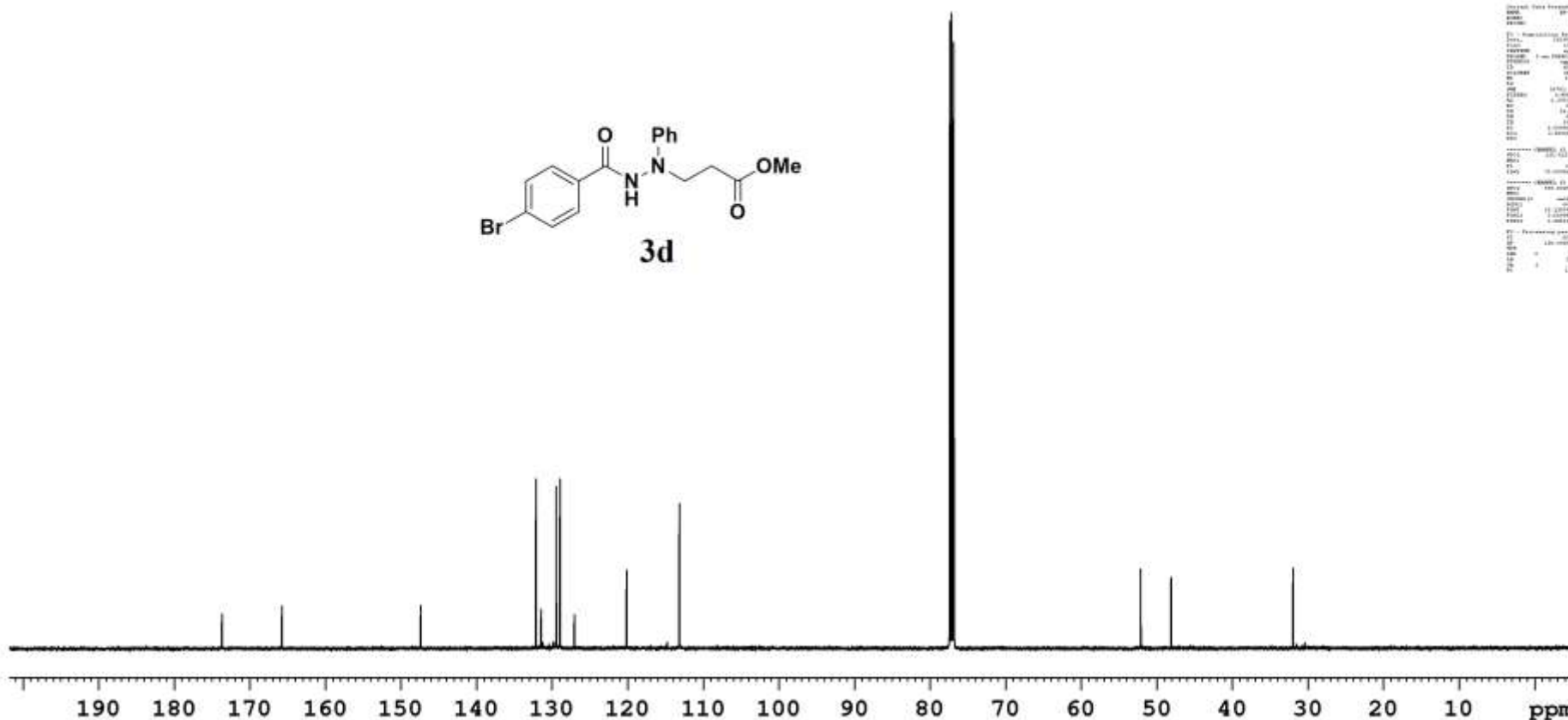
—52.067

—48.033

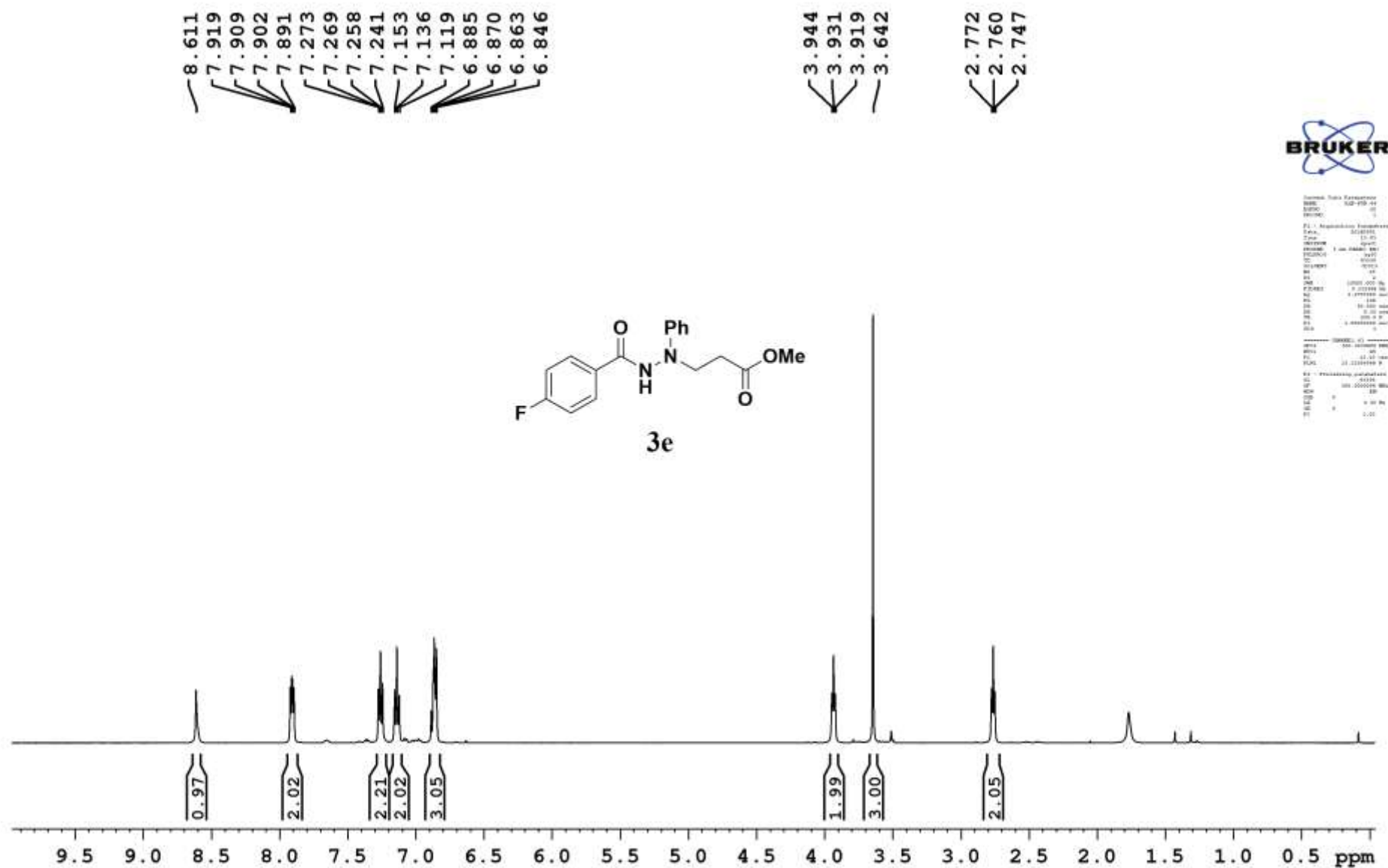
—31.888



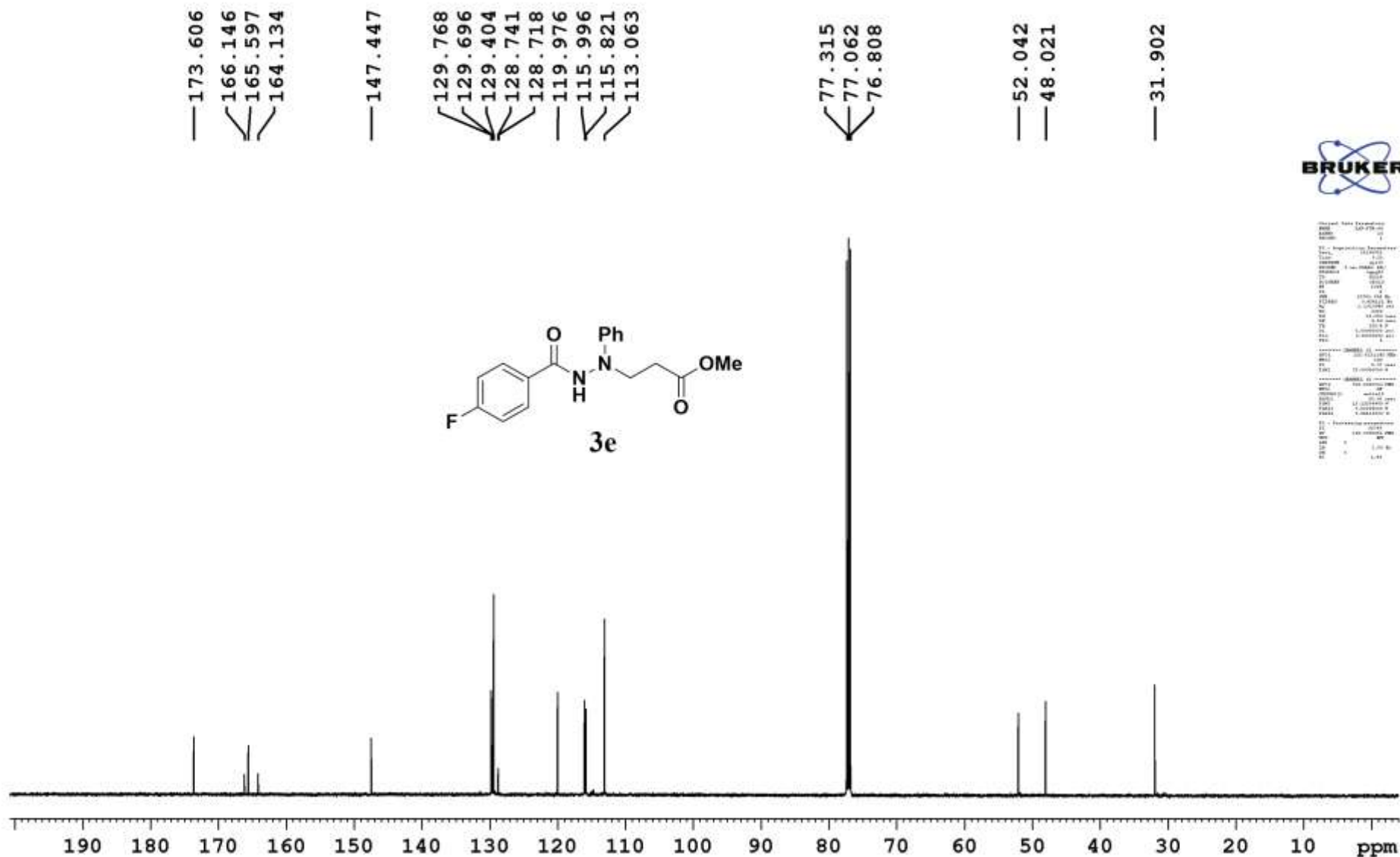
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 Size: 1.0 MB  
 Type: 13C NMR  
 Solvent: CDCl3  
 Temp: 25.0  
 Pres: 1.0  
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 F2: 125.76 MHz  
 F3: 125.76 MHz  
 F4: 125.76 MHz  
 F5: 125.76 MHz  
 F6: 125.76 MHz  
 F7: 125.76 MHz  
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 F96: 125.76 MHz  
 F97: 125.76 MHz  
 F98: 125.76 MHz  
 F99: 125.76 MHz  
 F100: 125.76 MHz



ES-RK-EXP-64P, 1H, CDCL3, 01/09/18



ES-RK-EXP-64, 13C, 02/09/18



Current Name: ES-RK-EXP-64  
 Date: 02/09/18  
 Time: 12:00:00  
 User: [illegible]  
 Instrument: spect  
 P1: 1.00  
 P2: 0.00  
 P3: 0.00  
 P4: 0.00  
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 P9: 0.00  
 P10: 0.00  
 P11: 0.00  
 P12: 0.00  
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 P16: 0.00  
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ES-RK-EXP-67P, 1H, 11/09/18

8.327  
7.904  
7.886  
7.301  
7.285  
7.269  
7.010  
6.993  
6.918  
6.902  
6.889  
6.875

4.001  
3.988  
3.976  
3.909  
3.678

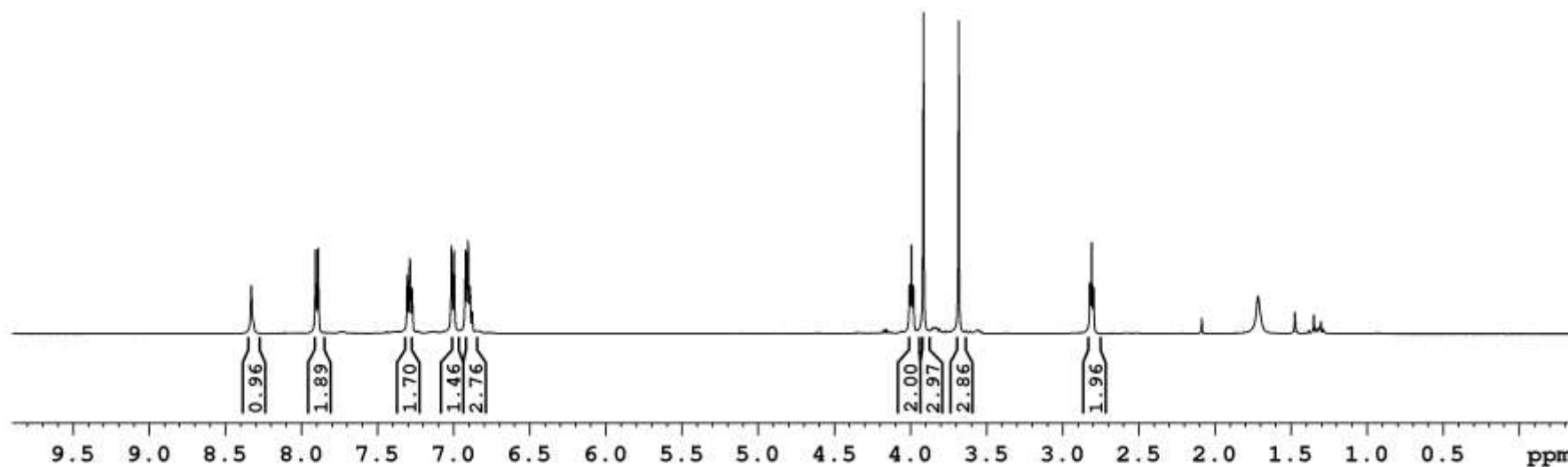
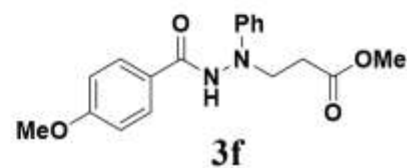
2.816  
2.804  
2.791



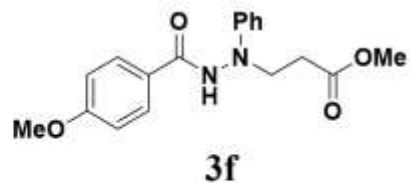
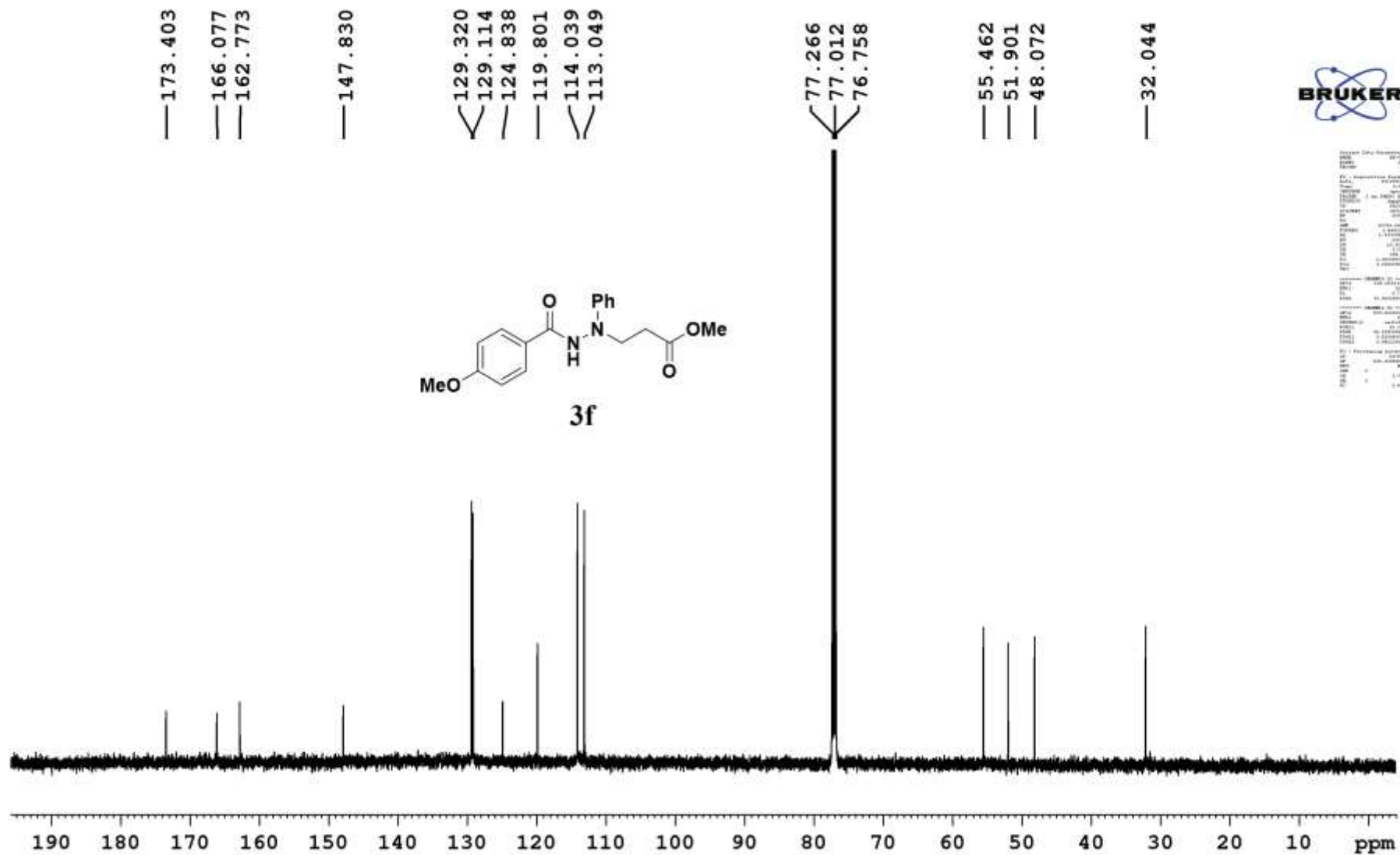
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Acquisition Parameters	
NAME	EXP001
TIME	11-12
DATE	11-12
PROBHD	5 mm HNPB
PROBHD	5 mm HNPB
NUC1	1H
NUC2	13C
NUC3	15N
NUC4	31P
NUC5	19F
NUC6	1H
NUC7	13C
NUC8	15N
NUC9	31P
NUC10	19F
NUC11	1H
NUC12	13C
NUC13	15N
NUC14	31P
NUC15	19F
NUC16	1H
NUC17	13C
NUC18	15N
NUC19	31P
NUC20	19F
NUC21	1H
NUC22	13C
NUC23	15N
NUC24	31P
NUC25	19F
NUC26	1H
NUC27	13C
NUC28	15N
NUC29	31P
NUC30	19F
NUC31	1H
NUC32	13C
NUC33	15N
NUC34	31P
NUC35	19F
NUC36	1H
NUC37	13C
NUC38	15N
NUC39	31P
NUC40	19F
NUC41	1H
NUC42	13C
NUC43	15N
NUC44	31P
NUC45	19F
NUC46	1H
NUC47	13C
NUC48	15N
NUC49	31P
NUC50	19F
NUC51	1H
NUC52	13C
NUC53	15N
NUC54	31P
NUC55	19F
NUC56	1H
NUC57	13C
NUC58	15N
NUC59	31P
NUC60	19F
NUC61	1H
NUC62	13C
NUC63	15N
NUC64	31P
NUC65	19F
NUC66	1H
NUC67	13C
NUC68	15N
NUC69	31P
NUC70	19F
NUC71	1H
NUC72	13C
NUC73	15N
NUC74	31P
NUC75	19F
NUC76	1H
NUC77	13C
NUC78	15N
NUC79	31P
NUC80	19F
NUC81	1H
NUC82	13C
NUC83	15N
NUC84	31P
NUC85	19F
NUC86	1H
NUC87	13C
NUC88	15N
NUC89	31P
NUC90	19F
NUC91	1H
NUC92	13C
NUC93	15N
NUC94	31P
NUC95	19F
NUC96	1H
NUC97	13C
NUC98	15N
NUC99	31P
NUC100	19F

=====



ES-RK-EXP-67P, 13C, CDCL3, 08/09/18

[illegible]



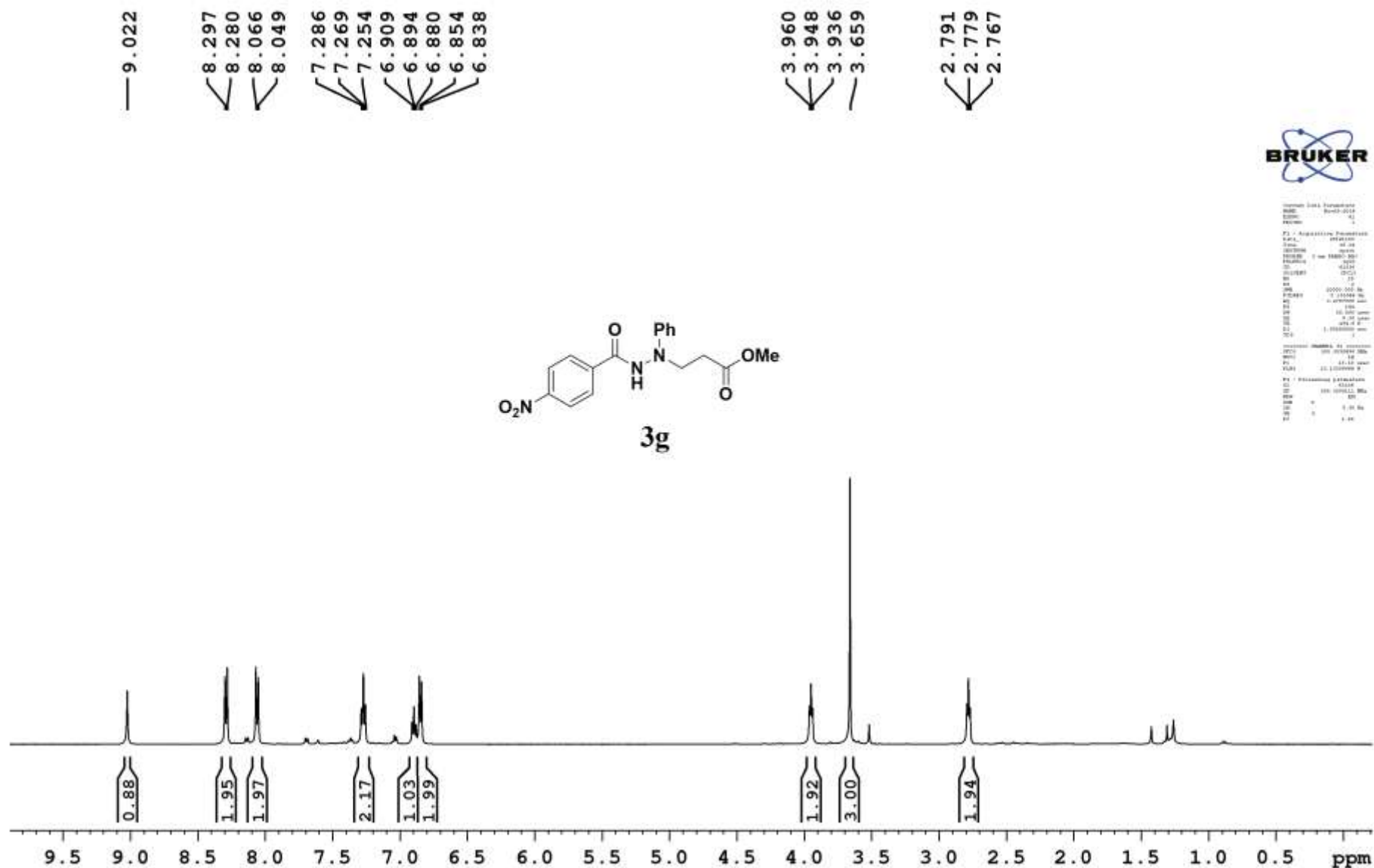
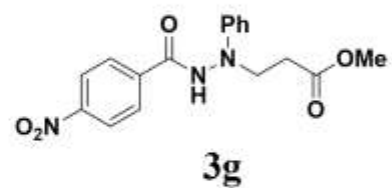
Version: 1.0.0  
Date: 2019-01-01  
Page: 1

Variable	Mean	SD	Min	Max
Age	34.5	10.2	21	55
Gender	0.5	0.5	0	1
Marital Status	0.6	0.5	0	1
Education	12.5	1.5	10	15
Income	3500	1500	1000	7000
Health	0.8	0.2	0	1
Smoking	0.3	0.5	0	1
Alcohol	0.2	0.4	0	1
Exercise	0.4	0.5	0	1
Stress	0.6	0.5	0	1
Depression	0.1	0.3	0	1
Loneliness	0.3	0.4	0	1
Life Satisfaction	0.7	0.2	0	1
Quality of Life	0.8	0.1	0	1

[illegible]

Material	Quantity	Unit
Steel	100	kg
Brass	50	kg
Aluminum	25	kg
Copper	10	kg
Iron	10	kg
Lead	5	kg
Gold	1	kg
Silver	1	kg
Platinum	1	kg
Palladium	1	kg
Rhodium	1	kg
Rosin	1	kg
Shellac	1	kg
Glue	1	kg
Paint	1	kg
Oil	1	kg
Wax	1	kg
Resin	1	kg
Acrylic	1	kg
Watercolor	1	kg
Charcoal	1	kg
Pencil	1	kg
Eraser	1	kg
Compass	1	kg
Protractor	1	kg
Scissors	1	kg
Knife	1	kg
Hammer	1	kg
Saw	1	kg
Drill	1	kg
Screwdriver	1	kg
Wrench	1	kg
Pliers	1	kg
File	1	kg
Sander	1	kg
Polisher	1	kg
Brush	1	kg
Roller	1	kg
Palette	1	kg
Mortar	1	kg
Plaster	1	kg
Concrete	1	kg
Brick	1	kg
Tile	1	kg
Stone	1	kg
Wood	1	kg
Glass	1	kg
Crystal	1	kg
Marble	1	kg
Granite	1	kg
Slate	1	kg
Shale	1	kg
Sandstone	1	kg
Limestone	1	kg
Dolomite	1	kg
Gypsum	1	kg
Plaster of Paris	1	kg
Putty	1	kg
Adhesive	1	kg
Sealant	1	kg
Grout	1	kg
Joint Compound	1	kg
Primer	1	kg
Sealer	1	kg
Finish	1	kg
Stain	1	kg
Paint	1	kg
Oil	1	kg
Wax	1	kg
Resin	1	kg
Acrylic	1	kg
Watercolor	1	kg
Charcoal	1	kg
Pencil	1	kg
Eraser	1	kg
Compass	1	kg
Protractor	1	kg
Scissors	1	kg
Knife	1	kg
Hammer	1	kg
Saw	1	kg
Drill	1	kg
Screwdriver	1	kg
Wrench	1	kg
Pliers	1	kg
File	1	kg
Sander	1	kg
Polisher	1	kg
Brush	1	kg
Roller	1	kg
Palette	1	kg
Mortar	1	kg
Plaster	1	kg
Concrete	1	kg
Brick	1	kg
Tile	1	kg
Stone	1	kg
Wood	1	kg
Glass	1	kg
Crystal	1	kg
Marble	1	kg
Granite	1	kg
Slate	1	kg
Shale	1	kg
Sandstone	1	kg
Limestone	1	kg
Dolomite	1	kg
Gypsum	1	kg
Plaster of Paris	1	kg
Putty	1	kg
Adhesive	1	kg
Sealant	1	kg
Grout	1	kg
Joint Compound	1	kg
Primer	1	kg
Sealer	1	kg
Finish	1	kg
Stain	1	kg
Paint	1	kg
Oil	1	kg
Wax	1	kg
Resin	1	kg
Acrylic	1	kg
Watercolor	1	kg
Charcoal	1	kg
Pencil	1	kg
Eraser	1	kg
Compass	1	kg
Protractor	1	kg
Scissors	1	kg
Knife	1	kg
Hammer	1	kg
Saw	1	kg
Drill	1	kg
Screwdriver	1	kg
Wrench	1	kg
Pliers	1	kg
File	1	kg
Sander	1	kg
Polisher	1	kg
Brush	1	kg
Roller	1</	

Year	Population	Population	Population
1970	1,000,000	1,000,000	1,000,000
1980	1,200,000	1,200,000	1,200,000
1990	1,400,000	1,400,000	1,400,000
2000	1,600,000	1,600,000	1,600,000
2010	1,800,000	1,800,000	1,800,000
2020	2,000,000	2,000,000	2,000,000



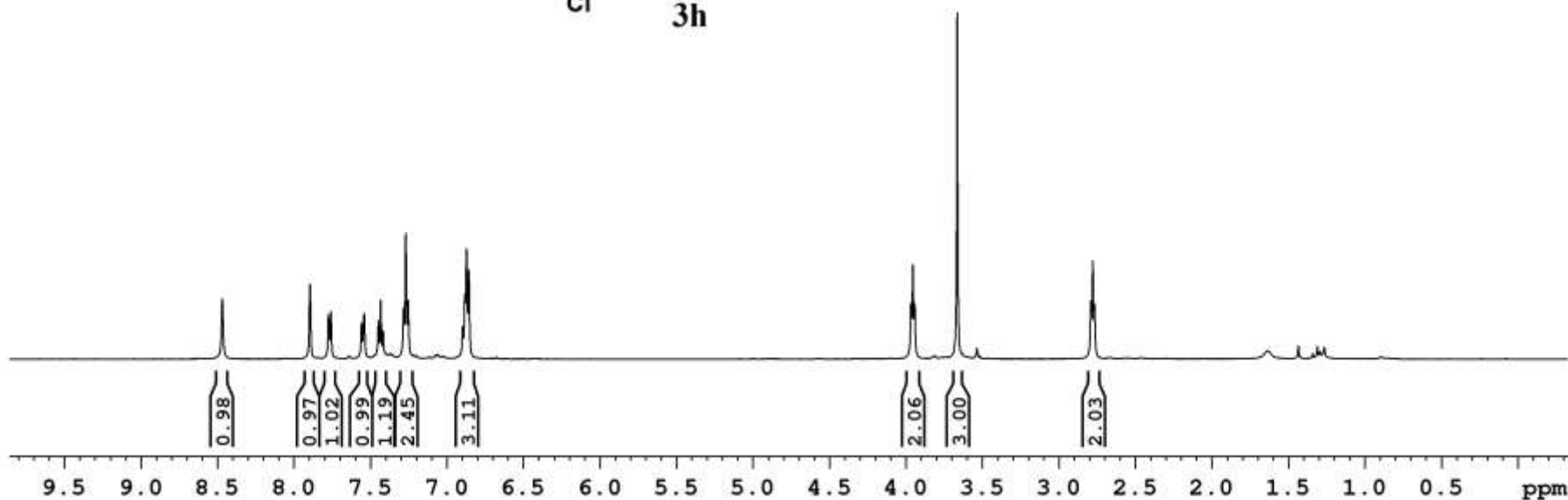
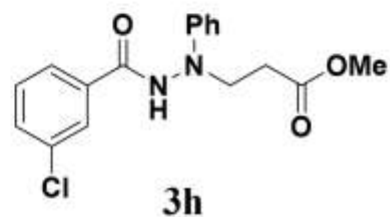


ES-AKJ-198-3; 09/11/2018

8.469  
7.895  
7.774  
7.759  
7.557  
7.541  
7.448  
7.432  
7.417  
7.284  
7.269  
7.253  
6.897  
6.883  
6.872  
6.856

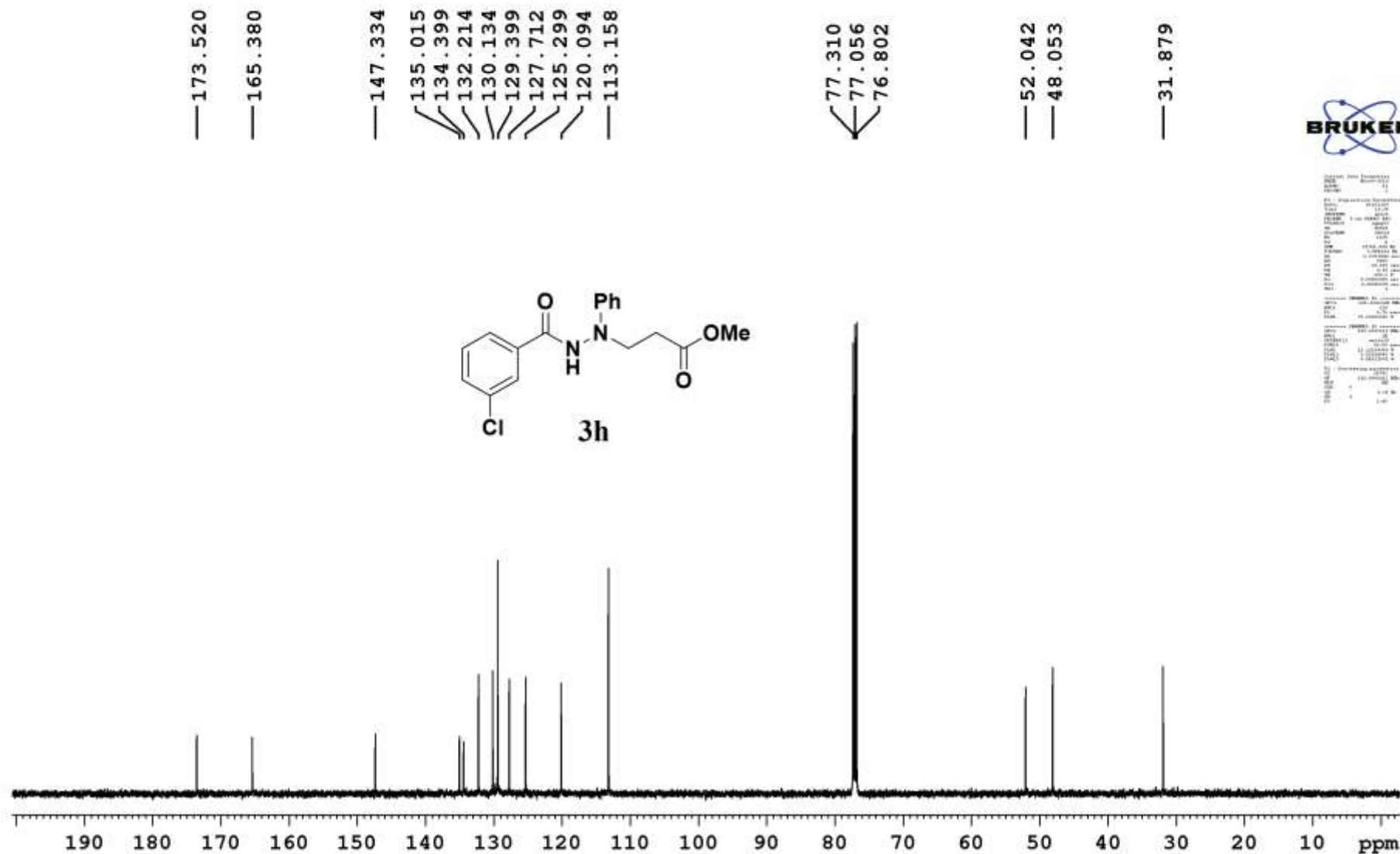
3.966  
3.954  
3.942  
3.663

2.790  
2.777  
2.765



Sample: ES-AKJ-198-3  
Date: 09/11/2018  
Time: 14:10:10  
Operator: [illegible]  
Acq: 1D  
P1: 1.00  
PC: 1.00  
PD: 0.00  
PE: 0.00  
PF: 0.00  
PG: 0.00  
PH: 0.00  
PI: 0.00  
PJ: 0.00  
PK: 0.00  
PL: 0.00  
PM: 0.00  
PN: 0.00  
PO: 0.00  
PP: 0.00  
PQ: 0.00  
PR: 0.00  
PS: 0.00  
PT: 0.00  
PU: 0.00  
PV: 0.00  
PW: 0.00  
PX: 0.00  
PY: 0.00  
PZ: 0.00  
Q1: 0.00  
Q2: 0.00  
Q3: 0.00  
Q4: 0.00  
Q5: 0.00  
Q6: 0.00  
Q7: 0.00  
Q8: 0.00  
Q9: 0.00  
Q0: 0.00  
R1: 0.00  
R2: 0.00  
R3: 0.00  
R4: 0.00  
R5: 0.00  
R6: 0.00  
R7: 0.00  
R8: 0.00  
R9: 0.00  
S1: 0.00  
S2: 0.00  
S3: 0.00  
S4: 0.00  
S5: 0.00  
S6: 0.00  
S7: 0.00  
S8: 0.00  
S9: 0.00  
T1: 0.00  
T2: 0.00  
T3: 0.00  
T4: 0.00  
T5: 0.00  
T6: 0.00  
T7: 0.00  
T8: 0.00  
T9: 0.00  
U1: 0.00  
U2: 0.00  
U3: 0.00  
U4: 0.00  
U5: 0.00  
U6: 0.00  
U7: 0.00  
U8: 0.00  
U9: 0.00  
V1: 0.00  
V2: 0.00  
V3: 0.00  
V4: 0.00  
V5: 0.00  
V6: 0.00  
V7: 0.00  
V8: 0.00  
V9: 0.00  
W1: 0.00  
W2: 0.00  
W3: 0.00  
W4: 0.00  
W5: 0.00  
W6: 0.00  
W7: 0.00  
W8: 0.00  
W9: 0.00  
X1: 0.00  
X2: 0.00  
X3: 0.00  
X4: 0.00  
X5: 0.00  
X6: 0.00  
X7: 0.00  
X8: 0.00  
X9: 0.00  
Y1: 0.00  
Y2: 0.00  
Y3: 0.00  
Y4: 0.00  
Y5: 0.00  
Y6: 0.00  
Y7: 0.00  
Y8: 0.00  
Y9: 0.00  
Z1: 0.00  
Z2: 0.00  
Z3: 0.00  
Z4: 0.00  
Z5: 0.00  
Z6: 0.00  
Z7: 0.00  
Z8: 0.00  
Z9: 0.00

ES-AKJ-198-3; 09/11/2018

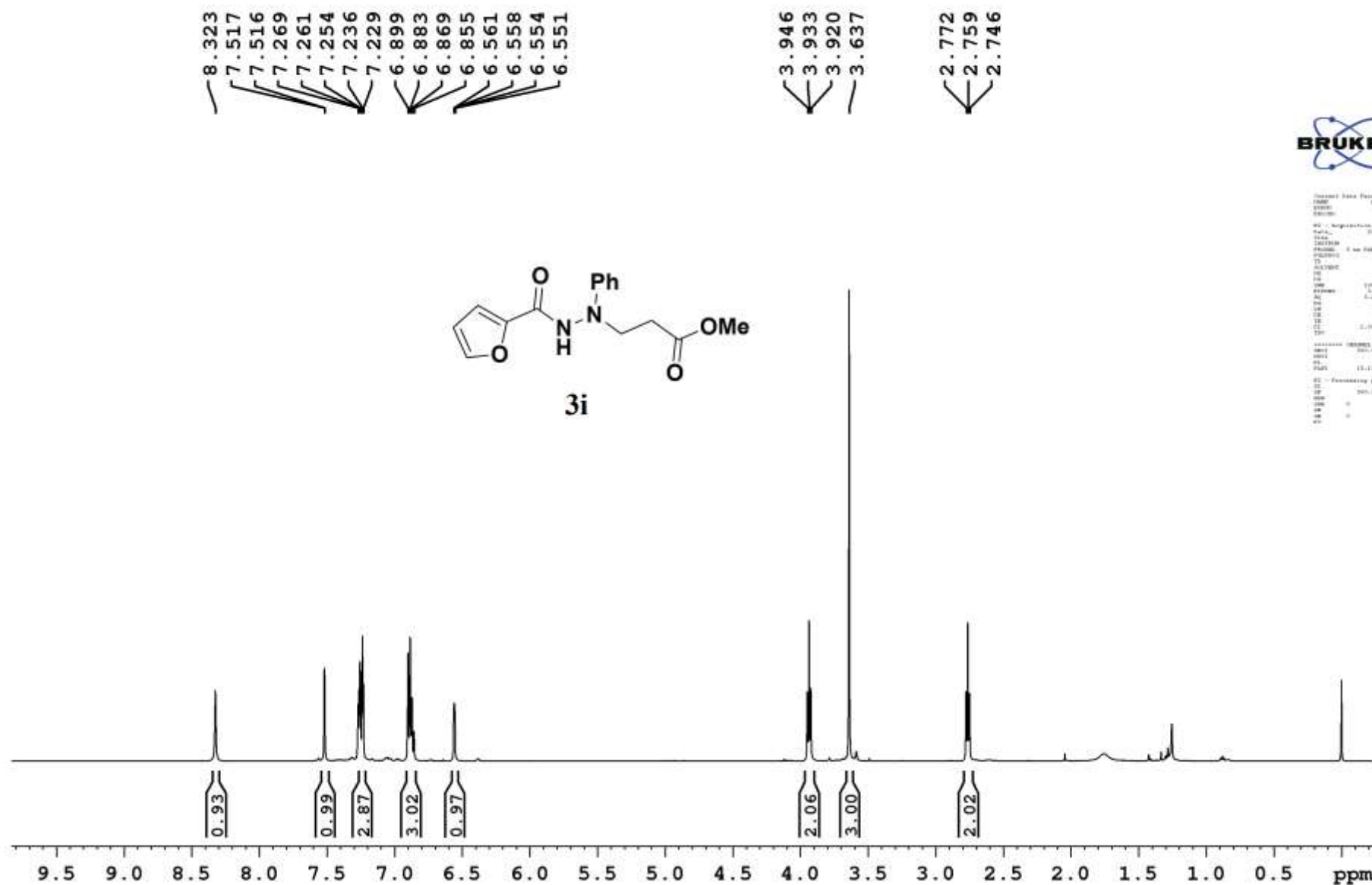
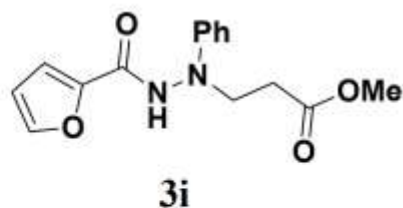


Date: 09/11/2018  
 Time: 11:11  
 File: 3h  
 Name: 3h  
 Solvent: CDCl3  
 Concentration: 100 mg/mL  
 Volume: 0.5 mL  
 Temperature: 25.0°C  
 P1: 12.00  
 P2: 12.00  
 P3: 12.00  
 P4: 12.00  
 P5: 12.00  
 P6: 12.00  
 P7: 12.00  
 P8: 12.00  
 P9: 12.00  
 P10: 12.00  
 P11: 12.00  
 P12: 12.00  
 P13: 12.00  
 P14: 12.00  
 P15: 12.00  
 P16: 12.00  
 P17: 12.00  
 P18: 12.00  
 P19: 12.00  
 P20: 12.00  
 P21: 12.00  
 P22: 12.00  
 P23: 12.00  
 P24: 12.00  
 P25: 12.00  
 P26: 12.00  
 P27: 12.00  
 P28: 12.00  
 P29: 12.00  
 P30: 12.00  
 P31: 12.00  
 P32: 12.00  
 P33: 12.00  
 P34: 12.00  
 P35: 12.00  
 P36: 12.00  
 P37: 12.00  
 P38: 12.00  
 P39: 12.00  
 P40: 12.00  
 P41: 12.00  
 P42: 12.00  
 P43: 12.00  
 P44: 12.00  
 P45: 12.00  
 P46: 12.00  
 P47: 12.00  
 P48: 12.00  
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 P91: 12.00  
 P92: 12.00  
 P93: 12.00  
 P94: 12.00  
 P95: 12.00  
 P96: 12.00  
 P97: 12.00  
 P98: 12.00  
 P99: 12.00  
 P100: 12.00

ES-AKJ-230; 23/08/2018



Name: 3i  
 Date: 23/08/2018  
 Time: 13:20  
 Location: 300 MHz  
 Solvent: CDCl<sub>3</sub>  
 Concentration: 10 mg/mL  
 Acquisition: 1D  
 Processing: 1D  
 Reference: TMS  
 Scale: 1.0000000  
 Gain: 1.0000000  
 Offset: 0.0000000  
 Phase: 0.0000000  
 F2 - Processing parameters  
 Name: 3i  
 Date: 23/08/2018  
 Time: 13:20  
 Location: 300 MHz  
 Solvent: CDCl<sub>3</sub>  
 Concentration: 10 mg/mL  
 Acquisition: 1D  
 Processing: 1D  
 Reference: TMS  
 Scale: 1.0000000  
 Gain: 1.0000000  
 Offset: 0.0000000  
 Phase: 0.0000000





ES-RK-EXP-72P; 30/10/2018

8.663

7.833

7.817

7.461

7.445

7.269

7.204

7.186

6.772

6.755

3.917

3.905

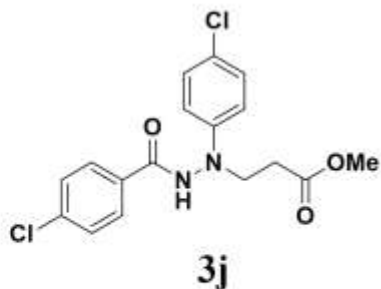
3.893

3.660

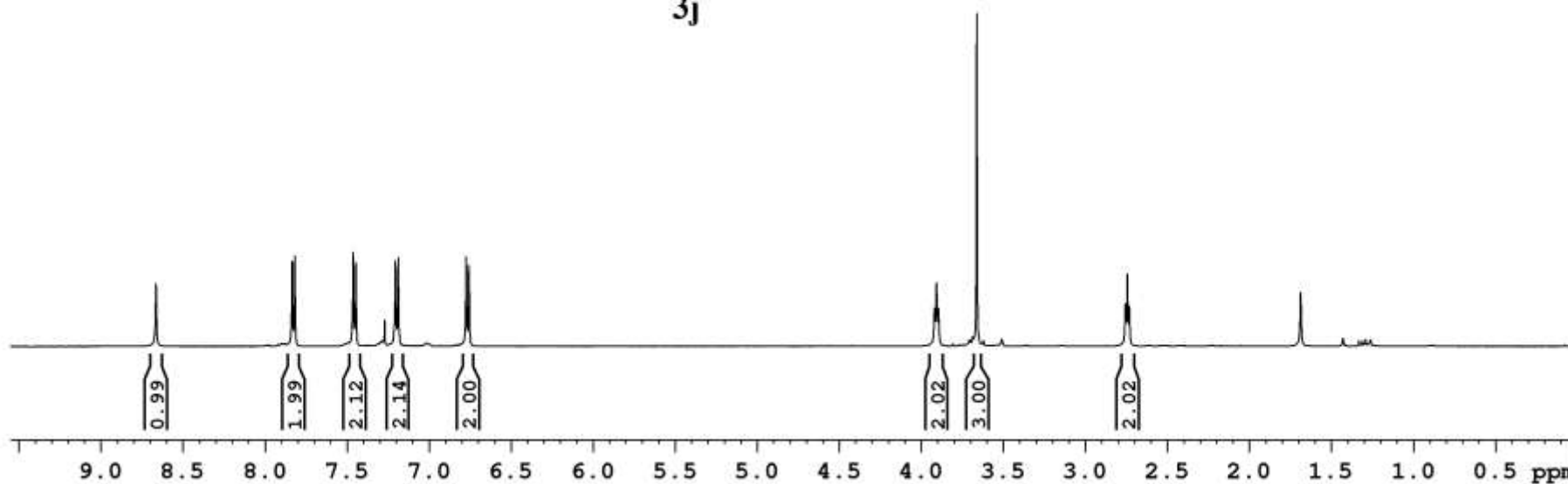
2.754

2.742

2.730

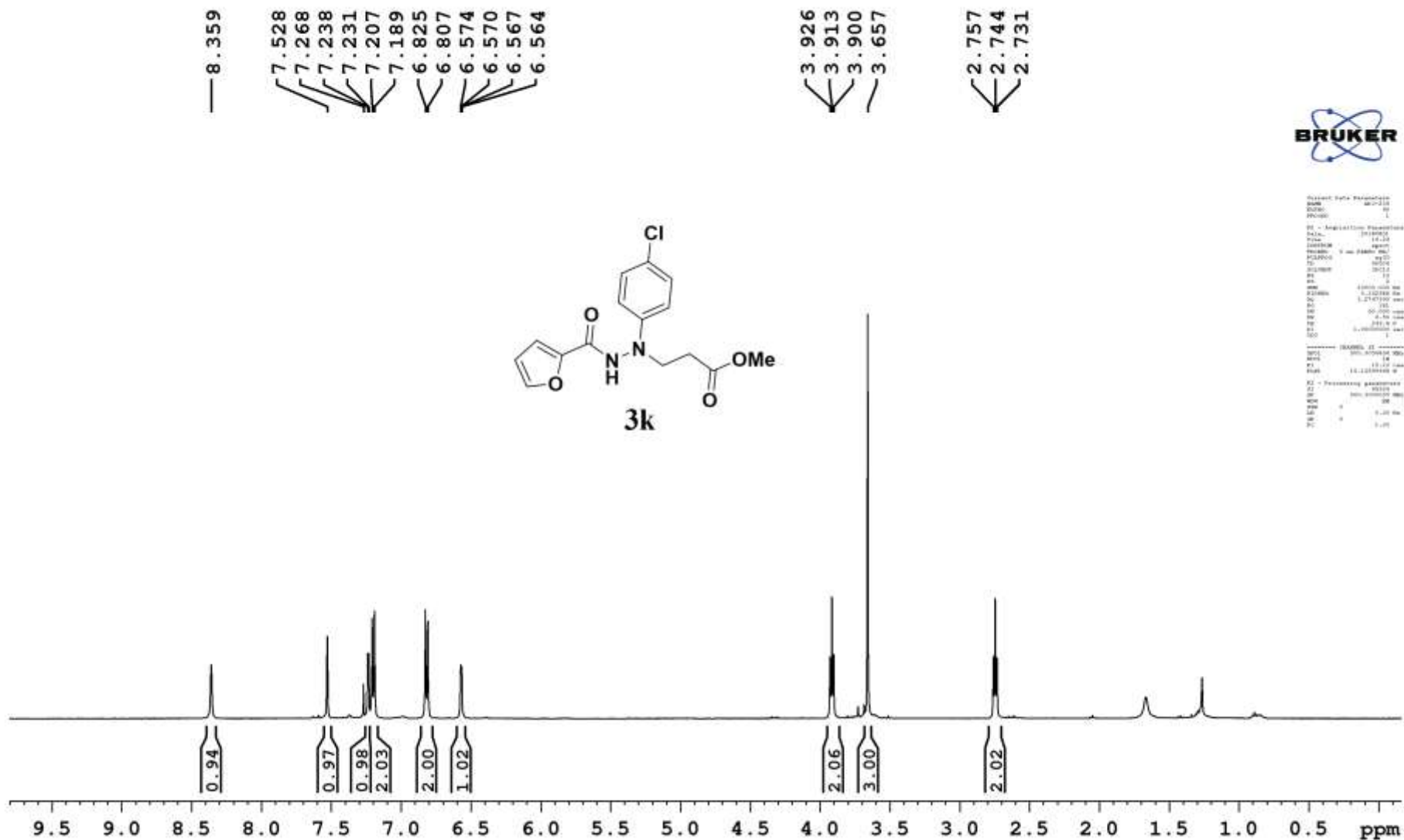


Current Data Acquisition  
NAME: 30-10-2018  
EXPNO: 1  
PROCNO: 1  
F2 - Acquisition Parameters  
Date\_ : 20181030  
Time : 12.15  
INSTRUM : spect  
PROBHD : 5 mm QNP 1H/13  
PULPROG : zgpg30  
TD : 65536  
SOLVENT : DMSO  
AQ : 0.10000000  
RG : 327.5  
DWDW : 1.00000000  
FIDRES : 0.00000000  
AQRES : 0.00000000  
F2 - Processing parameters  
SI : 32768  
SF : 400.1464000  
WDW : EM  
SSB : 0  
GB : 0  
PC : 1.0488000  
MC : 1.0000000  
LB : 0.3000000  
GB : 0  
PC : 1.0488000



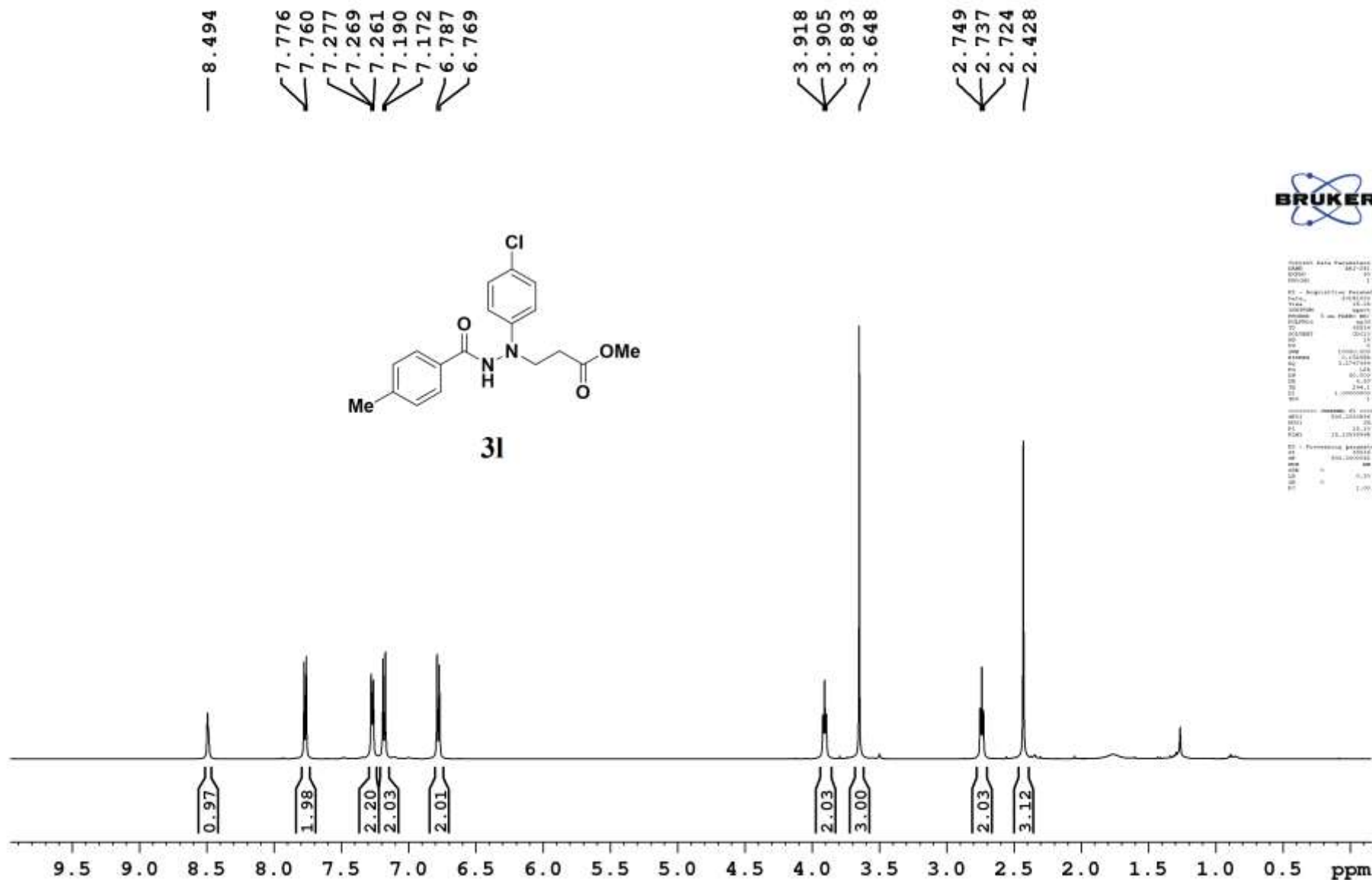




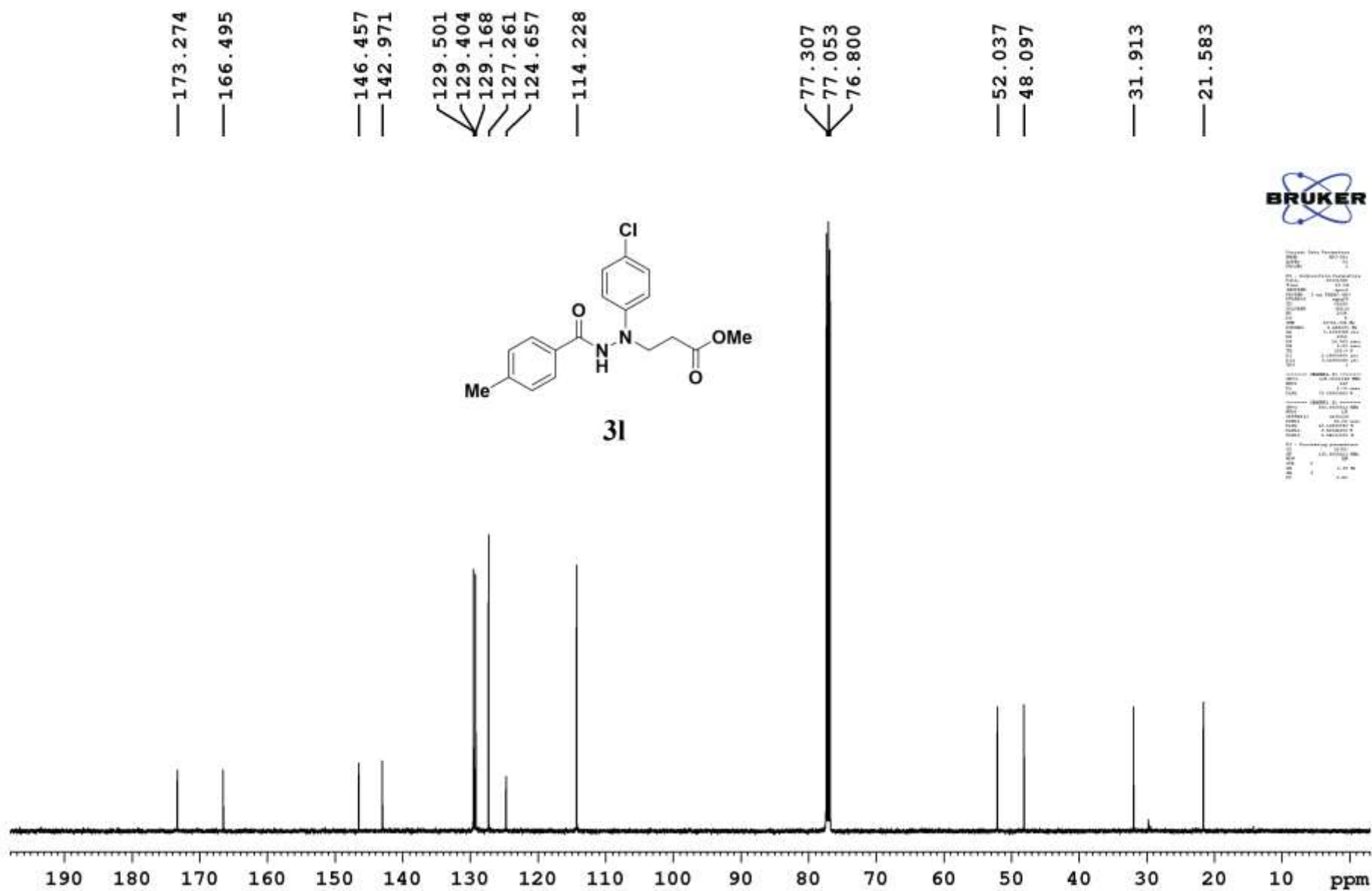




ES-AKJ-241; 30/10/2018



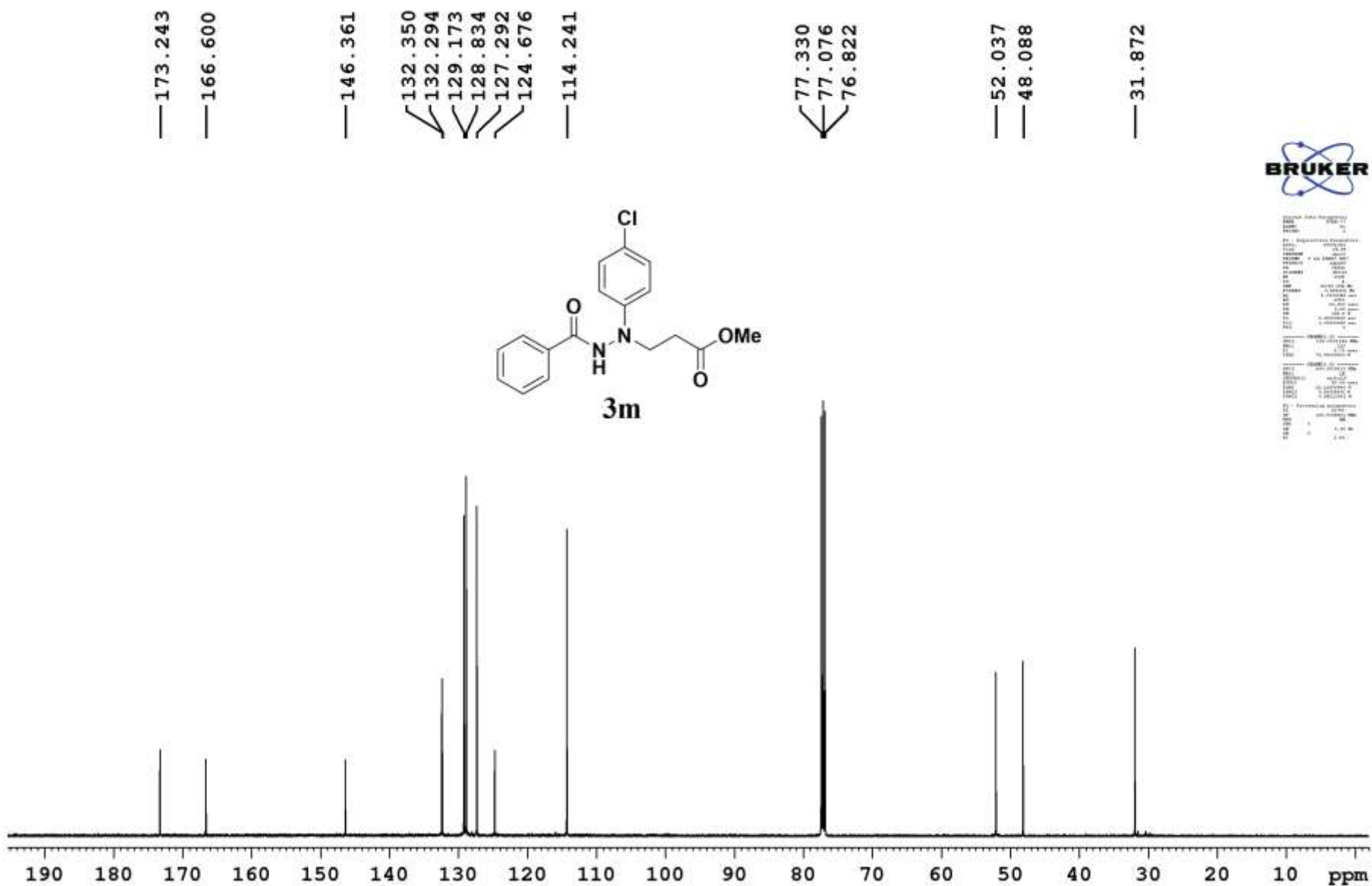
ES-AKJ-241; 30/10/2018



Sample Name: ES-AKJ-241  
 Date: 30/10/2018  
 Time: 14:00  
 Operator: [Name]  
 Instrument: Bruker Avance 400  
 P1: 12.00  
 PC: 1.00  
 PR: 1.00  
 PS: 1.00  
 PU: 1.00  
 PV: 1.00  
 PW: 1.00  
 PX: 1.00  
 PY: 1.00  
 PZ: 1.00  
 Q1: 1.00  
 Q2: 1.00  
 Q3: 1.00  
 Q4: 1.00  
 Q5: 1.00  
 Q6: 1.00  
 Q7: 1.00  
 Q8: 1.00  
 Q9: 1.00  
 Q10: 1.00  
 Q11: 1.00  
 Q12: 1.00  
 Q13: 1.00  
 Q14: 1.00  
 Q15: 1.00  
 Q16: 1.00  
 Q17: 1.00  
 Q18: 1.00  
 Q19: 1.00  
 Q20: 1.00  
 Q21: 1.00  
 Q22: 1.00  
 Q23: 1.00  
 Q24: 1.00  
 Q25: 1.00  
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 Q45: 1.00  
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 Q47: 1.00  
 Q48: 1.00  
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 Q50: 1.00  
 Q51: 1.00  
 Q52: 1.00  
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 Q54: 1.00  
 Q55: 1.00  
 Q56: 1.00  
 Q57: 1.00  
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 Q61: 1.00  
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 Q82: 1.00  
 Q83: 1.00  
 Q84: 1.00  
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 Q93: 1.00  
 Q94: 1.00  
 Q95: 1.00  
 Q96: 1.00  
 Q97: 1.00  
 Q98: 1.00  
 Q99: 1.00  
 Q100: 1.00



ES-RK-EXP-77P; 31/10/2018



ES-MC-58-3; 27/04/2018









ES-AKJ-MC-55; 24/04/2018

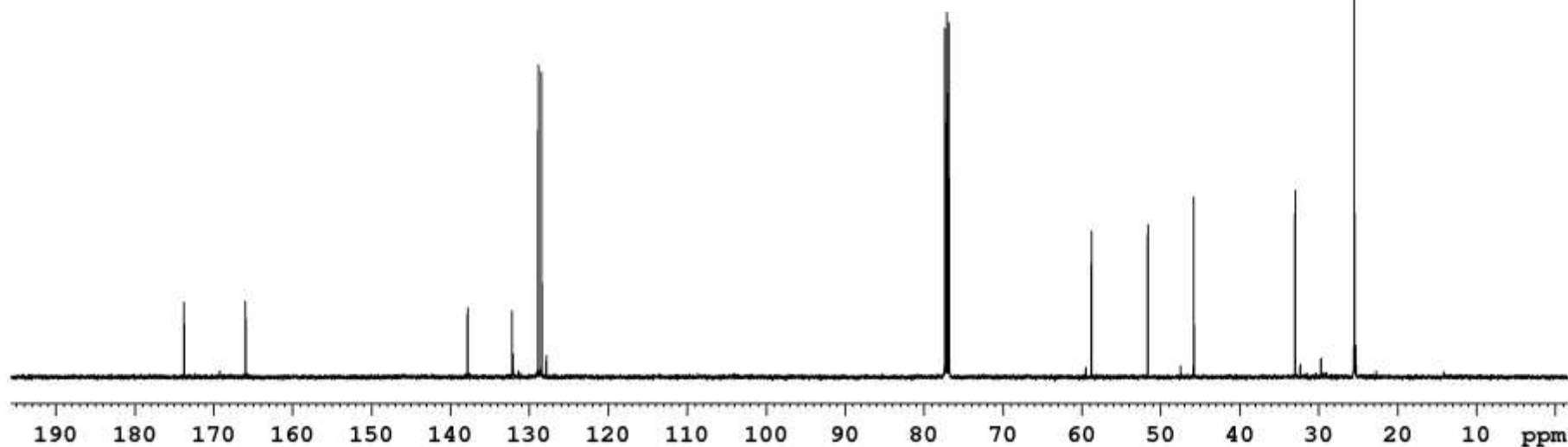
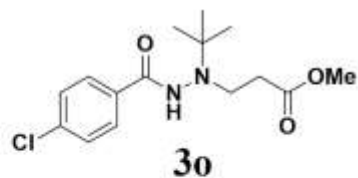
—173.743  
—165.951

—137.810  
—132.173  
—128.853  
—128.441

77.308  
77.054  
76.801

—58.745  
—51.620  
—45.792

—32.948  
—25.454



13C NMR (CDCl<sub>3</sub>)  
173.743, 165.951, 137.810, 132.173, 128.853, 128.441, 77.308, 77.054, 76.801, 58.745, 51.620, 45.792, 32.948, 25.454

ES-RK-EXP-60P, 1H, CDCL3, 31/08/18

7.613  
7.596  
7.565  
7.548  
7.269

6.638

3.508

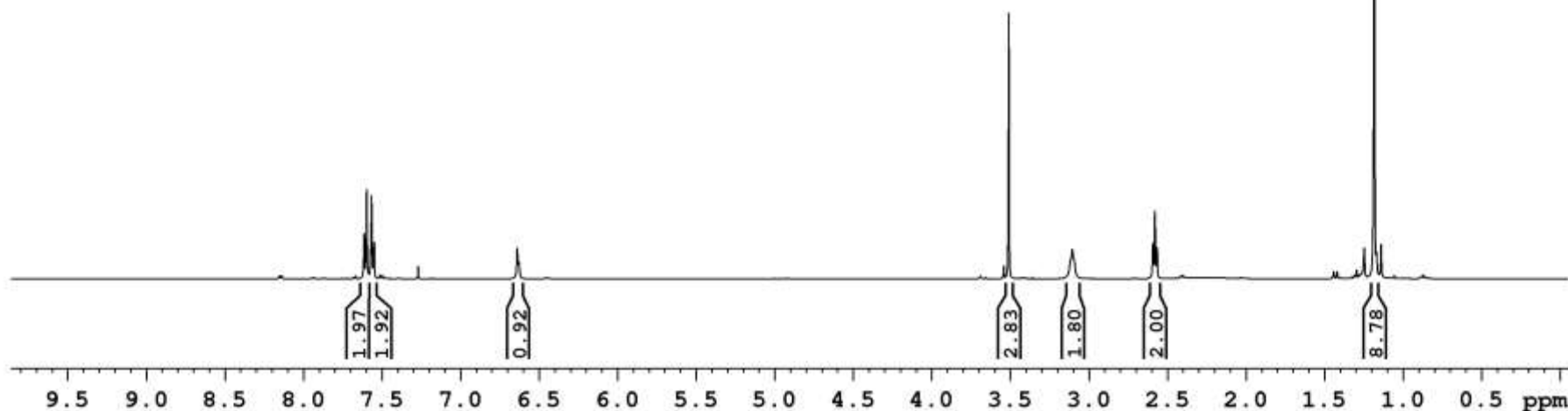
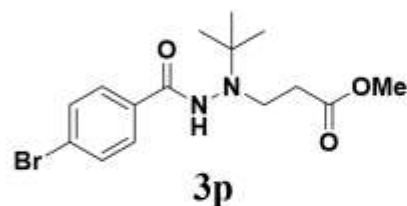
3.104

2.590  
2.577  
2.564

1.181



Experiment: 1H-EXP-60P  
Date: 31/08/18  
Time: 10:00  
Operator: [Name]  
Sample: [Name]  
Solvent: CDCl3  
P1: 12.00  
PC: 0.00  
PD: 0.00  
PE: 0.00  
PF: 0.00  
PG: 0.00  
PH: 0.00  
PI: 0.00  
PJ: 0.00  
PK: 0.00  
PL: 0.00  
PM: 0.00  
PN: 0.00  
PO: 0.00  
PP: 0.00  
PQ: 0.00  
PR: 0.00  
PS: 0.00  
PT: 0.00  
PU: 0.00  
PV: 0.00  
PW: 0.00  
PX: 0.00  
PY: 0.00  
PZ: 0.00  
Q1: 0.00  
Q2: 0.00  
Q3: 0.00  
Q4: 0.00  
Q5: 0.00  
Q6: 0.00  
Q7: 0.00  
Q8: 0.00  
Q9: 0.00  
Q0: 0.00  
R1: 0.00  
R2: 0.00  
R3: 0.00  
R4: 0.00  
R5: 0.00  
R6: 0.00  
R7: 0.00  
R8: 0.00  
R9: 0.00  
R0: 0.00  
S1: 0.00  
S2: 0.00  
S3: 0.00  
S4: 0.00  
S5: 0.00  
S6: 0.00  
S7: 0.00  
S8: 0.00  
S9: 0.00  
S0: 0.00  
T1: 0.00  
T2: 0.00  
T3: 0.00  
T4: 0.00  
T5: 0.00  
T6: 0.00  
T7: 0.00  
T8: 0.00  
T9: 0.00  
T0: 0.00  
U1: 0.00  
U2: 0.00  
U3: 0.00  
U4: 0.00  
U5: 0.00  
U6: 0.00  
U7: 0.00  
U8: 0.00  
U9: 0.00  
U0: 0.00  
V1: 0.00  
V2: 0.00  
V3: 0.00  
V4: 0.00  
V5: 0.00  
V6: 0.00  
V7: 0.00  
V8: 0.00  
V9: 0.00  
V0: 0.00  
W1: 0.00  
W2: 0.00  
W3: 0.00  
W4: 0.00  
W5: 0.00  
W6: 0.00  
W7: 0.00  
W8: 0.00  
W9: 0.00  
W0: 0.00  
X1: 0.00  
X2: 0.00  
X3: 0.00  
X4: 0.00  
X5: 0.00  
X6: 0.00  
X7: 0.00  
X8: 0.00  
X9: 0.00  
X0: 0.00  
Y1: 0.00  
Y2: 0.00  
Y3: 0.00  
Y4: 0.00  
Y5: 0.00  
Y6: 0.00  
Y7: 0.00  
Y8: 0.00  
Y9: 0.00  
Y0: 0.00  
Z1: 0.00  
Z2: 0.00  
Z3: 0.00  
Z4: 0.00  
Z5: 0.00  
Z6: 0.00  
Z7: 0.00  
Z8: 0.00  
Z9: 0.00  
Z0: 0.00



ES-RK-EXP-60P, 1H, CDCL3, 31/08/18

— 173.808

— 166.078

— 132.583

— 131.867

— 128.612

— 126.273

— 77.295

— 77.041

— 76.787

— 58.780

— 51.669

— 45.786

— 32.930

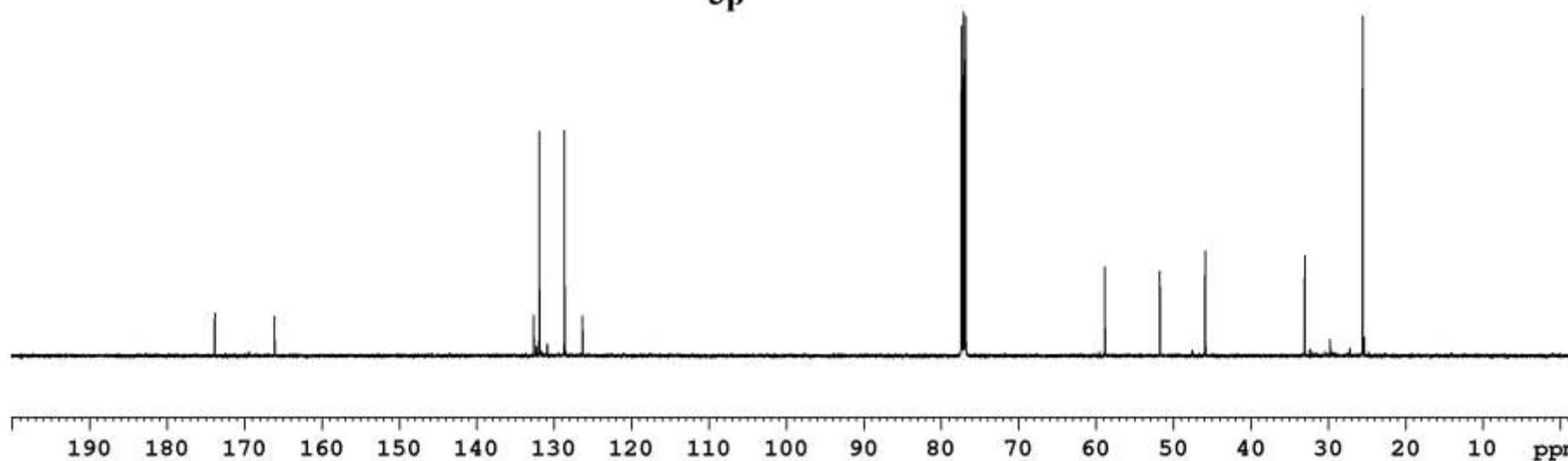
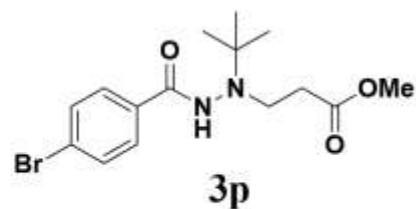
— 25.441



```

=====
NAME: ES-RK-EXP-60P
EXPNO: 1
PROCNO: 1
PROCNAME: 1
F2: 100.626150
AQ: 0.020000
RG: 327.680
SI: 327.680
SF: 100.626150
WDW: EM
SSB: 0
GB: 0
PC: 1.00
SCA: 0.000000
MC: 0.000000
DC: 0.000000
B0: 0.000000
B1: 0.000000
B2: 0.000000
B3: 0.000000
B4: 0.000000
B5: 0.000000
B6: 0.000000
B7: 0.000000
B8: 0.000000
B9: 0.000000
B10: 0.000000
B11: 0.000000
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B14: 0.000000
B15: 0.000000
B16: 0.000000
B17: 0.000000
B18: 0.000000
B19: 0.000000
B20: 0.000000
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B22: 0.000000
B23: 0.000000
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B45: 0.000000
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B50: 0.000000
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B69: 0.000000
B70: 0.000000
B71: 0.000000
B72: 0.000000
B73: 0.000000
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B77: 0.000000
B78: 0.000000
B79: 0.000000
B80: 0.000000
B81: 0.000000
B82: 0.000000
B83: 0.000000
B84: 0.000000
B85: 0.000000
B86: 0.000000
B87: 0.000000
B88: 0.000000
B89: 0.000000
B90: 0.000000
B91: 0.000000
B92: 0.000000
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B99: 0.000000
=====

```

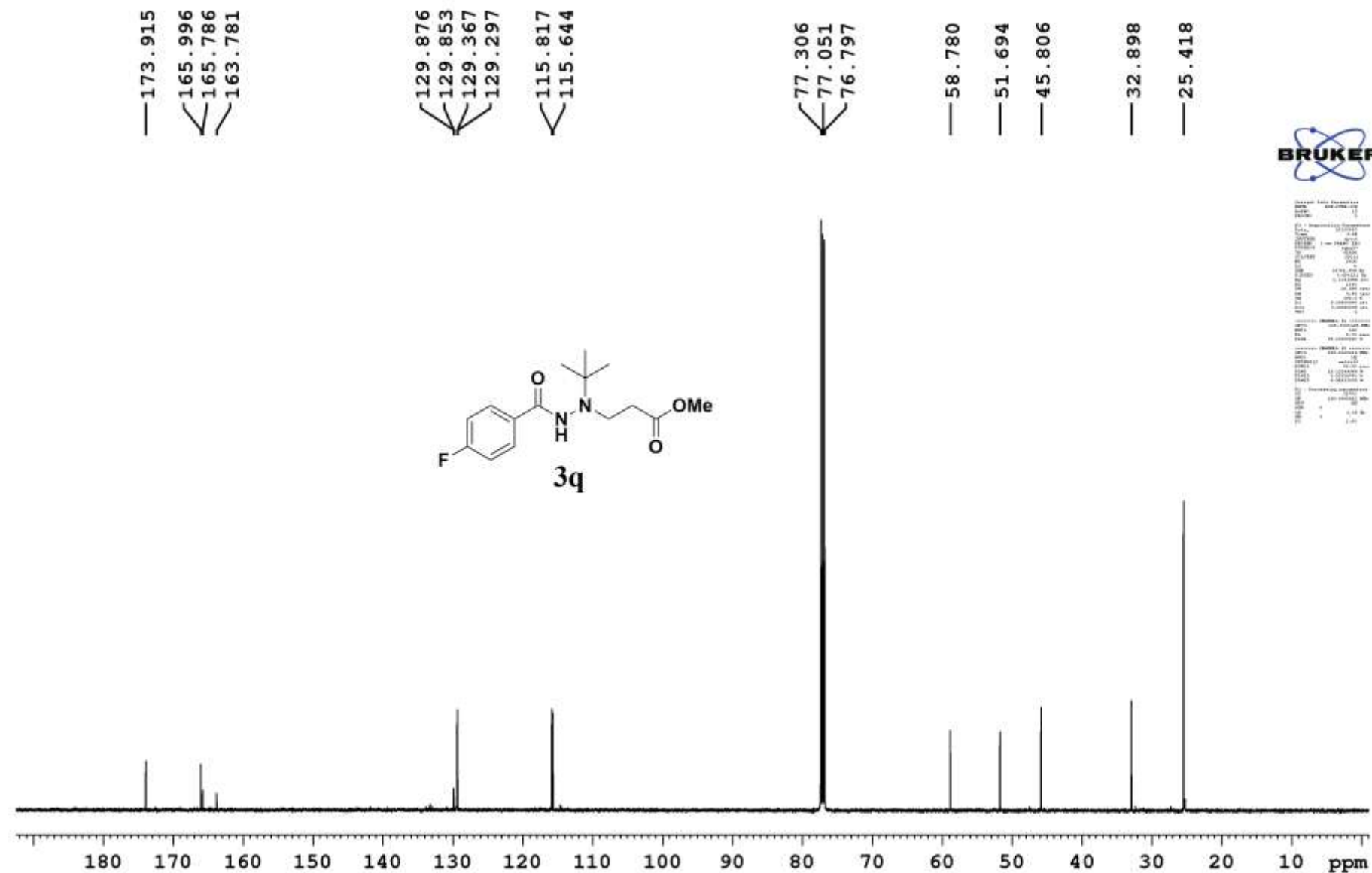


COCCN(C(C)(C)C)C(=O)c1ccc(F)cc1  
**3q**

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **3q**. The spectrum shows peaks at 7.767, 7.756, 7.749, 7.739, 7.130, 7.113, 7.095, 6.577, 3.505, 3.113, 2.605, 2.592, 2.578, and 1.194 ppm. Integration values are 1.93, 1.93, 0.91, 2.87, 1.82, 2.00, and 8.71.

Chemical Shift (ppm)	Integration
7.767, 7.756, 7.749, 7.739	1.93
7.130, 7.113, 7.095	1.93
6.577	0.91
3.505	2.87
3.113	1.82
2.605, 2.592, 2.578	2.00
1.194	8.71

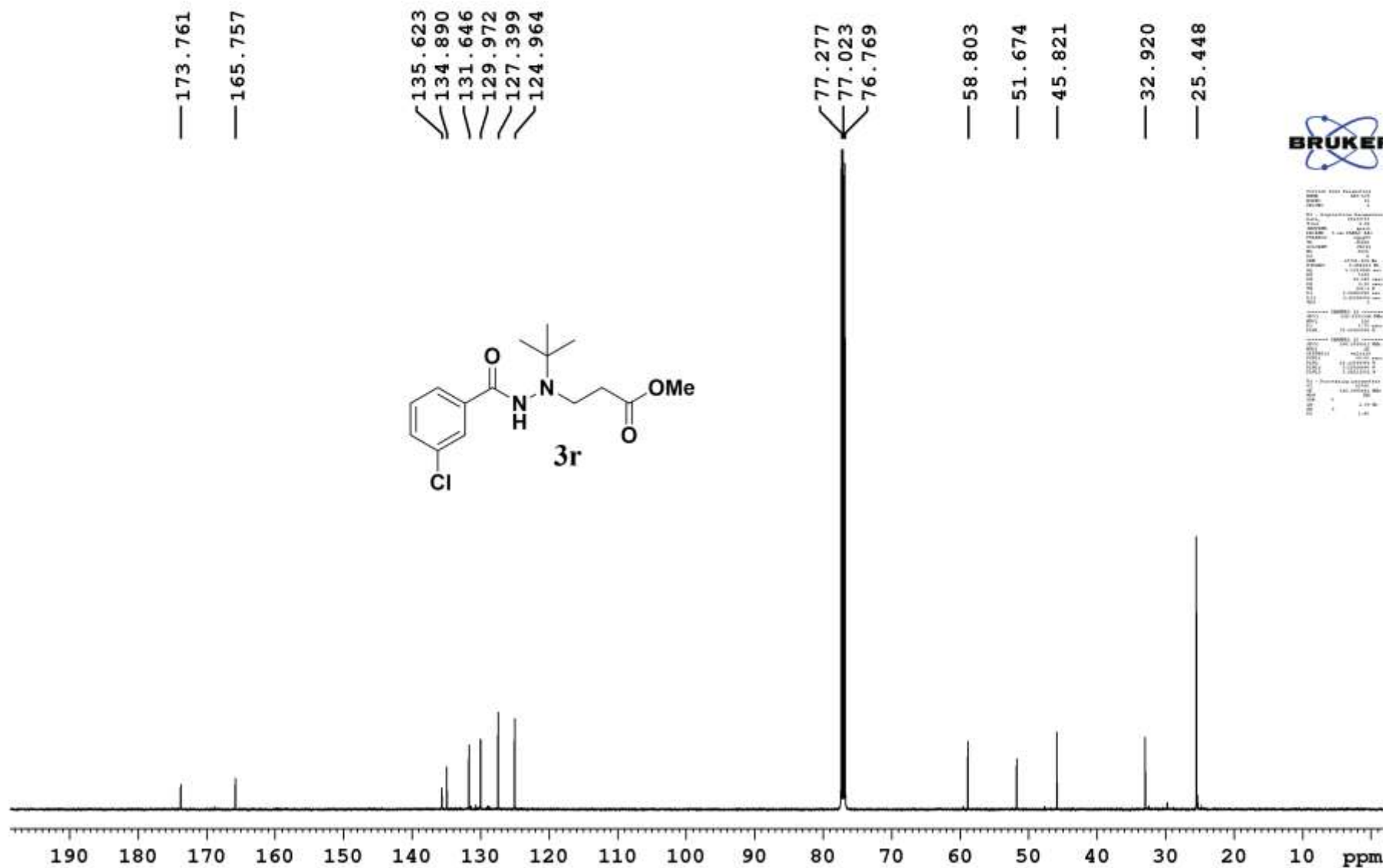
ES-RK-EXP-63P, <sup>13</sup>C, CDCl<sub>3</sub>, 01/09/18



Sample Name: 3q  
 Date: 01/09/18  
 Time: 14:00  
 Operator: ES-RK  
 Instrument: spect  
 P1: 12.00  
 PC: 1.00  
 PD: 0.00  
 PE: 0.00  
 PF: 0.00  
 PG: 0.00  
 PH: 0.00  
 PI: 0.00  
 PJ: 0.00  
 PK: 0.00  
 PL: 0.00  
 PM: 0.00  
 PN: 0.00  
 PO: 0.00  
 PP: 0.00  
 PQ: 0.00  
 PR: 0.00  
 PS: 0.00  
 PT: 0.00  
 PU: 0.00  
 PV: 0.00  
 PW: 0.00  
 PX: 0.00  
 PY: 0.00  
 PZ: 0.00  
 Q1: 0.00  
 Q2: 0.00  
 Q3: 0.00  
 Q4: 0.00  
 Q5: 0.00  
 Q6: 0.00  
 Q7: 0.00  
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 Q9: 0.00  
 Q10: 0.00  
 Q11: 0.00  
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 Q15: 0.00  
 Q16: 0.00  
 Q17: 0.00  
 Q18: 0.00  
 Q19: 0.00  
 Q20: 0.00  
 Q21: 0.00  
 Q22: 0.00  
 Q23: 0.00  
 Q24: 0.00  
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 Q26: 0.00  
 Q27: 0.00  
 Q28: 0.00  
 Q29: 0.00  
 Q30: 0.00  
 Q31: 0.00  
 Q32: 0.00  
 Q33: 0.00  
 Q34: 0.00  
 Q35: 0.00  
 Q36: 0.00  
 Q37: 0.00  
 Q38: 0.00  
 Q39: 0.00  
 Q40: 0.00  
 Q41: 0.00  
 Q42: 0.00  
 Q43: 0.00  
 Q44: 0.00  
 Q45: 0.00  
 Q46: 0.00  
 Q47: 0.00  
 Q48: 0.00  
 Q49: 0.00  
 Q50: 0.00  
 Q51: 0.00  
 Q52: 0.00  
 Q53: 0.00  
 Q54: 0.00  
 Q55: 0.00  
 Q56: 0.00  
 Q57: 0.00  
 Q58: 0.00  
 Q59: 0.00  
 Q60: 0.00  
 Q61: 0.00  
 Q62: 0.00  
 Q63: 0.00  
 Q64: 0.00  
 Q65: 0.00  
 Q66: 0.00  
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 Q69: 0.00  
 Q70: 0.00  
 Q71: 0.00  
 Q72: 0.00  
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 Q80: 0.00  
 Q81: 0.00  
 Q82: 0.00  
 Q83: 0.00  
 Q84: 0.00  
 Q85: 0.00  
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 Q91: 0.00  
 Q92: 0.00  
 Q93: 0.00  
 Q94: 0.00  
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 Q96: 0.00  
 Q97: 0.00  
 Q98: 0.00  
 Q99: 0.00  
 Q100: 0.00

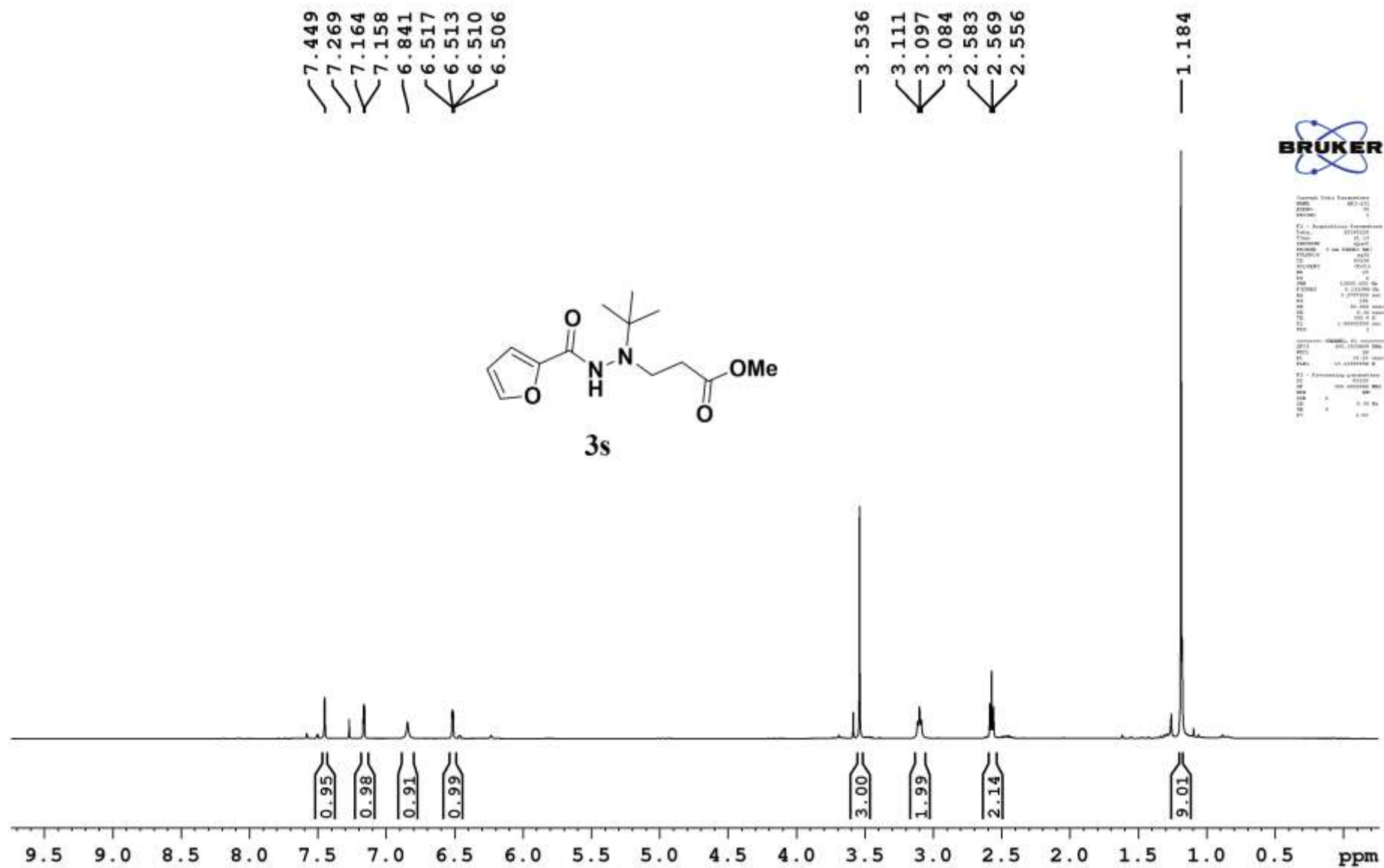
[illegible]

ES-AKJ-196-4-LB1; 06/07/2018



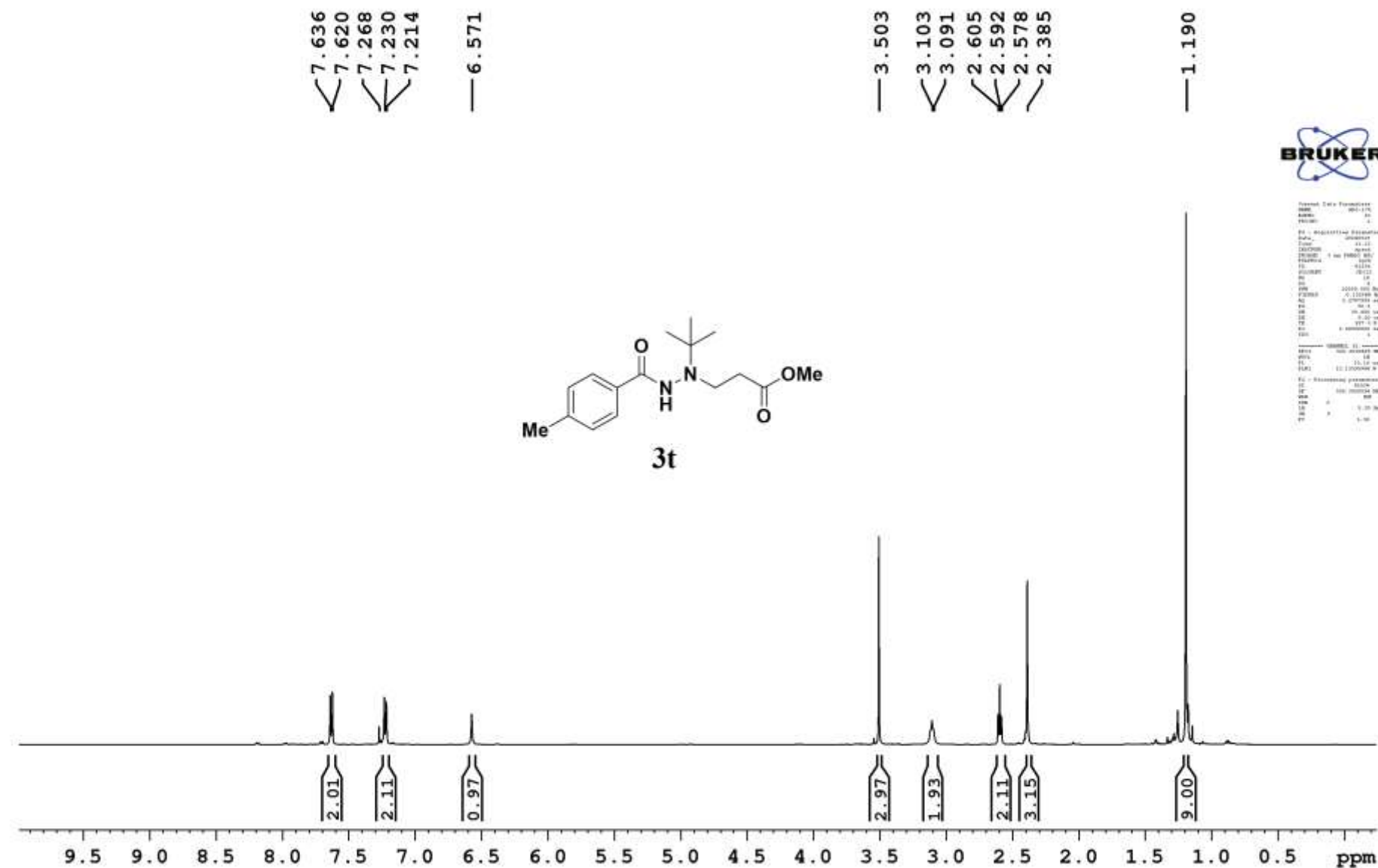
13C NMR (CDCl<sub>3</sub>)  
 173.761, 165.757, 135.623, 134.890, 131.646, 129.972, 127.399, 124.964, 77.277, 77.023, 76.769, 58.803, 51.674, 45.821, 32.920, 25.448







ES-AKJ-176-3-LB1; 19/05/2018





ES-RK-EXP-66-1H; CDC13; 26 OCT 2018

7.710  
7.693

7.269

6.920  
6.902

6.552

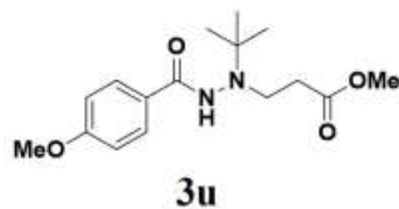
3.836

3.489

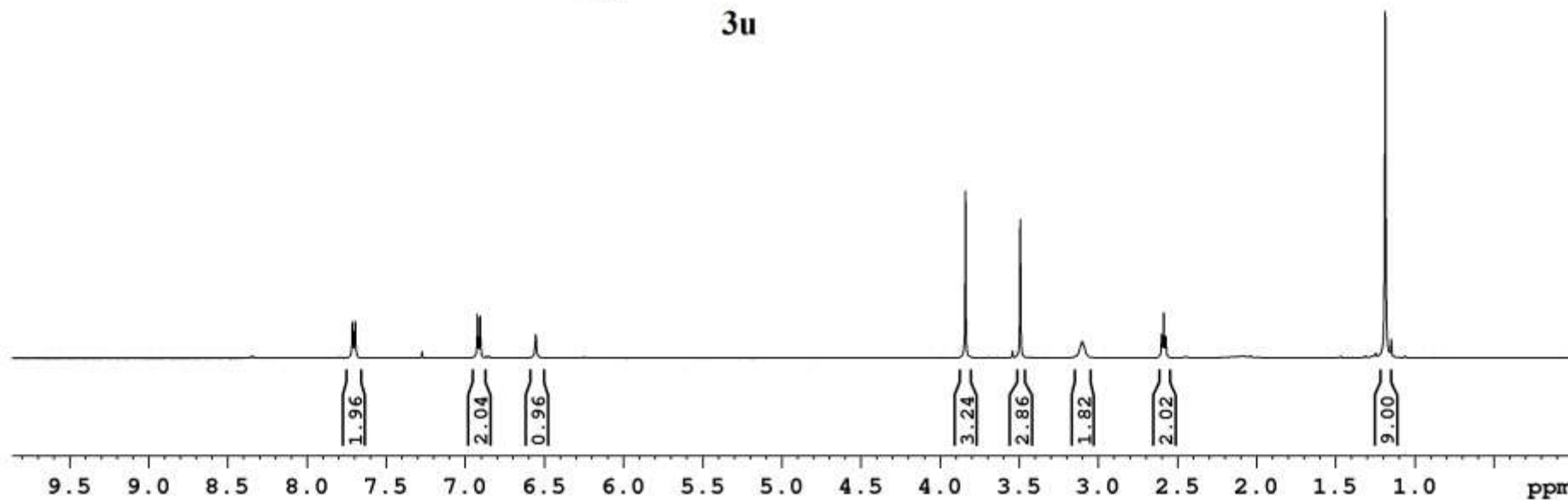
3.098

2.596  
2.583  
2.570

1.183



===== Data =====  
NAME: 3u  
EXPNO: 1  
PROCNO: 1  
F2 - Acquisition Parameters  
Date\_ : 20181026  
Time : 10:10  
INSTRUM : spect  
PROBHD : 5 mm BBO-1H  
PULPROG : zgpg30  
TD : 65536  
SFO : 400.146  
AQ : 1.00000000  
RG : 327.680000  
FIDRES : 0.333333 Hz  
AQRES : 0.333333 Hz  
F2 - Processing parameters  
SI : 32768  
SF : 400.146000 MHz  
WDW : EM  
SSB : 0  
LB : 3.00 Hz  
GB : 0  
PC : 2.00



ES-RK-EXP-66P; 29/10/2018

—173.927  
—166.494  
—162.270

—128.794  
—125.890

—113.816

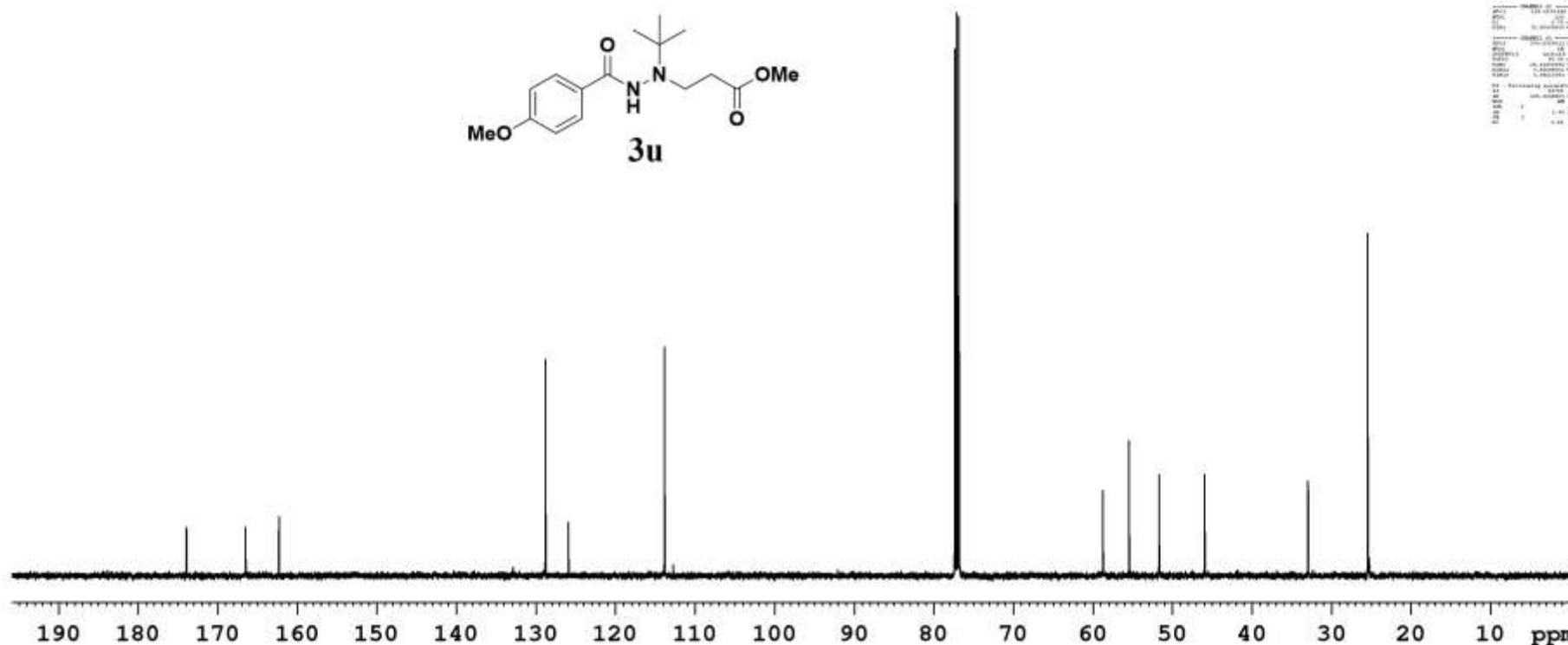
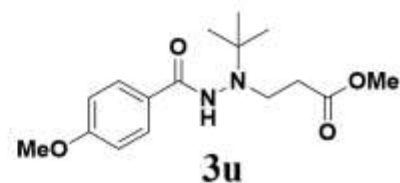
77.316  
77.062  
76.809

—58.709  
—55.425  
—51.643  
—45.905

—32.917  
—25.416



Acquired Data Parameters  
Date: 29/10/2018  
Time: 10:00:00  
F1: 400.138 MHz  
F2: 100.625 MHz  
F3: 400.138 MHz  
F4: 100.625 MHz  
F5: 400.138 MHz  
F6: 100.625 MHz  
F7: 400.138 MHz  
F8: 100.625 MHz  
F9: 400.138 MHz  
F10: 100.625 MHz  
F11: 400.138 MHz  
F12: 100.625 MHz  
F13: 400.138 MHz  
F14: 100.625 MHz  
F15: 400.138 MHz  
F16: 100.625 MHz  
F17: 400.138 MHz  
F18: 100.625 MHz  
F19: 400.138 MHz  
F20: 100.625 MHz  
F21: 400.138 MHz  
F22: 100.625 MHz  
F23: 400.138 MHz  
F24: 100.625 MHz  
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F26: 100.625 MHz  
F27: 400.138 MHz  
F28: 100.625 MHz  
F29: 400.138 MHz  
F30: 100.625 MHz  
F31: 400.138 MHz  
F32: 100.625 MHz  
F33: 400.138 MHz  
F34: 100.625 MHz  
F35: 400.138 MHz  
F36: 100.625 MHz  
F37: 400.138 MHz  
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F39: 400.138 MHz  
F40: 100.625 MHz  
F41: 400.138 MHz  
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F59: 400.138 MHz  
F60: 100.625 MHz  
F61: 400.138 MHz  
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F63: 400.138 MHz  
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F84: 100.625 MHz  
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F86: 100.625 MHz  
F87: 400.138 MHz  
F88: 100.625 MHz  
F89: 400.138 MHz  
F90: 100.625 MHz  
F91: 400.138 MHz  
F92: 100.625 MHz  
F93: 400.138 MHz  
F94: 100.625 MHz  
F95: 400.138 MHz  
F96: 100.625 MHz  
F97: 400.138 MHz  
F98: 100.625 MHz  
F99: 400.138 MHz  
F100: 100.625 MHz



ES-AKJ-T; 28/11/2017

8.446  
7.904  
7.889  
7.584  
7.569  
7.554  
7.495  
7.480  
7.465  
7.274  
7.269  
7.258  
7.242  
6.892  
6.877  
6.866  
6.851

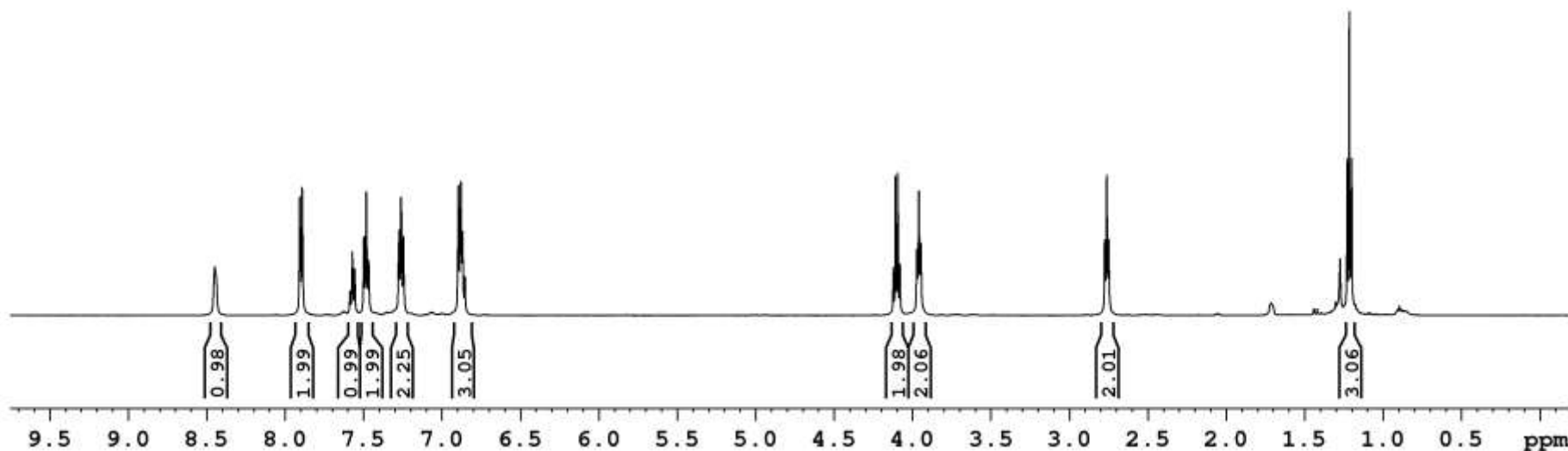
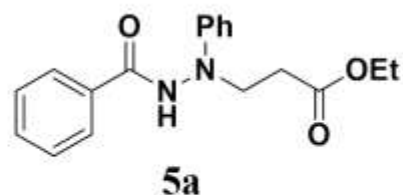
4.120  
4.105  
4.091  
4.077  
3.969  
3.956  
3.944

2.771  
2.758  
2.746

1.225  
1.211  
1.196



NAME: 28/11/17  
EXPNO: 1  
PROCNO: 1  
PROCPS: 1  
F2 - Acquisition Parameters  
Date\_ 28/11/17  
Time 12:54  
INSTRUM spect  
PROBHD 1 mm BBO-1H/13  
PULPROG zgpg30  
TD 65536  
SOLVENT dms  
AQ 1.00  
RG 320  
RT 300.2 K  
FIDRES 0.000000 Hz  
AQ 1.00  
F2 - Processing parameters  
SI 32768  
SF 400.146400 MHz  
WDW EM  
SSB 0  
GB 0  
PC 1.0000000  
F2 - Integration parameters  
SI 32768  
SF 400.146400 MHz  
WDW EM  
SSB 0  
GB 0  
PC 1.0000000



ES-AKJ-T; 28/11/2017

—172.971

—166.515

—147.677

132.678

132.152

129.337

128.794

127.268

—119.850

—113.094

77.295

77.041

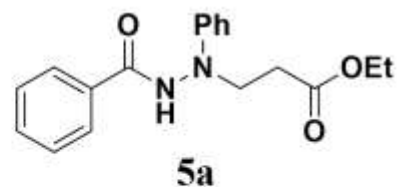
76.787

—60.902

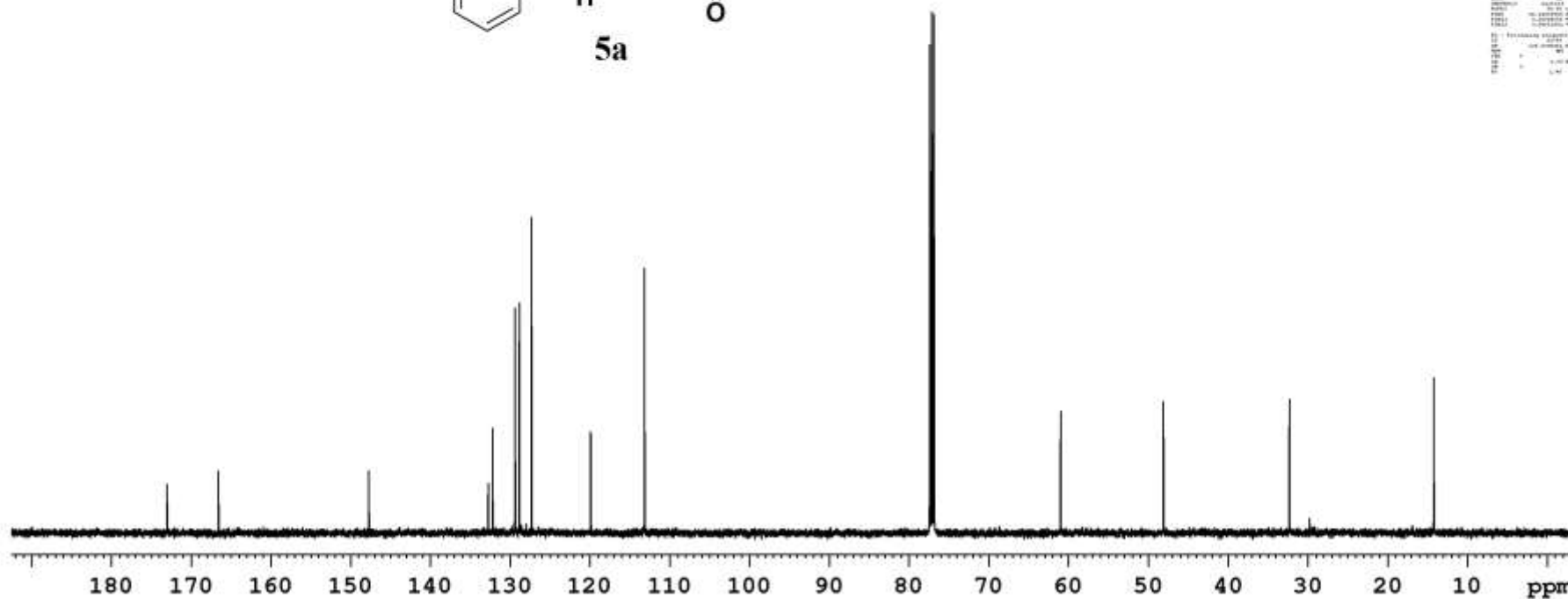
—48.024

—32.214

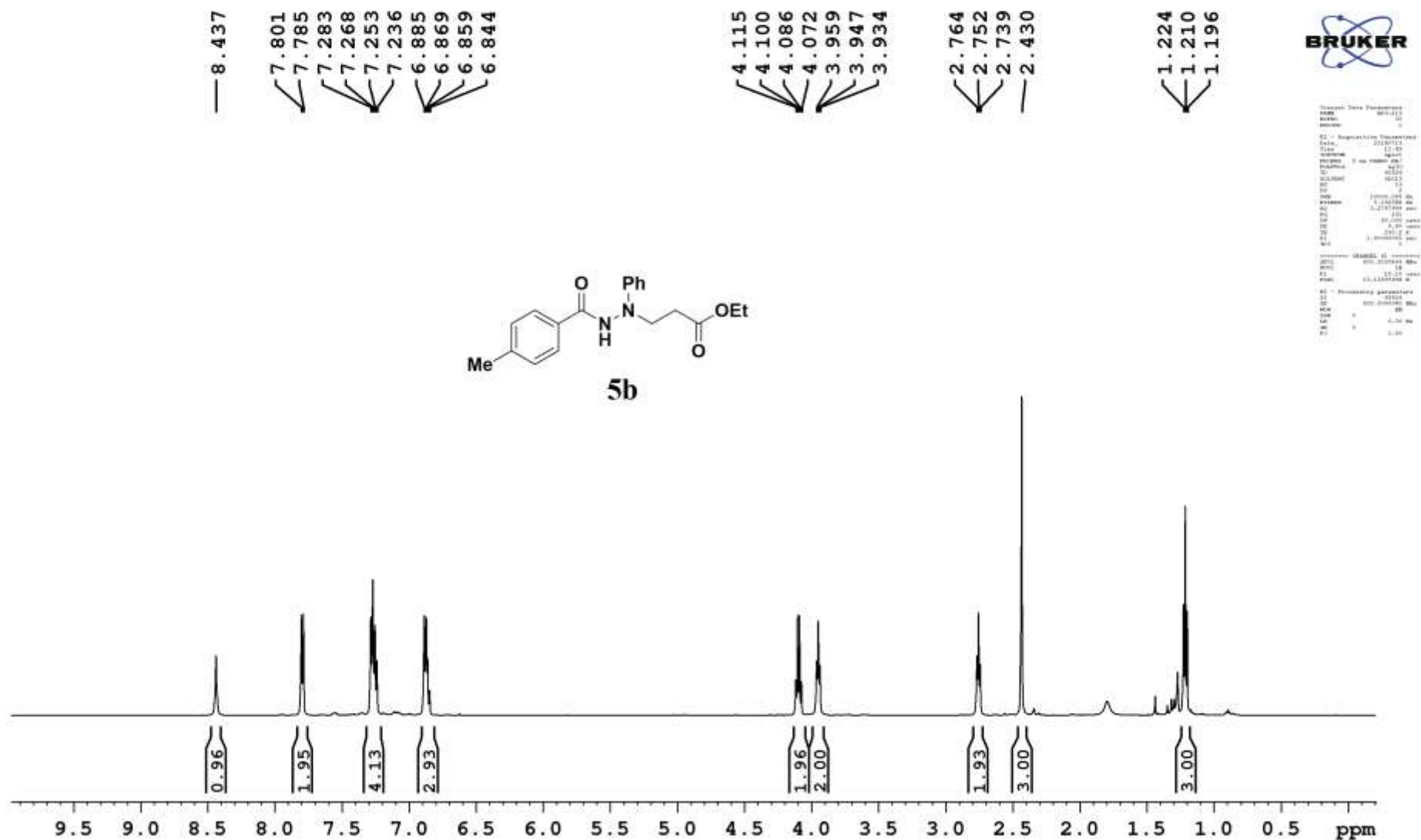
—14.104



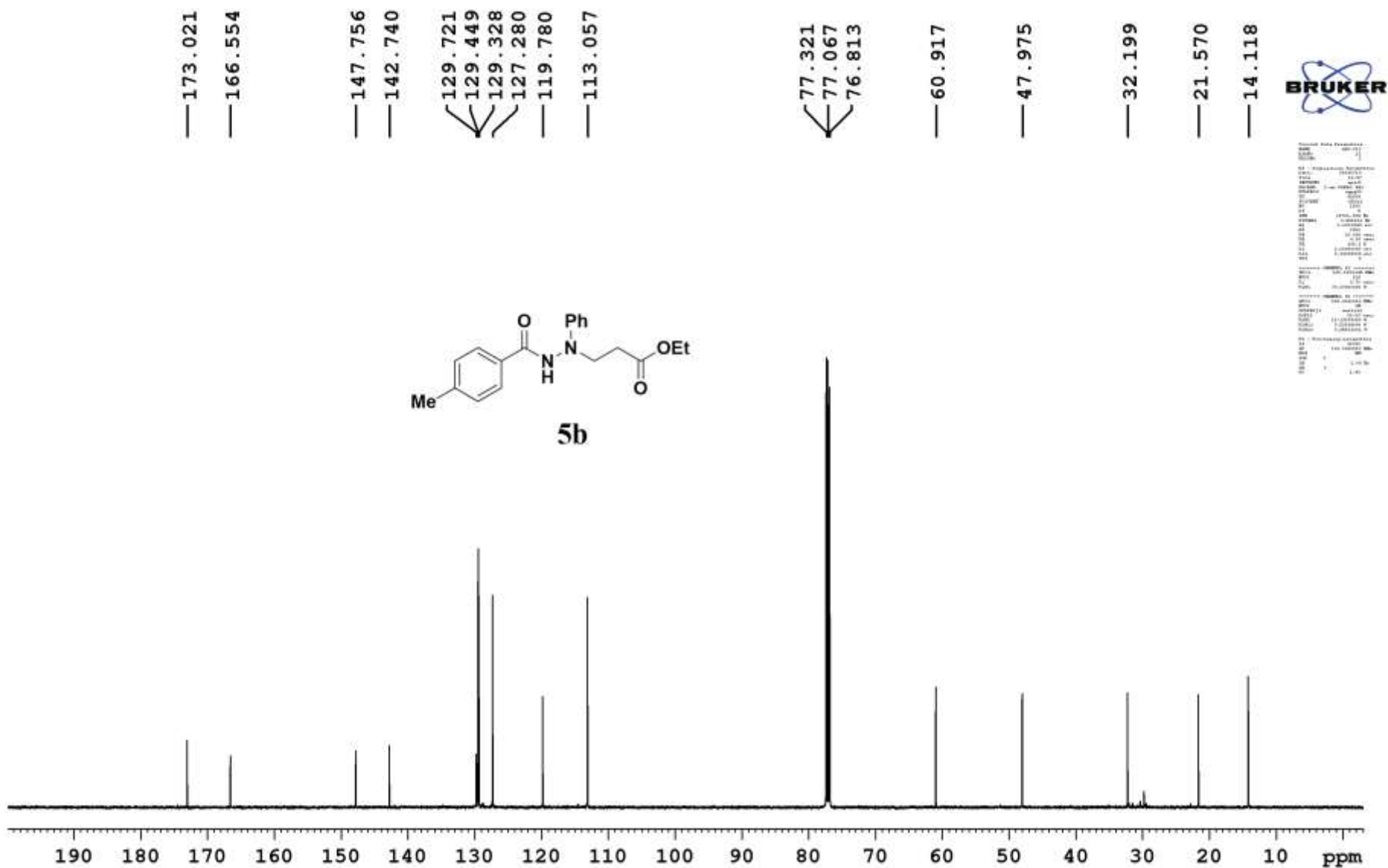
Acquired: 2017-11-28 10:00:00  
 Date: 2017-11-28 10:00:00  
 Time: 10:00:00  
 File: 2017-11-28 10:00:00  
 Name: 2017-11-28 10:00:00  
 Path: 2017-11-28 10:00:00  
 Size: 2017-11-28 10:00:00  
 Type: 2017-11-28 10:00:00  
 Unit: 2017-11-28 10:00:00  
 User: 2017-11-28 10:00:00  
 Version: 2017-11-28 10:00:00  
 Project: 2017-11-28 10:00:00  
 Experiment: 2017-11-28 10:00:00  
 Acquisition: 2017-11-28 10:00:00  
 Processing: 2017-11-28 10:00:00  
 Reference: 2017-11-28 10:00:00  
 Comments: 2017-11-28 10:00:00







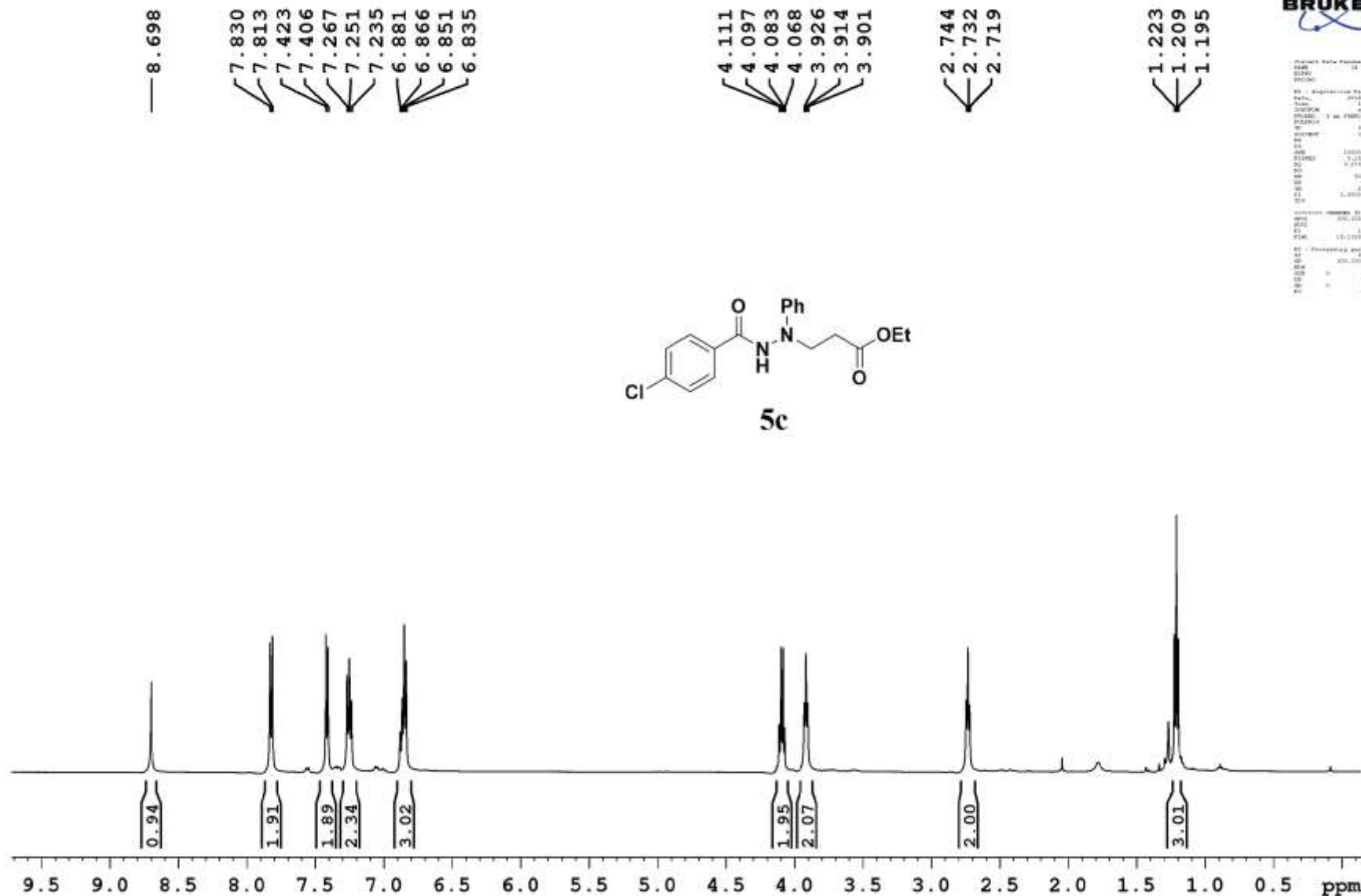
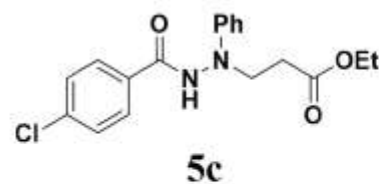
ES-AKJ-213-LB1; 19/07/2018

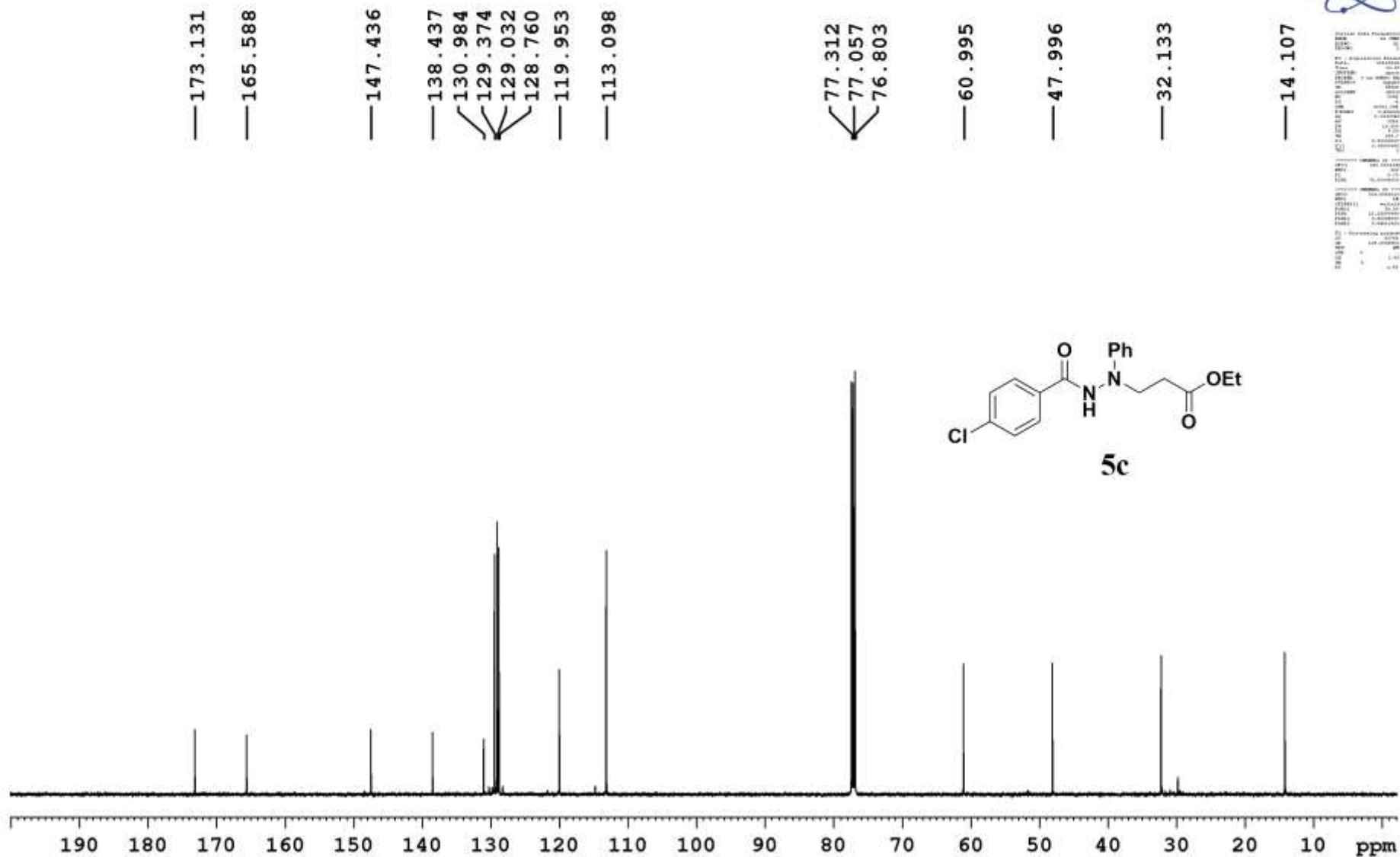


ES-AKJ-190-3LB1; 14/06/2018

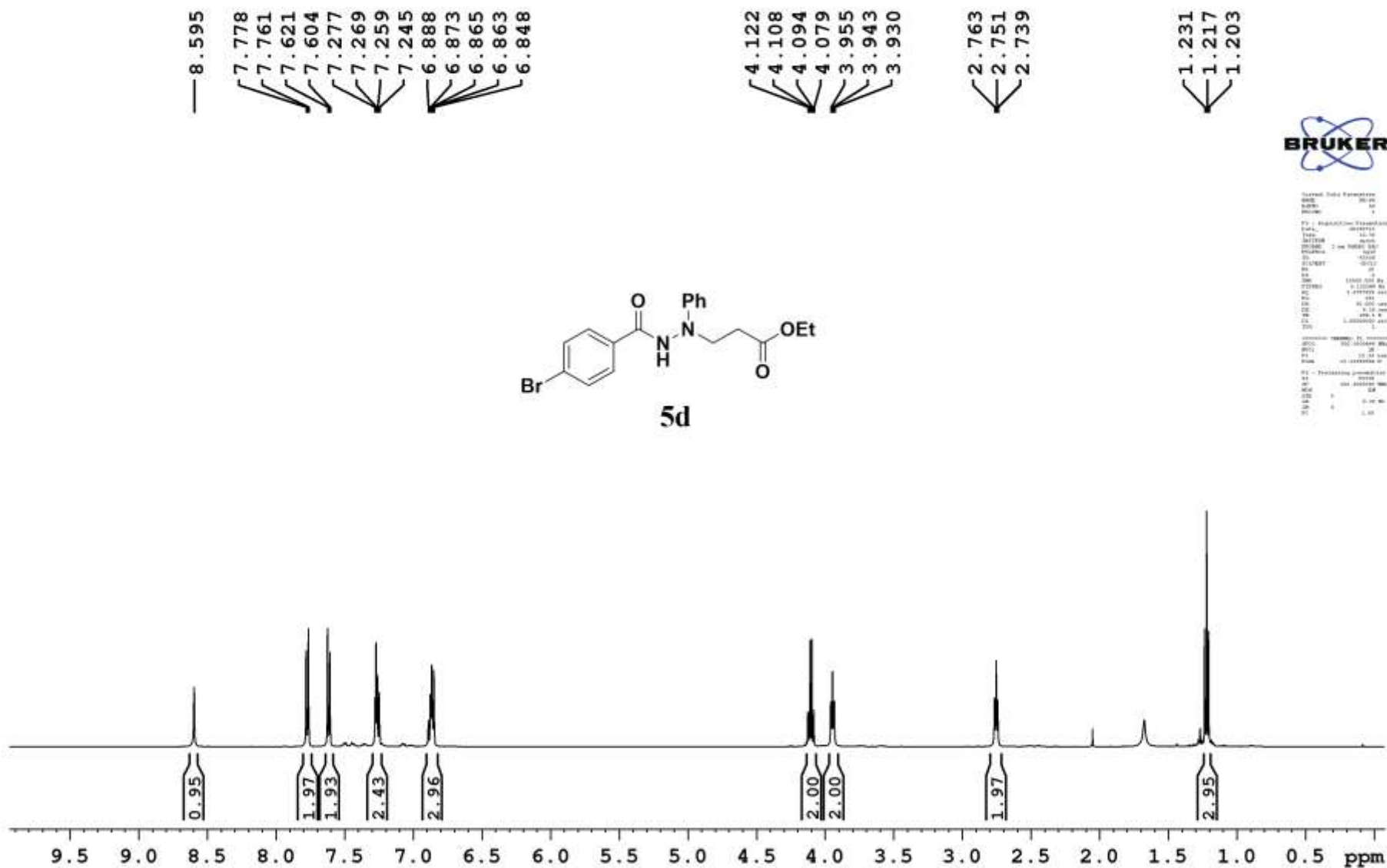


Project Name: ES-AKJ-190-3LB1  
 Date: 14/06/2018  
 Time: 11:34  
 Operator: [blank]  
 Sample: [blank]  
 Solvent: CDCl3  
 Concentration: 10 mg/mL  
 Volume: 0.5 mL  
 Weight: 5.00 mg  
 Purity: 100%  
 Acquisition Parameters:  
 Name: ES-AKJ-190-3LB1  
 Date: 14/06/2018  
 Time: 11:34  
 Operator: [blank]  
 Sample: [blank]  
 Solvent: CDCl3  
 Concentration: 10 mg/mL  
 Volume: 0.5 mL  
 Weight: 5.00 mg  
 Purity: 100%  
 Acquisition Parameters:  
 Name: ES-AKJ-190-3LB1  
 Date: 14/06/2018  
 Time: 11:34  
 Operator: [blank]  
 Sample: [blank]  
 Solvent: CDCl3  
 Concentration: 10 mg/mL  
 Volume: 0.5 mL  
 Weight: 5.00 mg  
 Purity: 100%

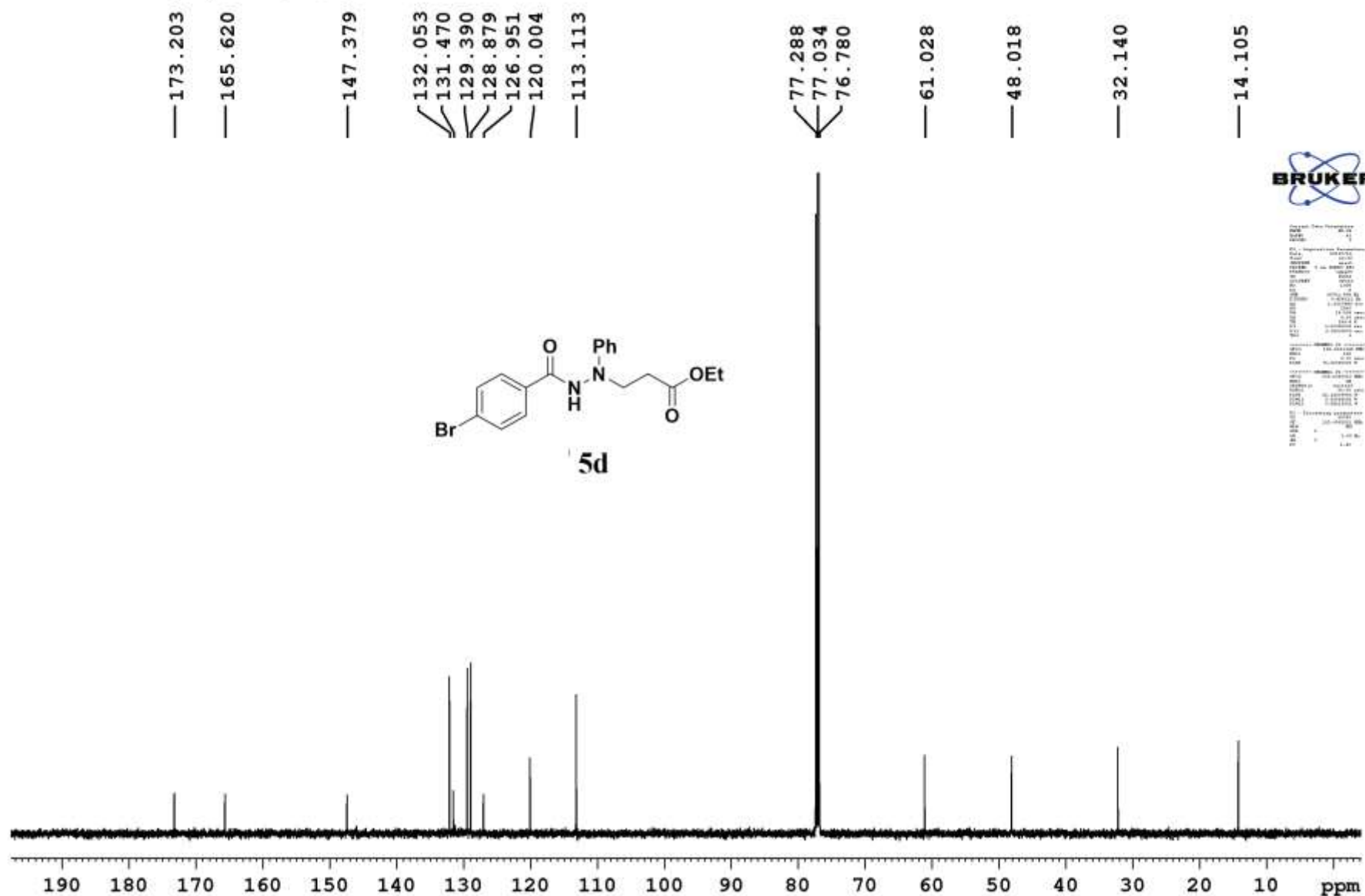


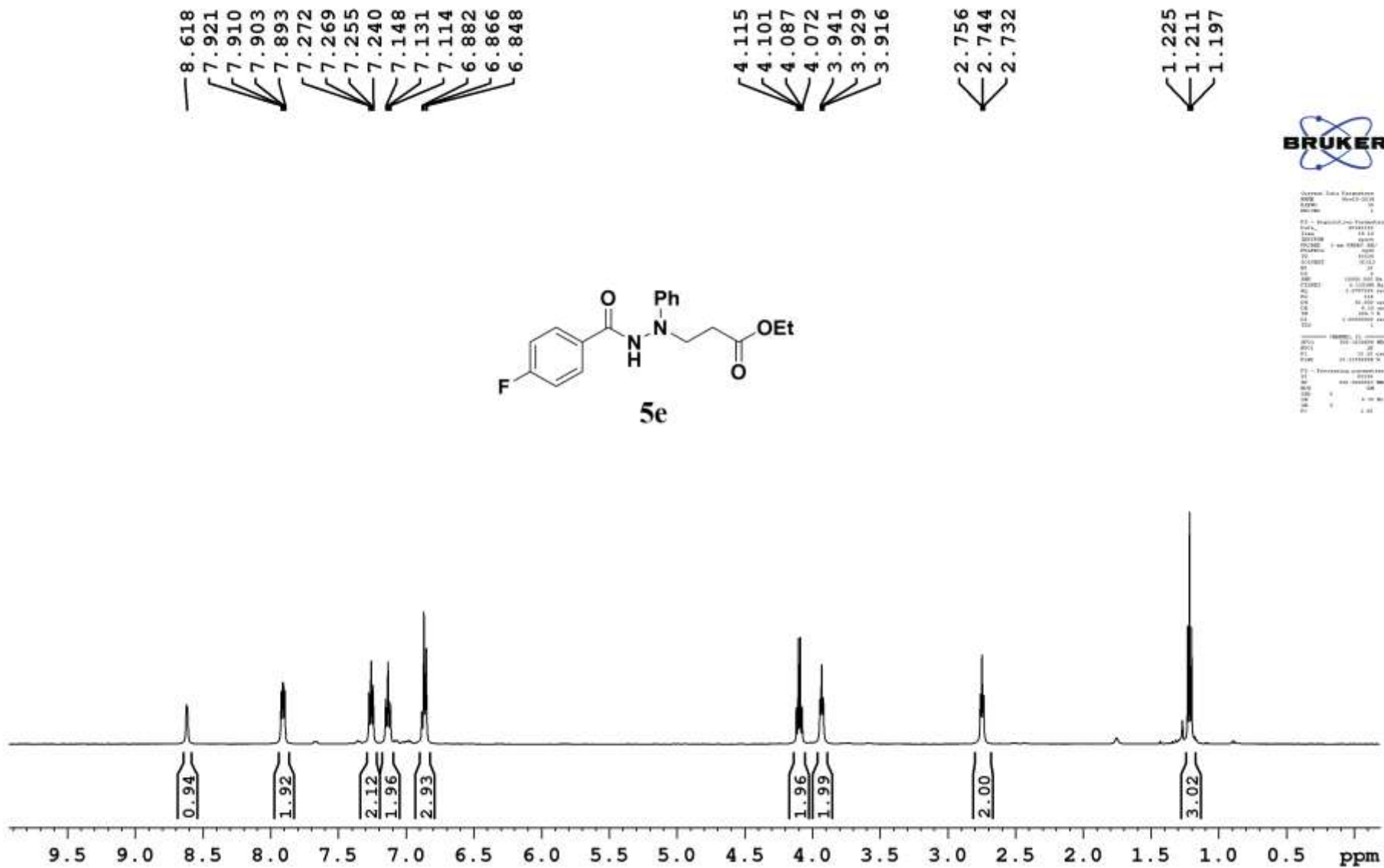


ES-RK-84P, 1H, CDC13, 13/7/19

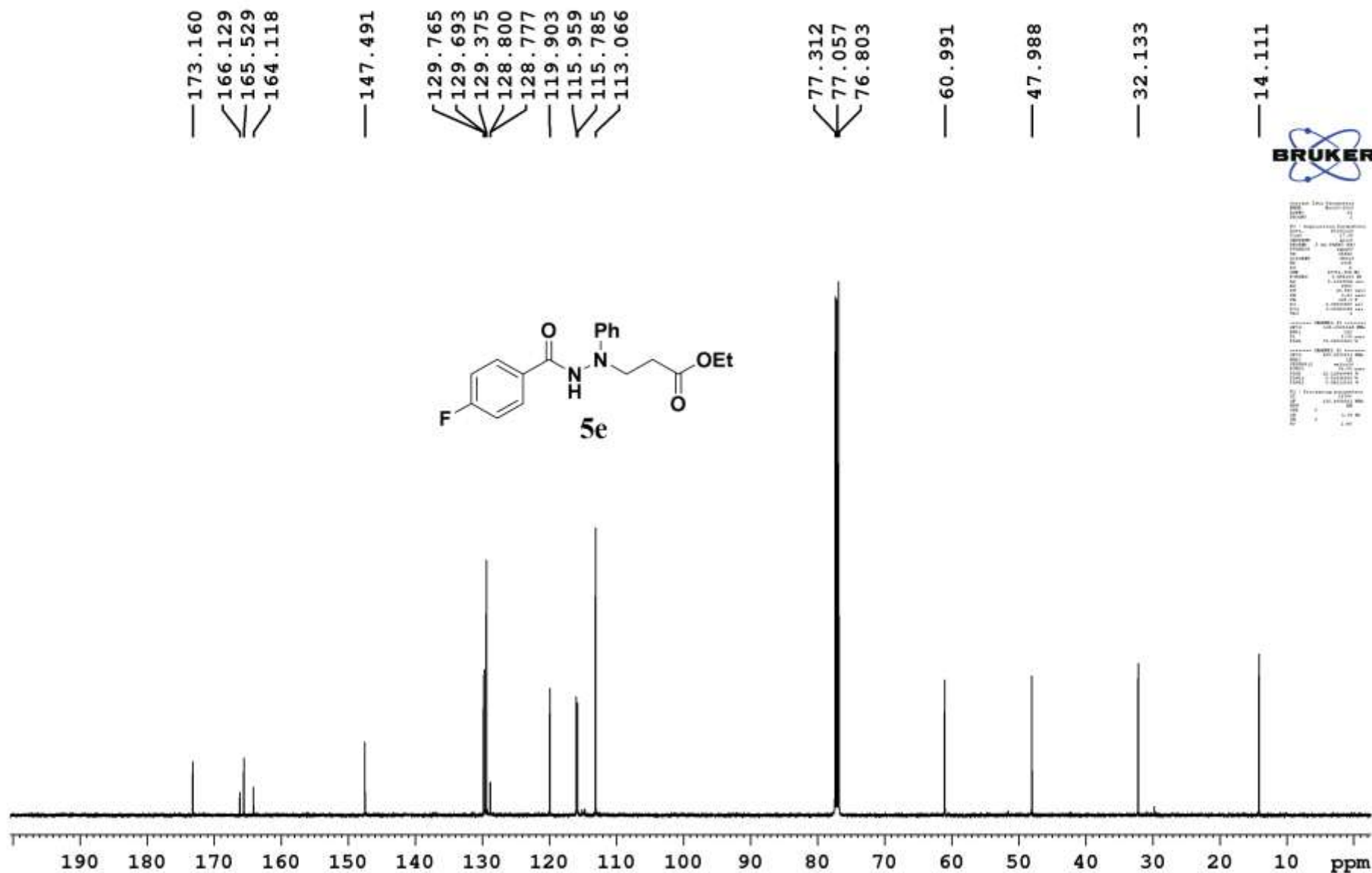


ES-RK-84P, 1H, CDC13, 13/7/19



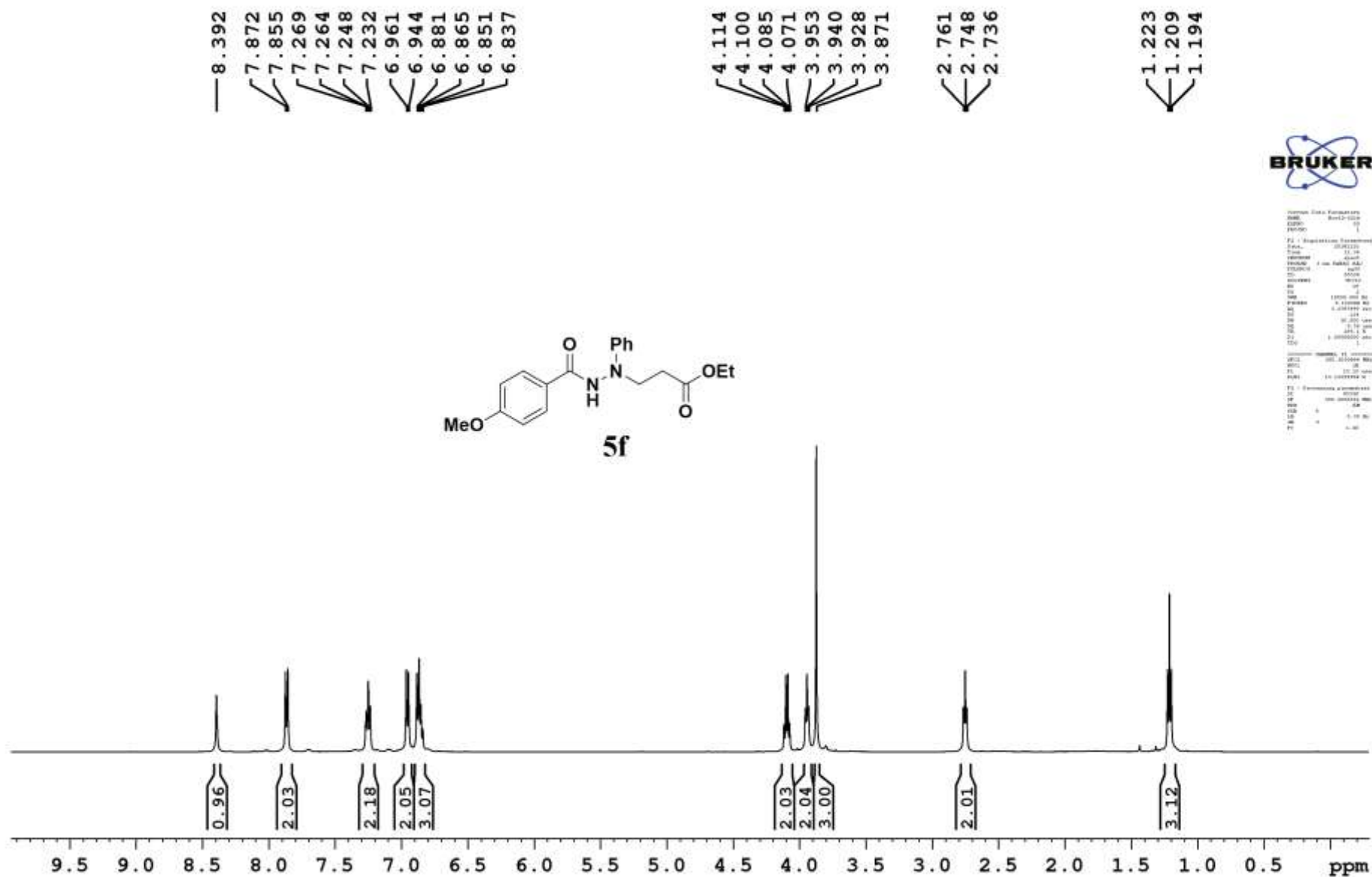


ES-AKJ-202-3; 10/11/2018

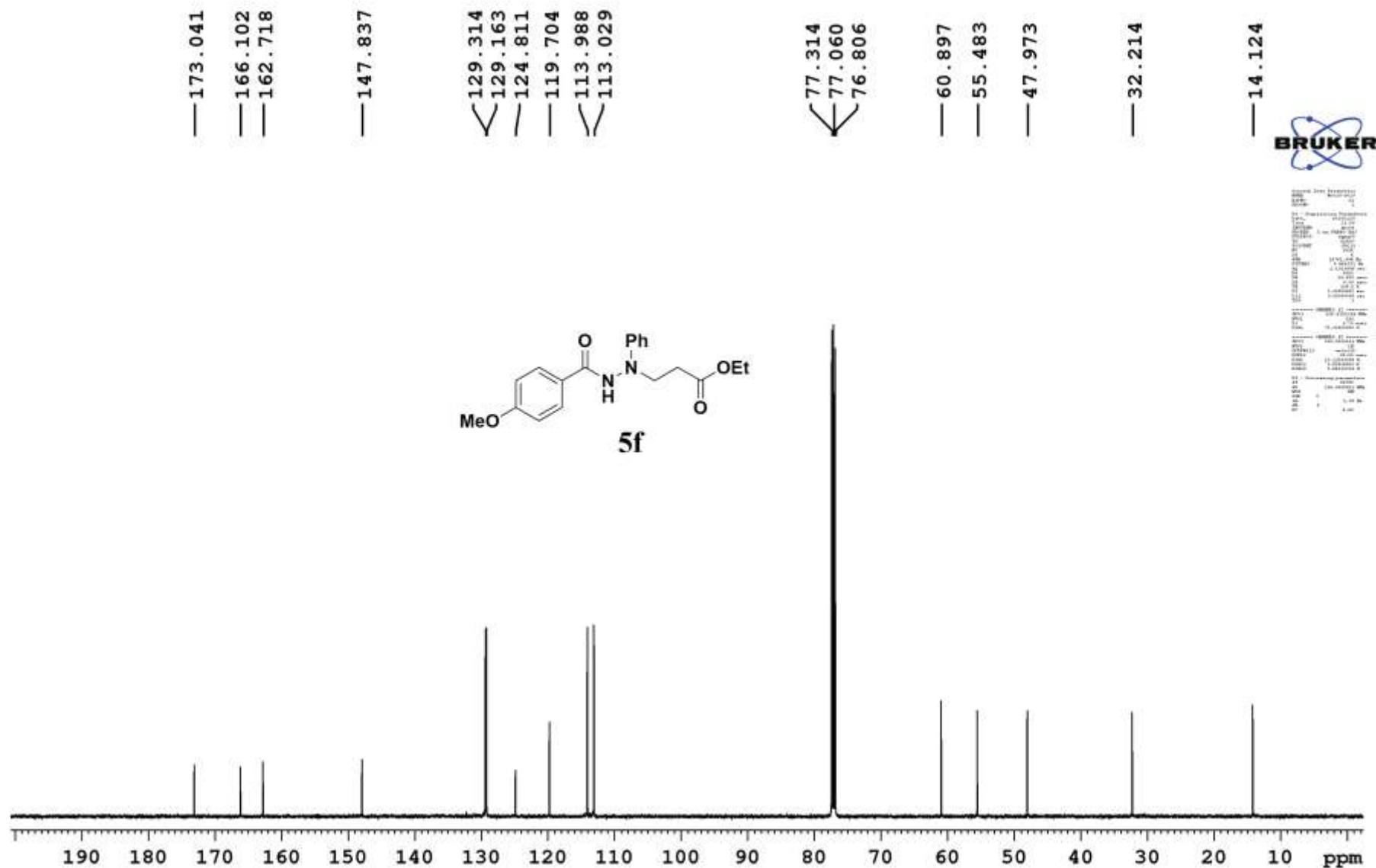




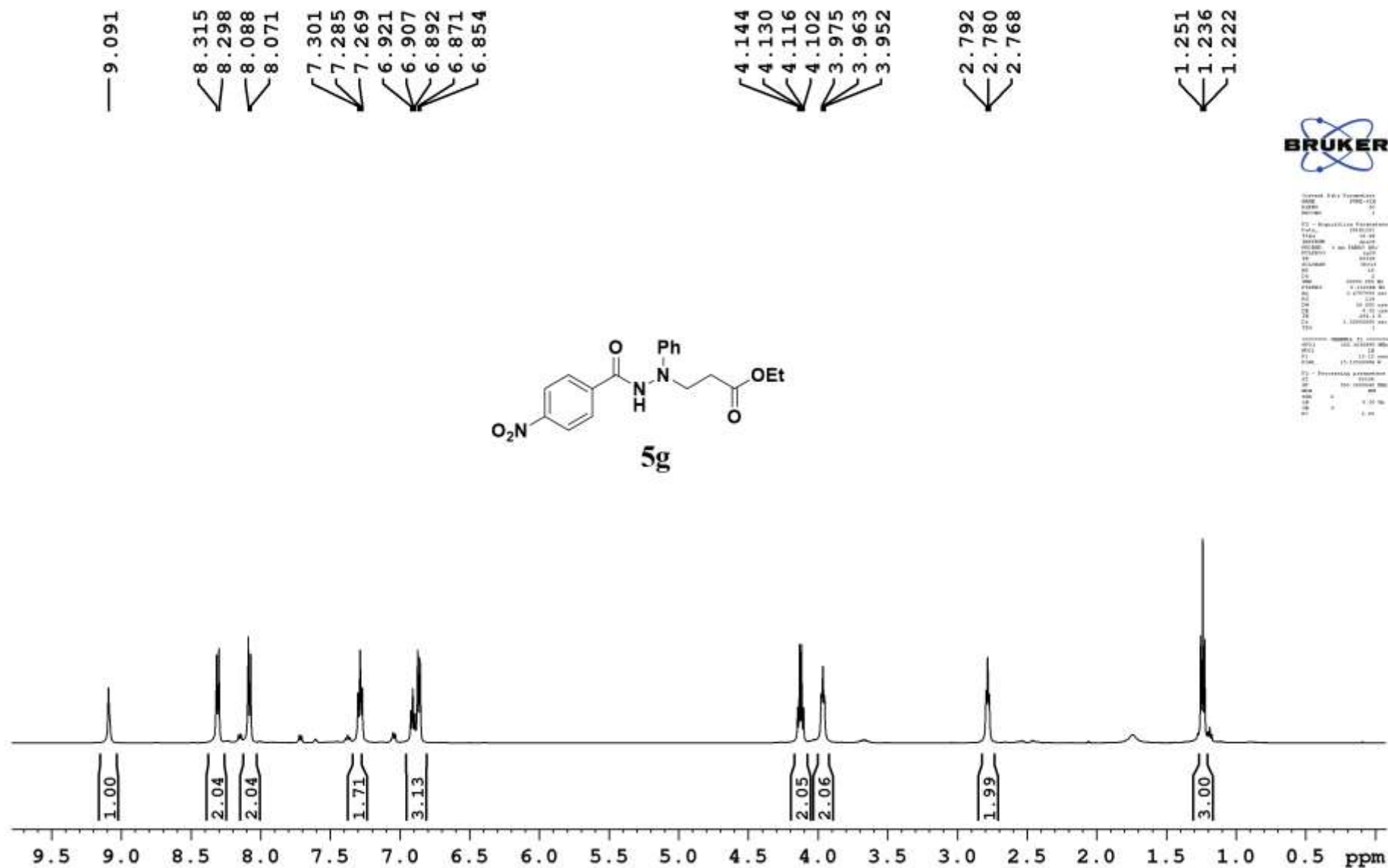
ES-AKJ-MC-49; 10/11/2018



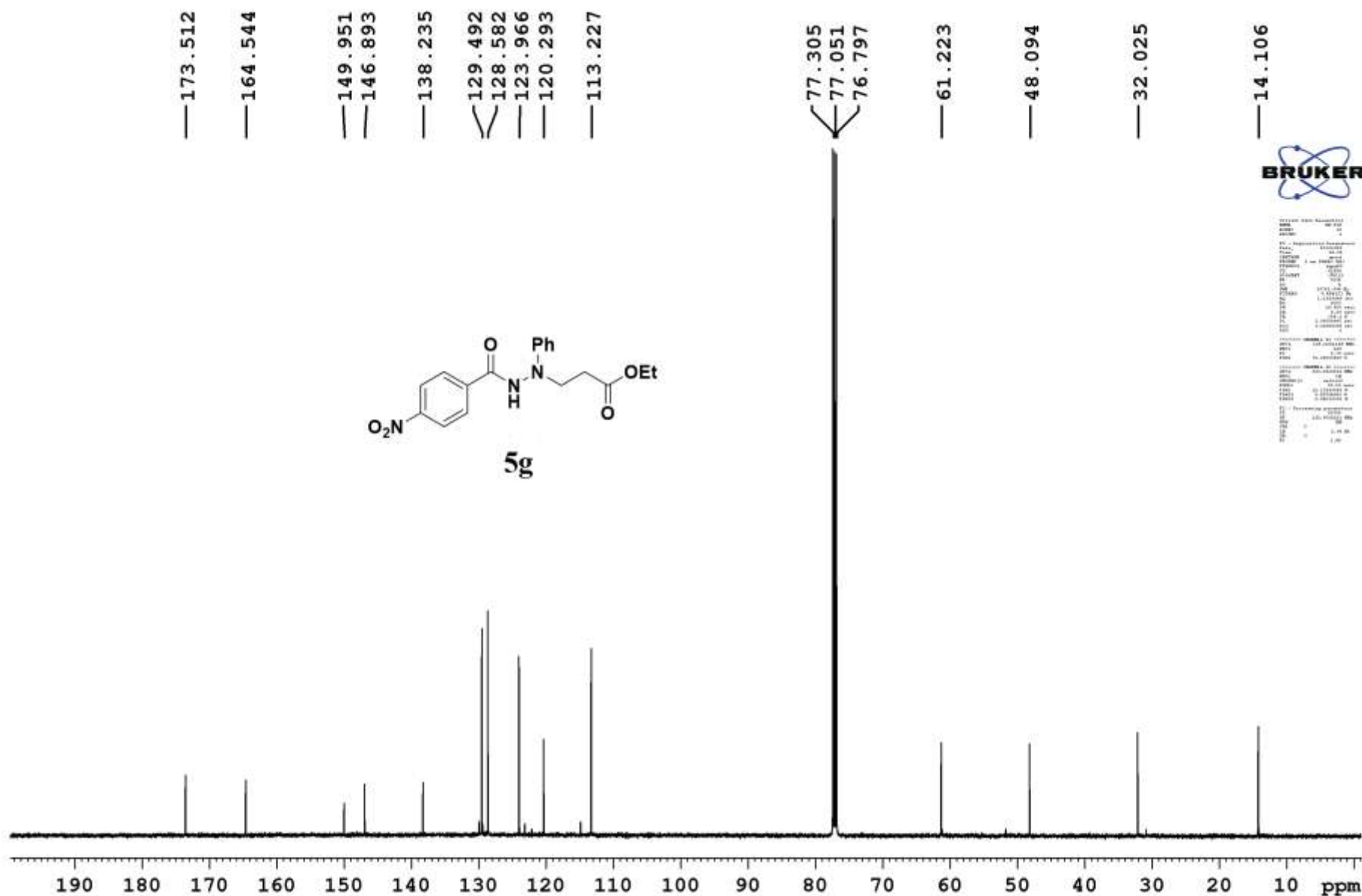
ES-AKJ-MC-49; 10/11/2018



ES-RK-EXP-91;1H;CDCL3;1/11/18



ES-RK-EXP-91P, 13C, CHCL3; 31/10/18



BRUKER

ES-AKJ-216; 09/11/2018

8.705  
7.886  
7.883  
7.879  
7.754  
7.739  
7.531  
7.515  
7.397  
7.382  
7.366  
7.269  
7.258  
7.243  
7.226  
6.877  
6.862  
6.842  
6.826

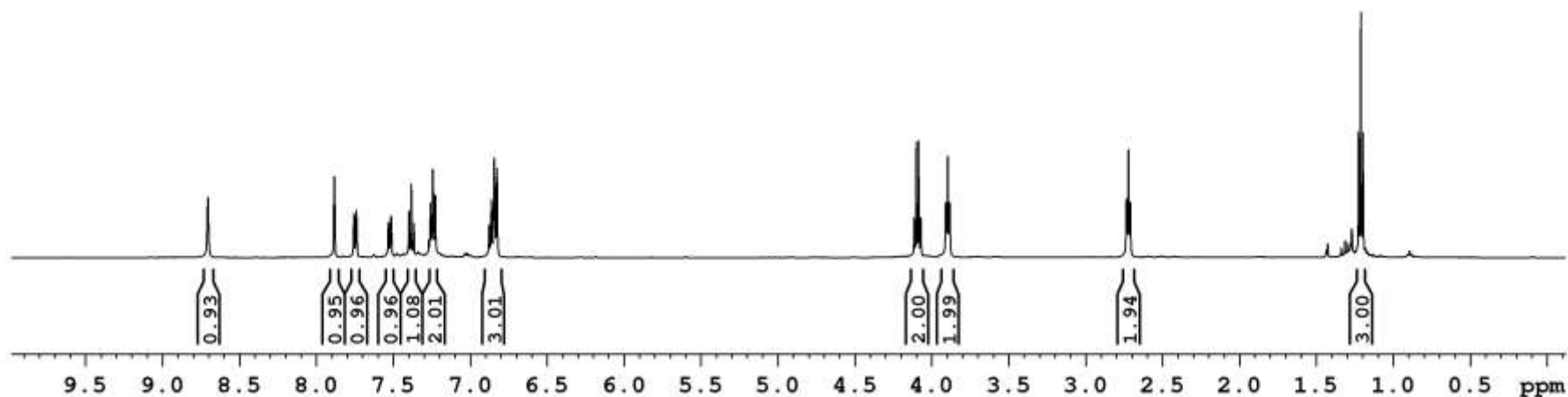
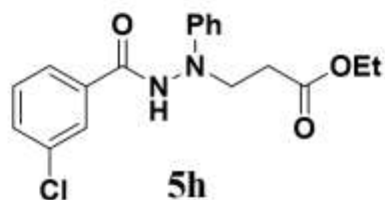
4.113  
4.099  
4.084  
4.070  
3.907  
3.895  
3.882

2.733  
2.721  
2.708

1.224  
1.209  
1.195

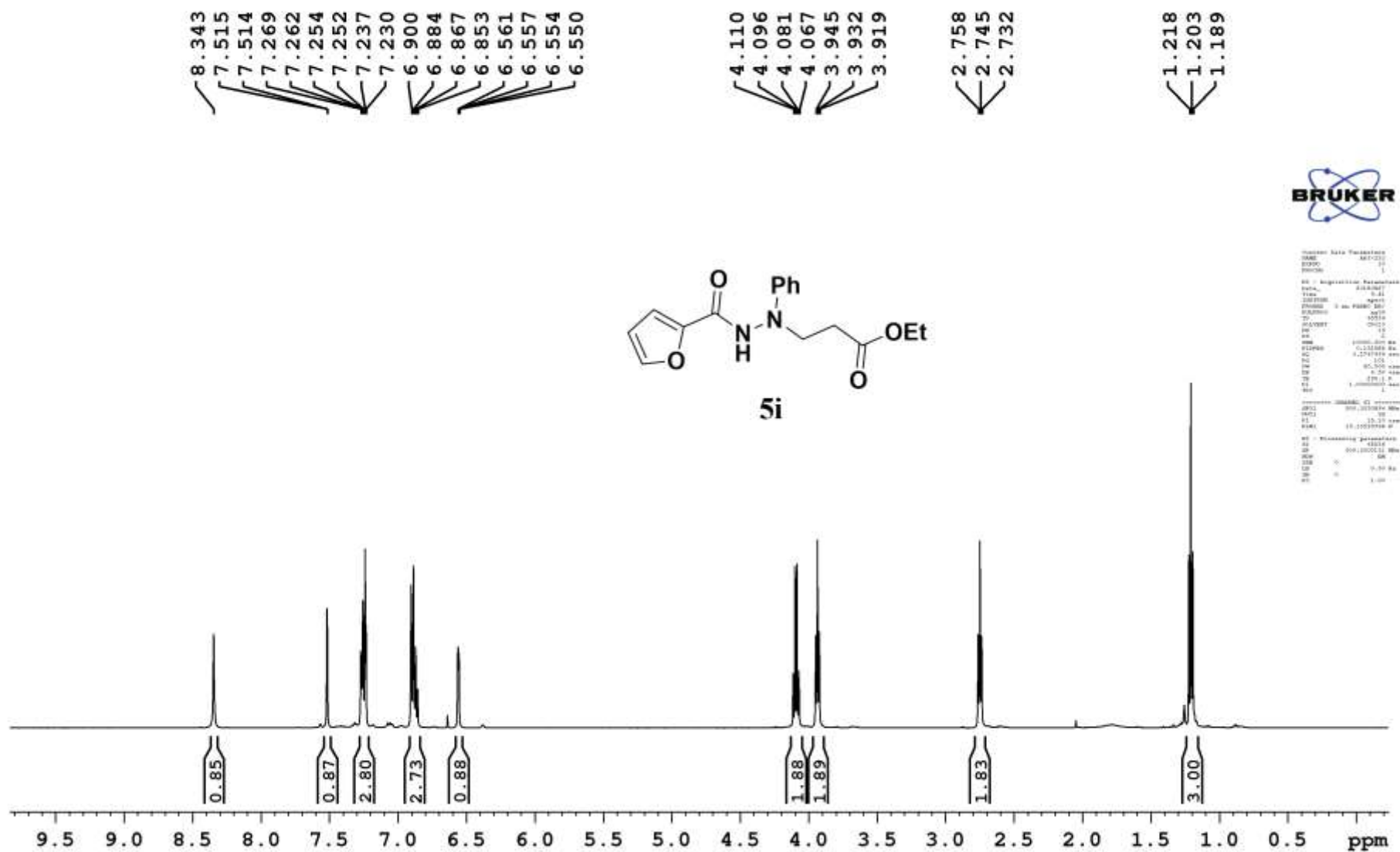


Acquired Date Parameters  
Date: 09/11/2018  
Time: 10:10:10  
Operator: [illegible]  
Sample: [illegible]  
Pulse Program: zgpg30  
Acquisition: 400 MHz, 1H  
F2: 400.146 MHz  
SFO: 400.146 MHz  
AQ: 1.19999996 sec  
RG: 655.36  
SF: 400.146 MHz  
WDW: EM  
SSB: 0  
GB: 0  
PC: 1.00  
FIDRES: 0.000180 Hz  
AQRES: 0.000180 Hz  
F2 - Acquisition Parameters  
Date: 09/11/2018  
Time: 10:10:10  
Operator: [illegible]  
Sample: [illegible]  
Pulse Program: zgpg30  
Acquisition: 400 MHz, 1H  
F2: 400.146 MHz  
SFO: 400.146 MHz  
AQ: 1.19999996 sec  
RG: 655.36  
SF: 400.146 MHz  
WDW: EM  
SSB: 0  
GB: 0  
PC: 1.00  
FIDRES: 0.000180 Hz  
AQRES: 0.000180 Hz





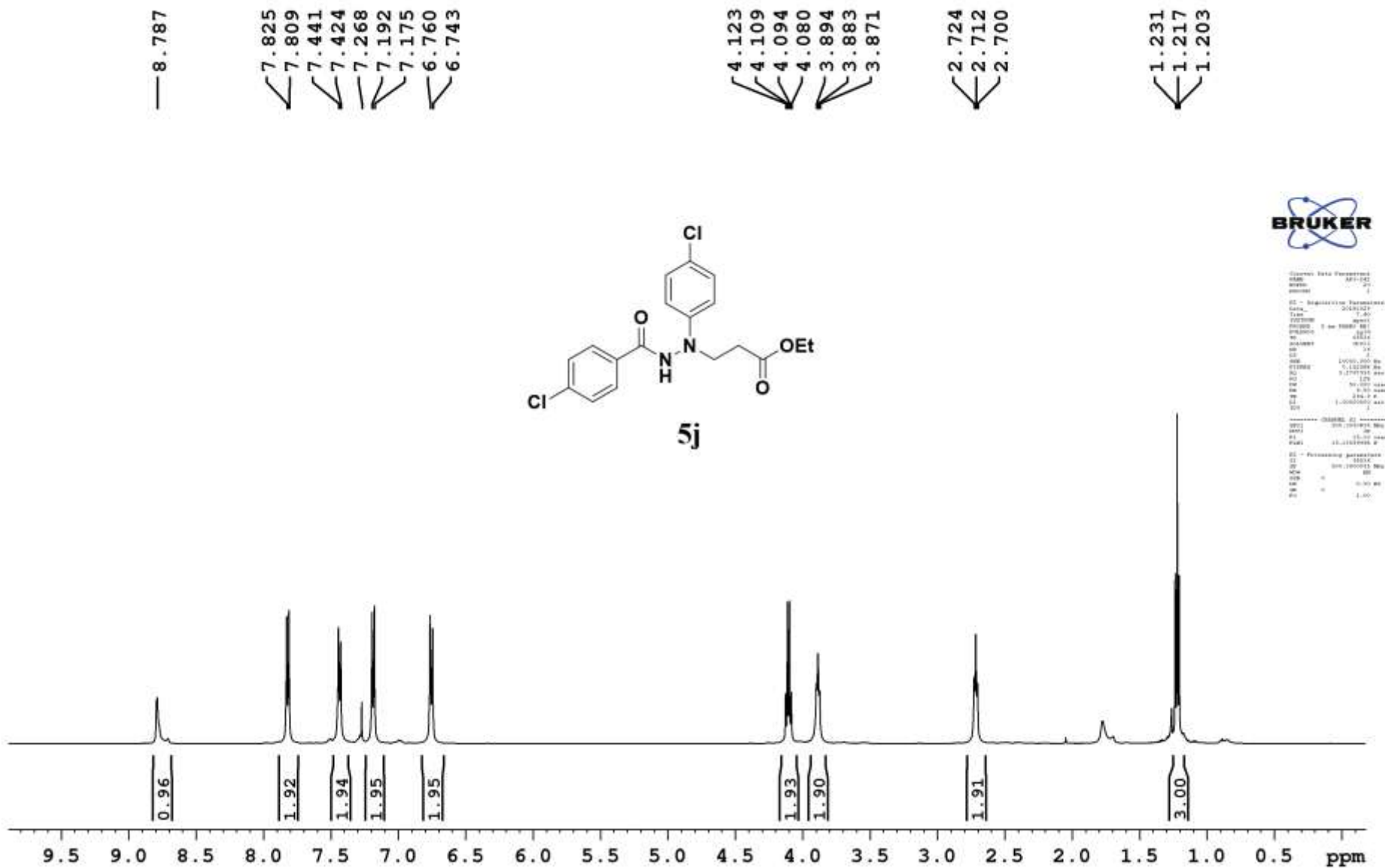
ES-AKJ-233; 27/08/2018





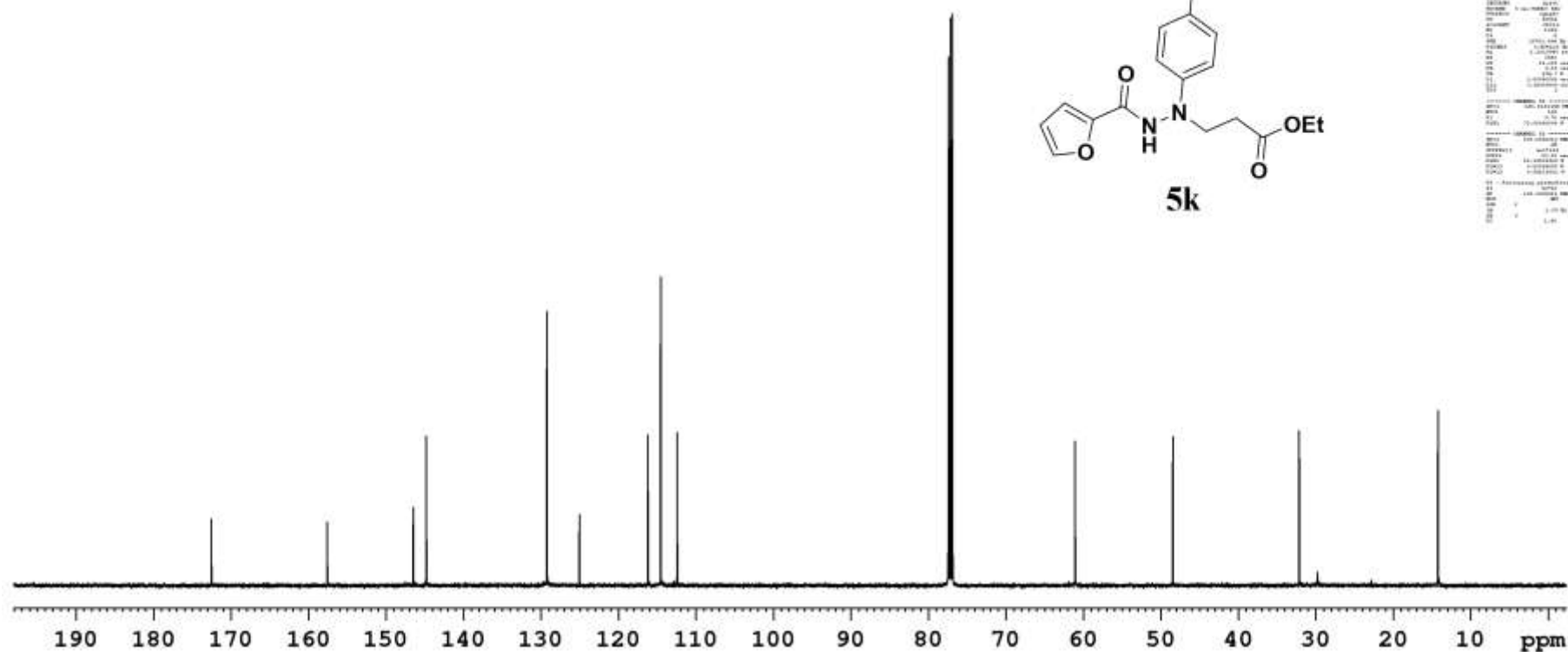
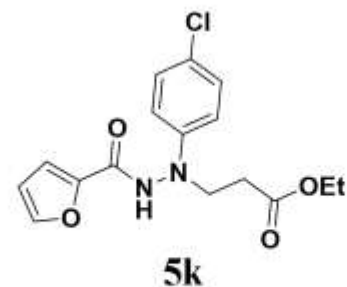


ES-AKJ-242; 29/10/2018

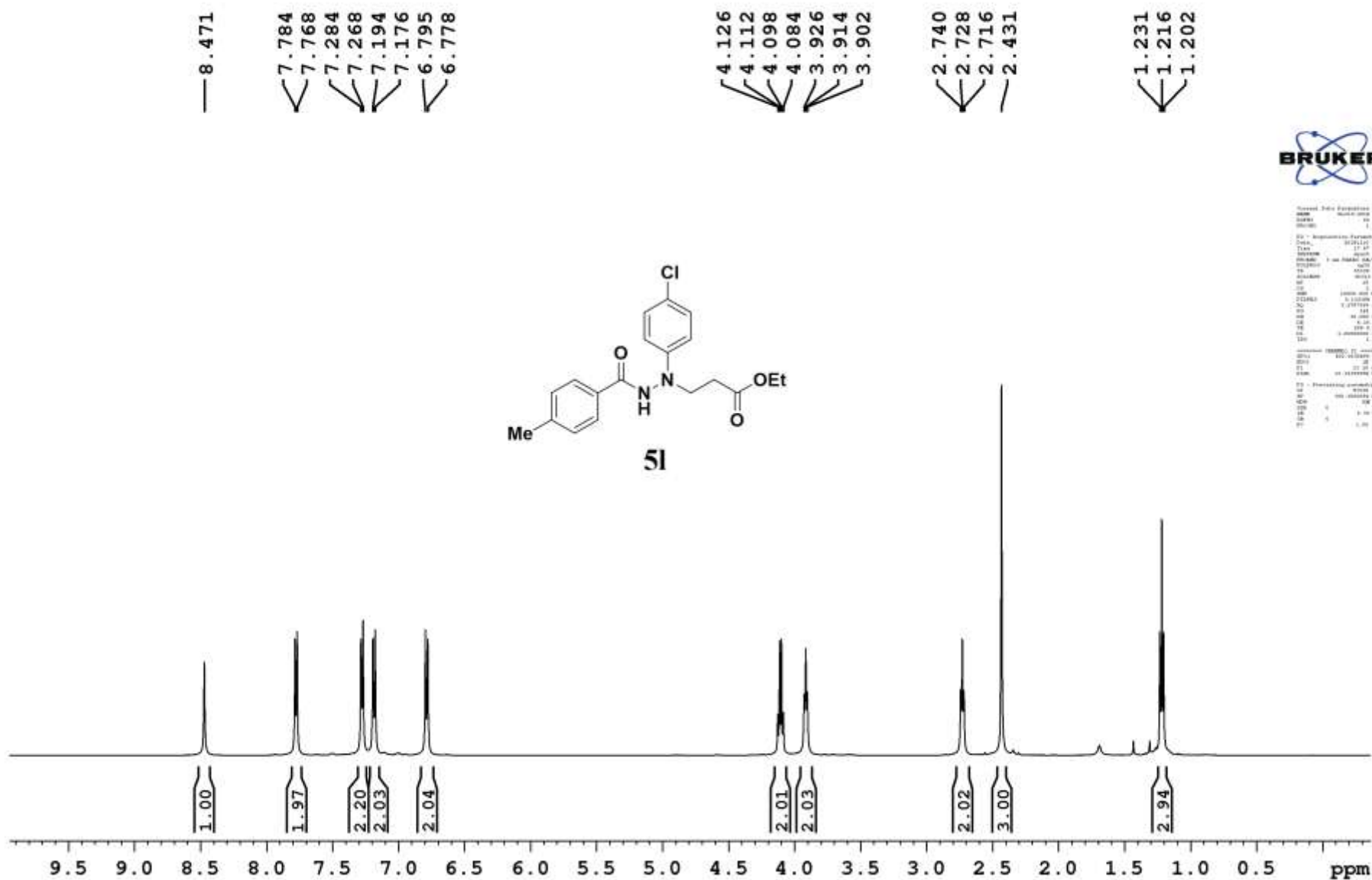




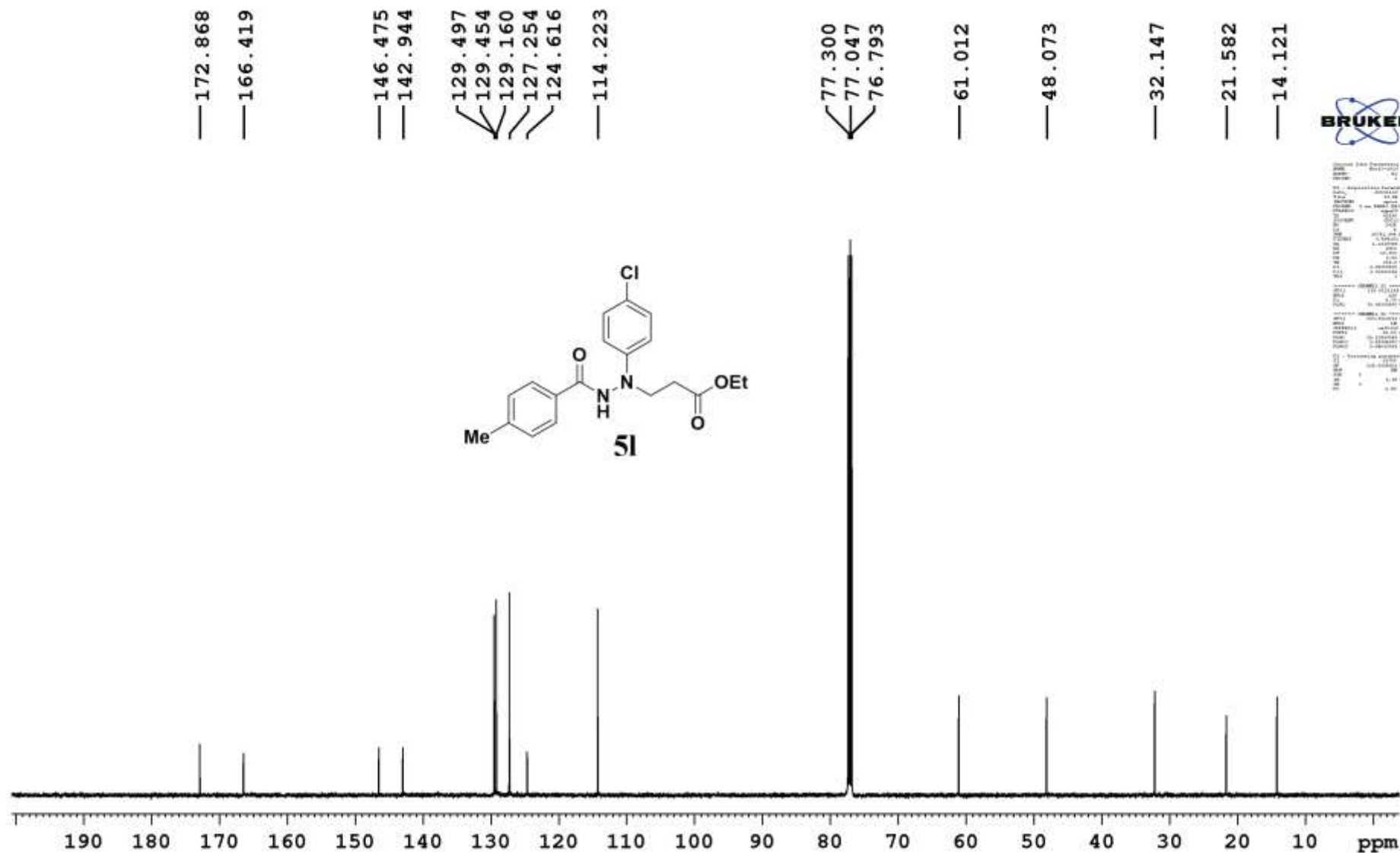




ES-AKJ-225; 10/11/2018



ES-AKJ-225; 10/11/2018





ES-AKJ-239; CDC13; 20/02/2019

—172.877  
—165.986  
—162.865

—146.581

—129.140  
—124.566  
—124.546

—114.202  
—114.051

—77.278  
—77.024  
—76.770

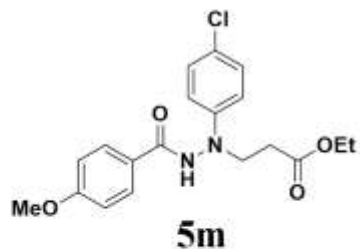
—60.982

—55.482

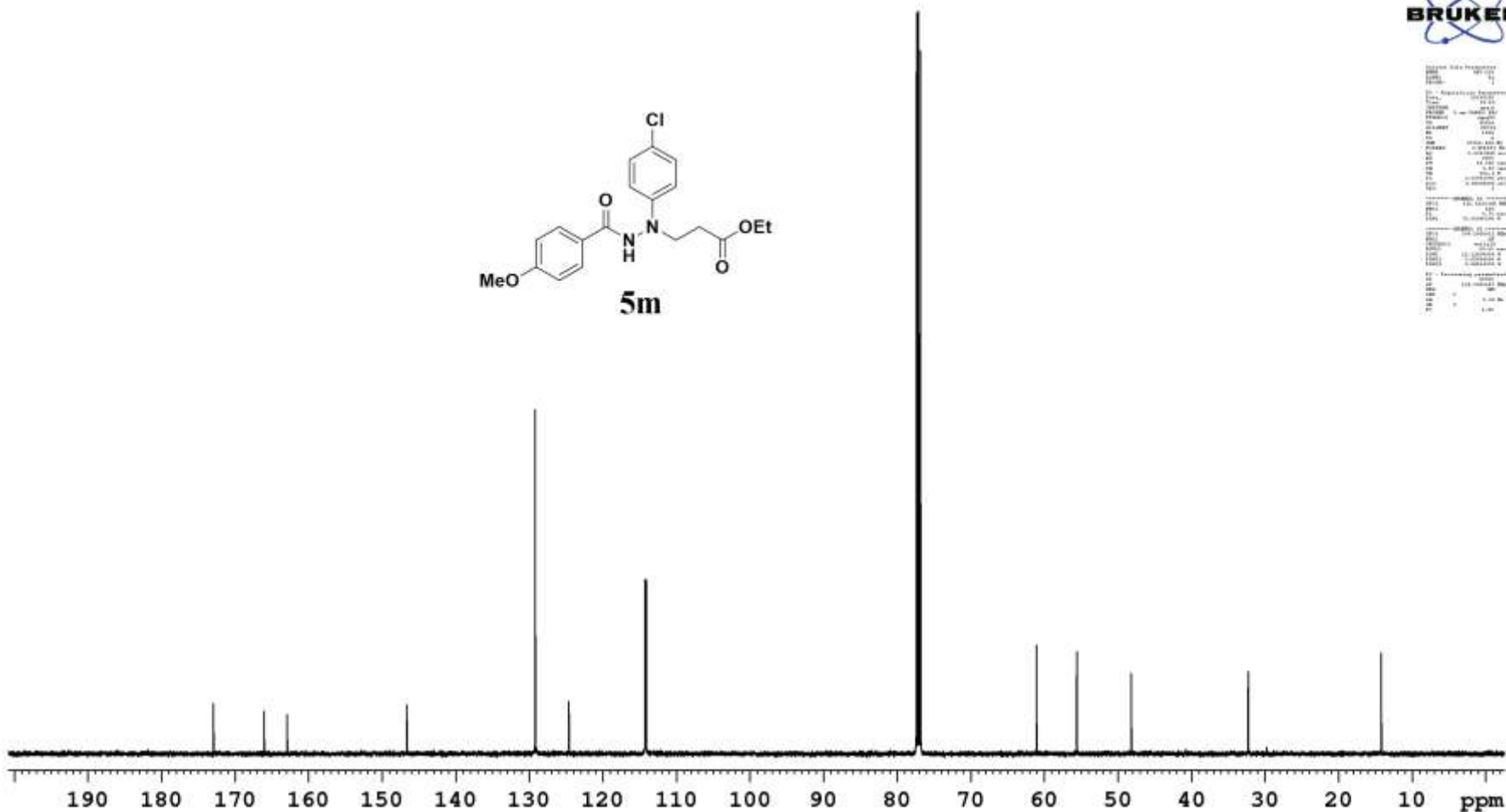
—48.092

—32.194

—14.107

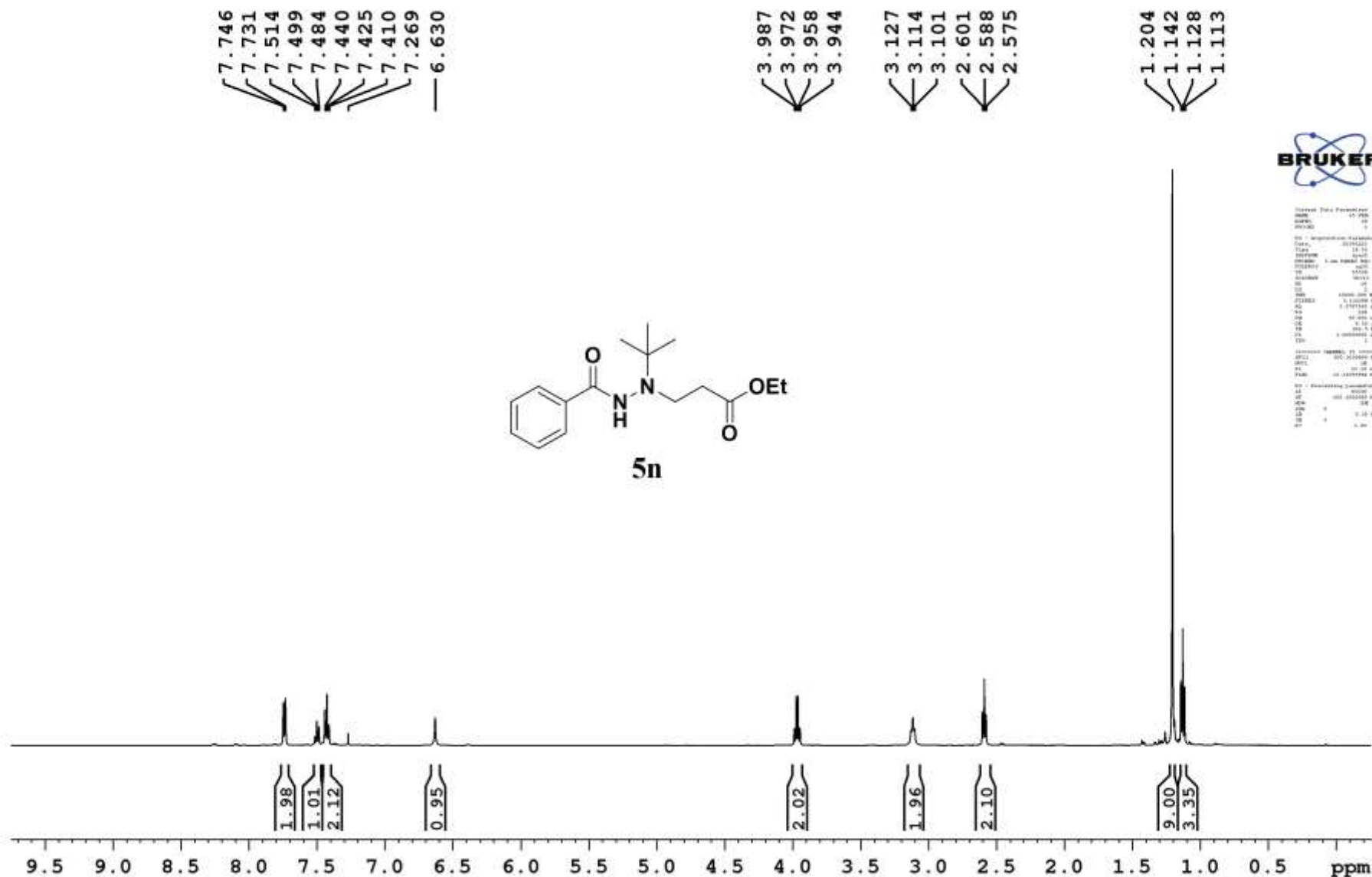


1D 13C NMR Spectrum  
 Date: 20/02/2019  
 Time: 10:11:14  
 File: ES-AKJ-239  
 F2: 125.76 MHz  
 F1: 500.13 MHz  
 A1: 13C  
 P1: 12.00  
 SFO: 100.625 MHz  
 A2: 13C  
 P2: 12.00  
 SFO: 100.625 MHz  
 A3: 13C  
 P3: 12.00  
 SFO: 100.625 MHz  
 A4: 13C  
 P4: 12.00  
 SFO: 100.625 MHz  
 A5: 13C  
 P5: 12.00  
 SFO: 100.625 MHz  
 A6: 13C  
 P6: 12.00  
 SFO: 100.625 MHz  
 A7: 13C  
 P7: 12.00  
 SFO: 100.625 MHz  
 A8: 13C  
 P8: 12.00  
 SFO: 100.625 MHz  
 A9: 13C  
 P9: 12.00  
 SFO: 100.625 MHz  
 A10: 13C  
 P10: 12.00  
 SFO: 100.625 MHz  
 A11: 13C  
 P11: 12.00  
 SFO: 100.625 MHz  
 A12: 13C  
 P12: 12.00  
 SFO: 100.625 MHz  
 A13: 13C  
 P13: 12.00  
 SFO: 100.625 MHz  
 A14: 13C  
 P14: 12.00  
 SFO: 100.625 MHz  
 A15: 13C  
 P15: 12.00  
 SFO: 100.625 MHz  
 A16: 13C  
 P16: 12.00  
 SFO: 100.625 MHz  
 A17: 13C  
 P17: 12.00  
 SFO: 100.625 MHz  
 A18: 13C  
 P18: 12.00  
 SFO: 100.625 MHz  
 A19: 13C  
 P19: 12.00  
 SFO: 100.625 MHz  
 A20: 13C  
 P20: 12.00  
 SFO: 100.625 MHz  
 A21: 13C  
 P21: 12.00  
 SFO: 100.625 MHz  
 A22: 13C  
 P22: 12.00  
 SFO: 100.625 MHz  
 A23: 13C  
 P23: 12.00  
 SFO: 100.625 MHz  
 A24: 13C  
 P24: 12.00  
 SFO: 100.625 MHz  
 A25: 13C  
 P25: 12.00  
 SFO: 100.625 MHz  
 A26: 13C  
 P26: 12.00  
 SFO: 100.625 MHz  
 A27: 13C  
 P27: 12.00  
 SFO: 100.625 MHz  
 A28: 13C  
 P28: 12.00  
 SFO: 100.625 MHz  
 A29: 13C  
 P29: 12.00  
 SFO: 100.625 MHz  
 A30: 13C  
 P30: 12.00  
 SFO: 100.625 MHz  
 A31: 13C  
 P31: 12.00  
 SFO: 100.625 MHz  
 A32: 13C  
 P32: 12.00  
 SFO: 100.625 MHz  
 A33: 13C  
 P33: 12.00  
 SFO: 100.625 MHz  
 A34: 13C  
 P34: 12.00  
 SFO: 100.625 MHz  
 A35: 13C  
 P35: 12.00  
 SFO: 100.625 MHz  
 A36: 13C  
 P36: 12.00  
 SFO: 100.625 MHz  
 A37: 13C  
 P37: 12.00  
 SFO: 100.625 MHz  
 A38: 13C  
 P38: 12.00  
 SFO: 100.625 MHz  
 A39: 13C  
 P39: 12.00  
 SFO: 100.625 MHz  
 A40: 13C  
 P40: 12.00  
 SFO: 100.625 MHz  
 A41: 13C  
 P41: 12.00  
 SFO: 100.625 MHz  
 A42: 13C  
 P42: 12.00  
 SFO: 100.625 MHz  
 A43: 13C  
 P43: 12.00  
 SFO: 100.625 MHz  
 A44: 13C  
 P44: 12.00  
 SFO: 100.625 MHz  
 A45: 13C  
 P45: 12.00  
 SFO: 100.625 MHz  
 A46: 13C  
 P46: 12.00  
 SFO: 100.625 MHz  
 A47: 13C  
 P47: 12.00  
 SFO: 100.625 MHz  
 A48: 13C  
 P48: 12.00  
 SFO: 100.625 MHz  
 A49: 13C  
 P49: 12.00  
 SFO: 100.625 MHz  
 A50: 13C  
 P50: 12.00  
 SFO: 100.625 MHz  
 A51: 13C  
 P51: 12.00  
 SFO: 100.625 MHz  
 A52: 13C  
 P52: 12.00  
 SFO: 100.625 MHz  
 A53: 13C  
 P53: 12.00  
 SFO: 100.625 MHz  
 A54: 13C  
 P54: 12.00  
 SFO: 100.625 MHz  
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 P55: 12.00  
 SFO: 100.625 MHz  
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 P56: 12.00  
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 A57: 13C  
 P57: 12.00  
 SFO: 100.625 MHz  
 A58: 13C  
 P58: 12.00  
 SFO: 100.625 MHz  
 A59: 13C  
 P59: 12.00  
 SFO: 100.625 MHz  
 A60: 13C  
 P60: 12.00  
 SFO: 100.625 MHz  
 A61: 13C  
 P61: 12.00  
 SFO: 100.625 MHz  
 A62: 13C  
 P62: 12.00  
 SFO: 100.625 MHz  
 A63: 13C  
 P63: 12.00  
 SFO: 100.625 MHz  
 A64: 13C  
 P64: 12.00  
 SFO: 100.625 MHz  
 A65: 13C  
 P65: 12.00  
 SFO: 100.625 MHz  
 A66: 13C  
 P66: 12.00  
 SFO: 100.625 MHz  
 A67: 13C  
 P67: 12.00  
 SFO: 100.625 MHz  
 A68: 13C  
 P68: 12.00  
 SFO: 100.625 MHz  
 A69: 13C  
 P69: 12.00  
 SFO: 100.625 MHz  
 A70: 13C  
 P70: 12.00  
 SFO: 100.625 MHz  
 A71: 13C  
 P71: 12.00  
 SFO: 100.625 MHz  
 A72: 13C  
 P72: 12.00  
 SFO: 100.625 MHz  
 A73: 13C  
 P73: 12.00  
 SFO: 100.625 MHz  
 A74: 13C  
 P74: 12.00  
 SFO: 100.625 MHz  
 A75: 13C  
 P75: 12.00  
 SFO: 100.625 MHz  
 A76: 13C  
 P76: 12.00  
 SFO: 100.625 MHz  
 A77: 13C  
 P77: 12.00  
 SFO: 100.625 MHz  
 A78: 13C  
 P78: 12.00  
 SFO: 100.625 MHz  
 A79: 13C  
 P79: 12.00  
 SFO: 100.625 MHz  
 A80: 13C  
 P80: 12.00  
 SFO: 100.625 MHz  
 A81: 13C  
 P81: 12.00  
 SFO: 100.625 MHz  
 A82: 13C  
 P82: 12.00  
 SFO: 100.625 MHz  
 A83: 13C  
 P83: 12.00  
 SFO: 100.625 MHz  
 A84: 13C  
 P84: 12.00  
 SFO: 100.625 MHz  
 A85: 13C  
 P85: 12.00  
 SFO: 100.625 MHz  
 A86: 13C  
 P86: 12.00  
 SFO: 100.625 MHz  
 A87: 13C  
 P87: 12.00  
 SFO: 100.625 MHz  
 A88: 13C  
 P88: 12.00  
 SFO: 100.625 MHz  
 A89: 13C  
 P89: 12.00  
 SFO: 100.625 MHz  
 A90: 13C  
 P90: 12.00  
 SFO: 100.625 MHz  
 A91: 13C  
 P91: 12.00  
 SFO: 100.625 MHz  
 A92: 13C  
 P92: 12.00  
 SFO: 100.625 MHz  
 A93: 13C  
 P93: 12.00  
 SFO: 100.625 MHz  
 A94: 13C  
 P94: 12.00  
 SFO: 100.625 MHz  
 A95: 13C  
 P95: 12.00  
 SFO: 100.625 MHz  
 A96: 13C  
 P96: 12.00  
 SFO: 100.625 MHz  
 A97: 13C  
 P97: 12.00  
 SFO: 100.625 MHz  
 A98: 13C  
 P98: 12.00  
 SFO: 100.625 MHz  
 A99: 13C  
 P99: 12.00  
 SFO: 100.625 MHz  
 A100: 13C  
 P100: 12.00  
 SFO: 100.625 MHz

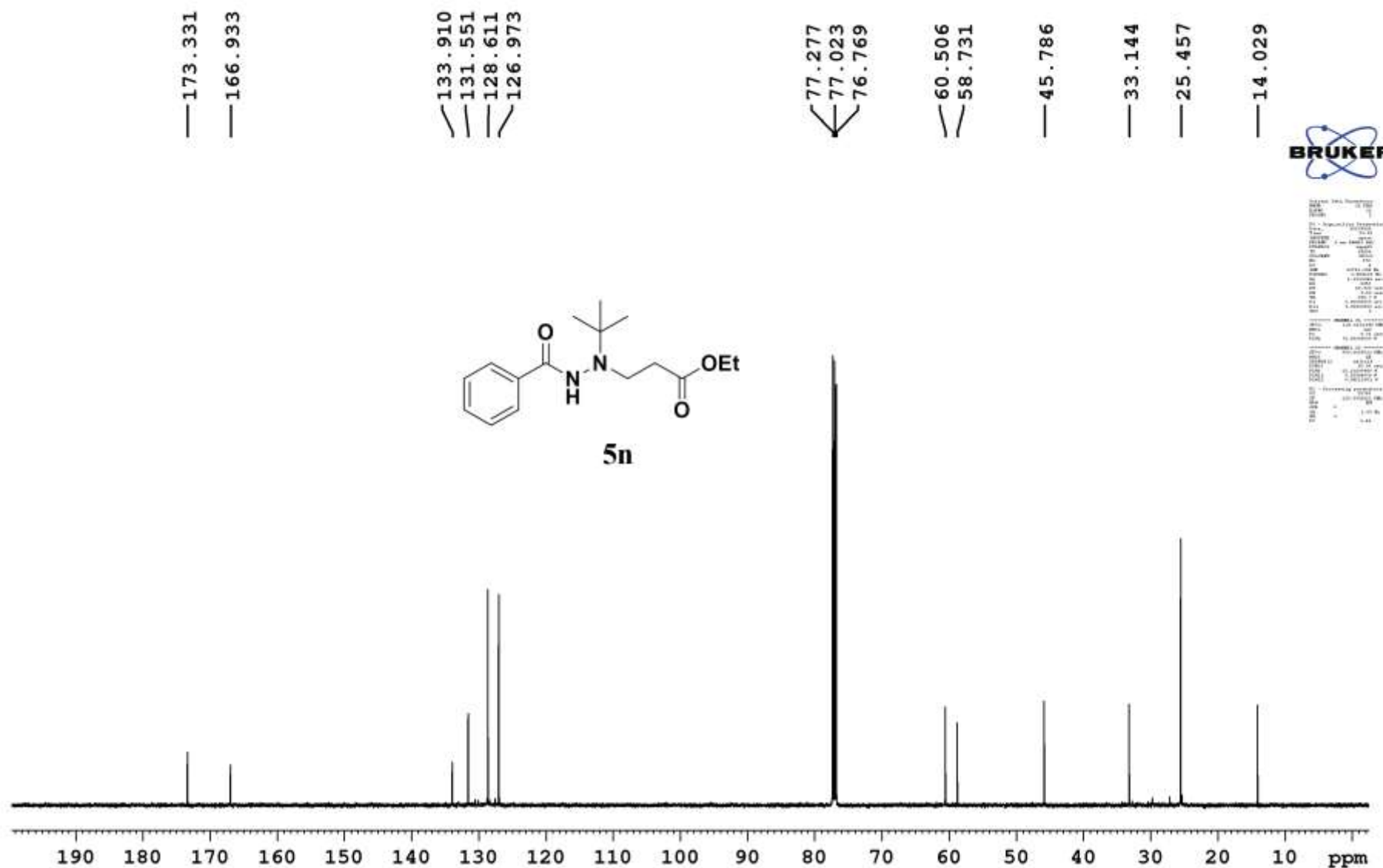




ES-AKJ-MC-54; CDC13; 25/02/2019



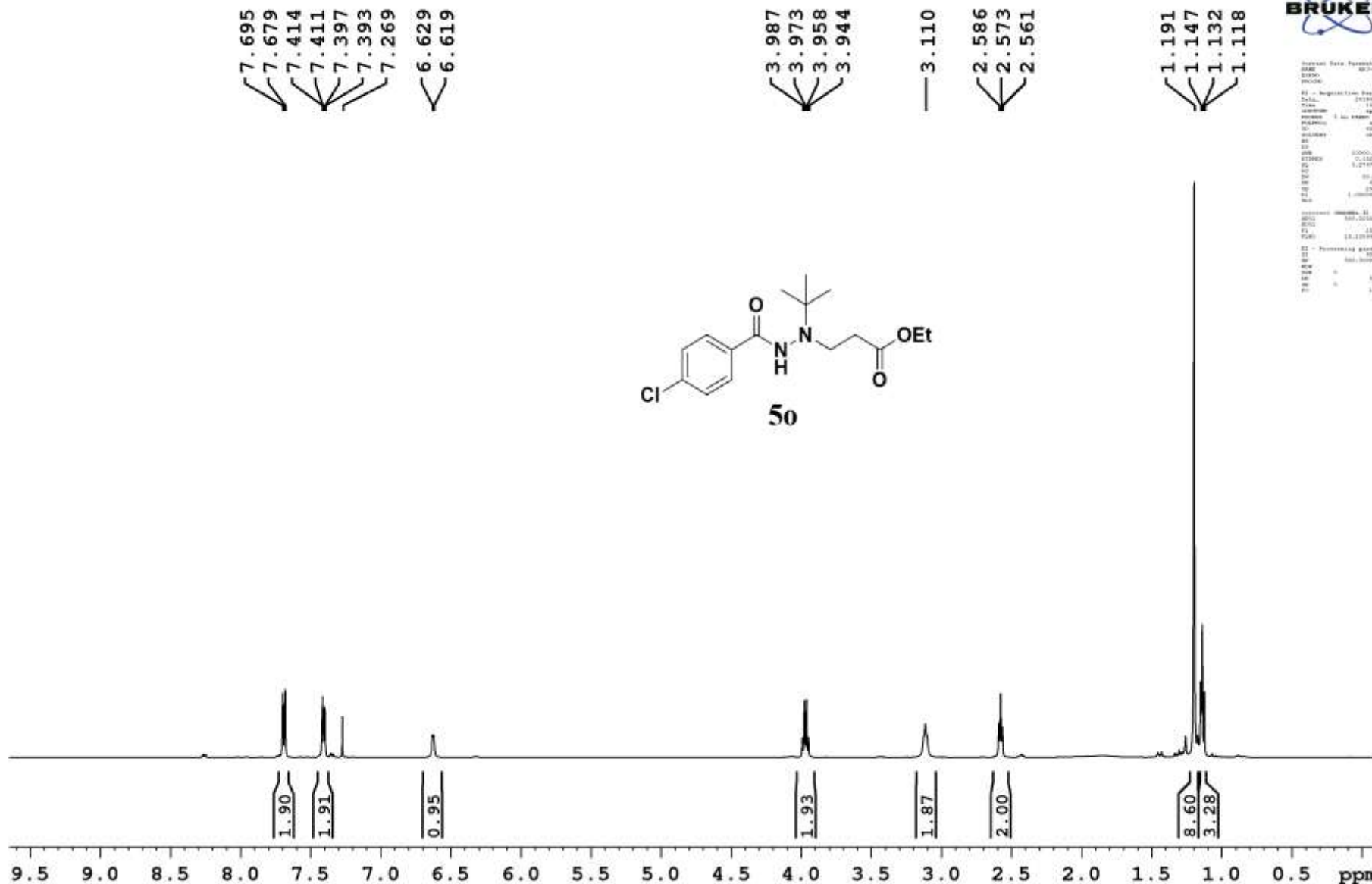
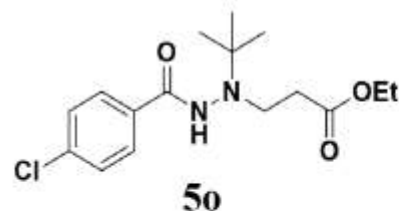
ES-AKJ-MC-54; CDC13; 25/02/2019

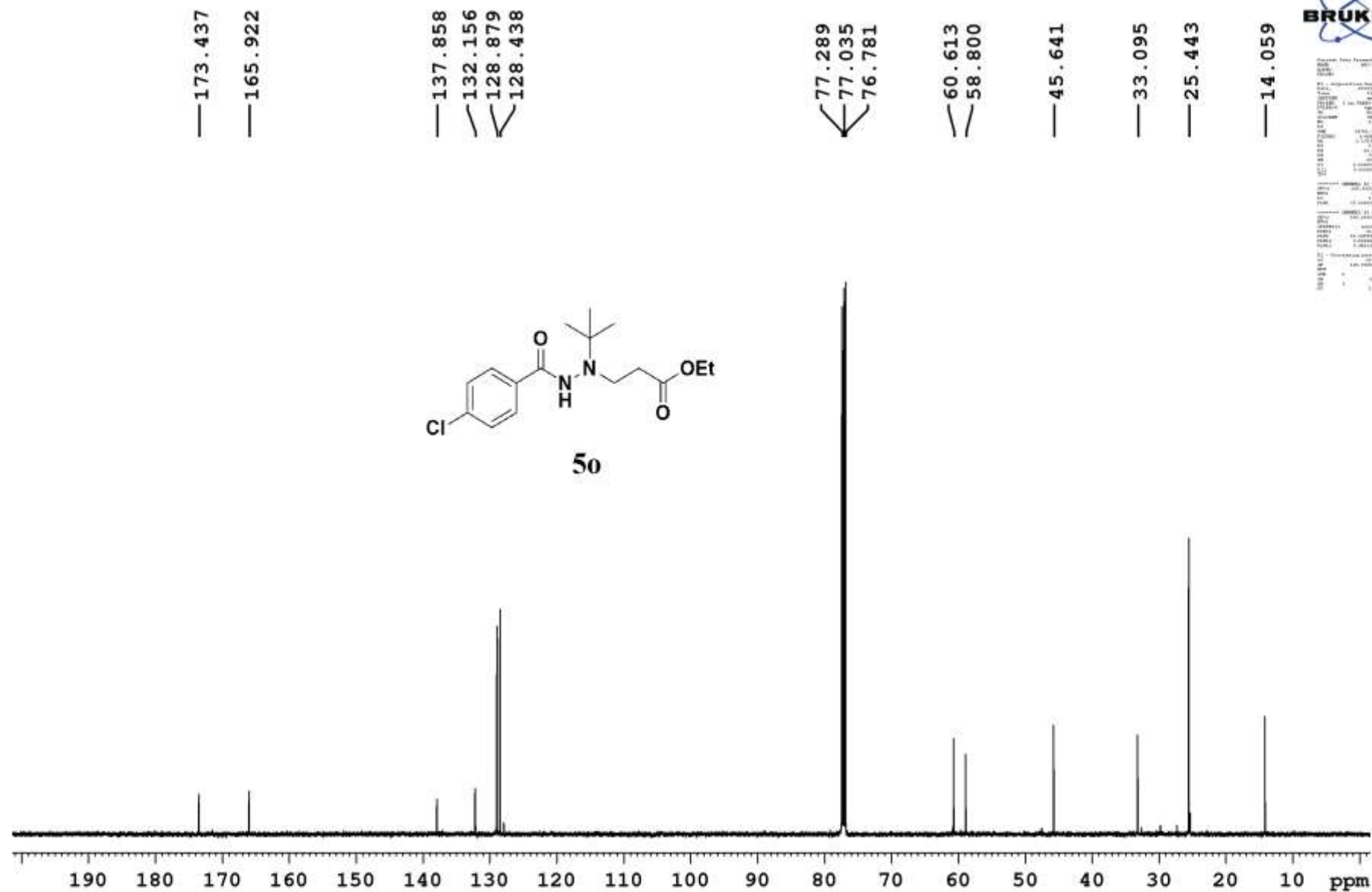


Sample Name: ES-AKJ-MC-54  
 Date: 25/02/2019  
 Time: 10:10  
 Operator: [illegible]  
 Instrument: Bruker Avance 400  
 P1: 12.00  
 PC: 1.00  
 PR: 1.00  
 PS: 1.00  
 PT: 1.00  
 PU: 1.00  
 PV: 1.00  
 PW: 1.00  
 PX: 1.00  
 PY: 1.00  
 PZ: 1.00  
 Q1: 1.00  
 Q2: 1.00  
 Q3: 1.00  
 Q4: 1.00  
 Q5: 1.00  
 Q6: 1.00  
 Q7: 1.00  
 Q8: 1.00  
 Q9: 1.00  
 Q10: 1.00  
 Q11: 1.00  
 Q12: 1.00  
 Q13: 1.00  
 Q14: 1.00  
 Q15: 1.00  
 Q16: 1.00  
 Q17: 1.00  
 Q18: 1.00  
 Q19: 1.00  
 Q20: 1.00  
 Q21: 1.00  
 Q22: 1.00  
 Q23: 1.00  
 Q24: 1.00  
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 Q26: 1.00  
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 Q45: 1.00  
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 Q53: 1.00  
 Q54: 1.00  
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 Q56: 1.00  
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 Q58: 1.00  
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 Q66: 1.00  
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 Q77: 1.00  
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 Q86: 1.00  
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 Q88: 1.00  
 Q89: 1.00  
 Q90: 1.00  
 Q91: 1.00  
 Q92: 1.00  
 Q93: 1.00  
 Q94: 1.00  
 Q95: 1.00  
 Q96: 1.00  
 Q97: 1.00  
 Q98: 1.00  
 Q99: 1.00  
 Q100: 1.00



Instrument Data Parameters  
 NAME: ES-AKJ-189-3LB1  
 PROJECT: 189-3LB1  
 Date: 14/06/2018  
 Time: 14:10  
 Operator: [blank]  
 Sample: 1.00 mg/ml  
 Solvent: CDCl<sub>3</sub>  
 Concentration: 0.025 g/ml  
 Acquisition: 128  
 Resolution: 0.000000 Hz  
 F2 (MHz): 500.136260  
 F1 (MHz): 125.761150  
 SWH (Hz): 5000.000  
 FID (Hz): 1.2747733  
 AQ (s): 1.28  
 S/N: 4.54  
 IN: 145.3  
 FI: 1.0000000  
 RG: 4  
 Processing parameters  
 SI: 32768  
 SF: 500.136260 MHz  
 WF: 0  
 LG: 3.00 Hz  
 HG: 0  
 PC: 1.00



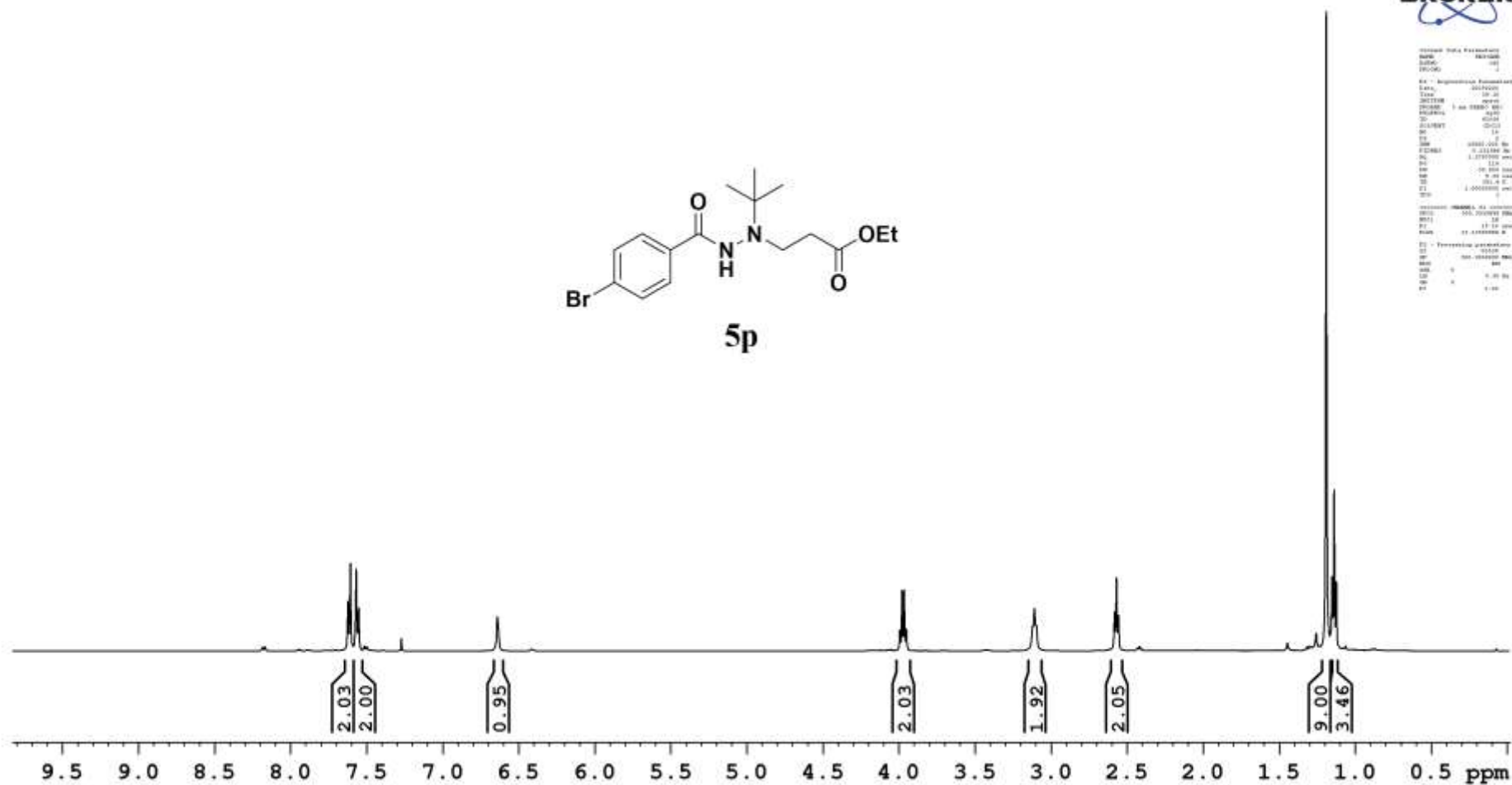
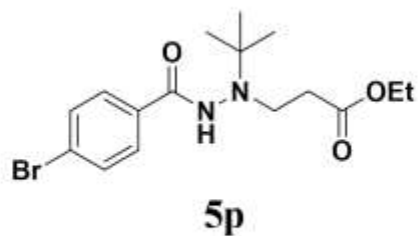


7.621  
7.605  
7.566  
7.550  
7.269

— 6.639

$\begin{array}{r} 3.118 \\ 3.106 \\ 3.094 \end{array}$ 
 $\begin{array}{r} 2.579 \\ 2.566 \\ 2.553 \end{array}$

1.187  
1.148  
1.134  
1.120



ES-RK-EXP-86P-13C-CDC13-30 AUG 18

— 173.452

— 166.082

132.561

131.846

128.635

126.279

77.328

77.074

76.820

60.645

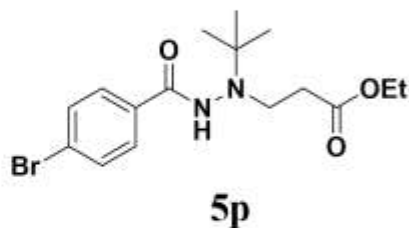
58.812

— 45.608

— 33.071

— 25.437

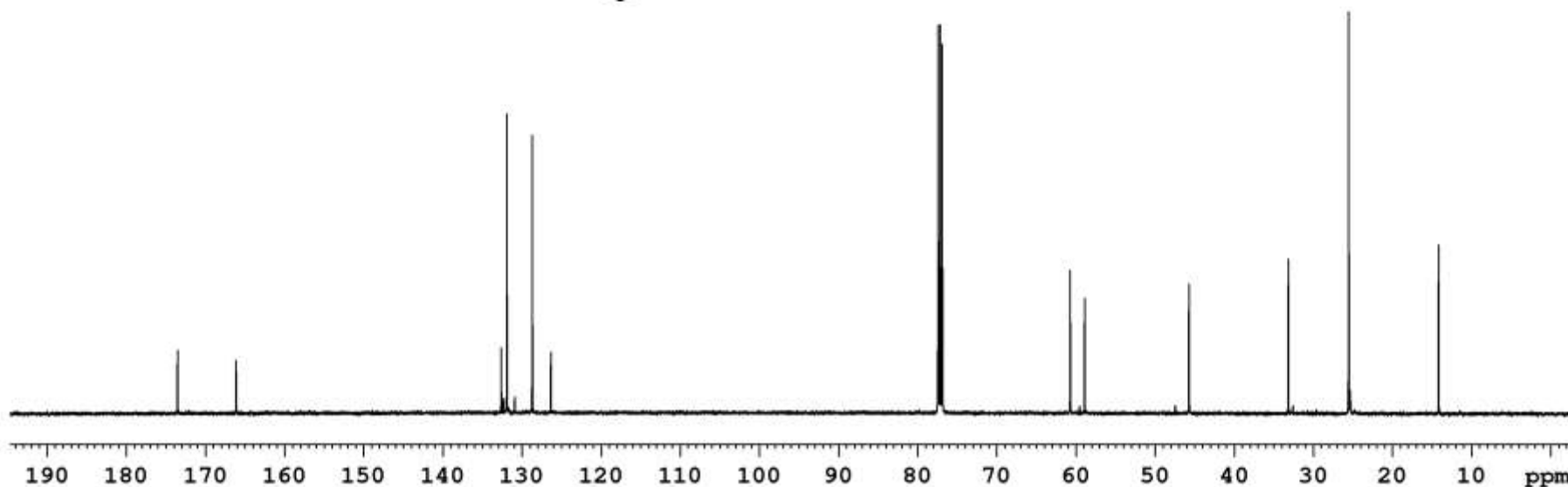
— 14.069

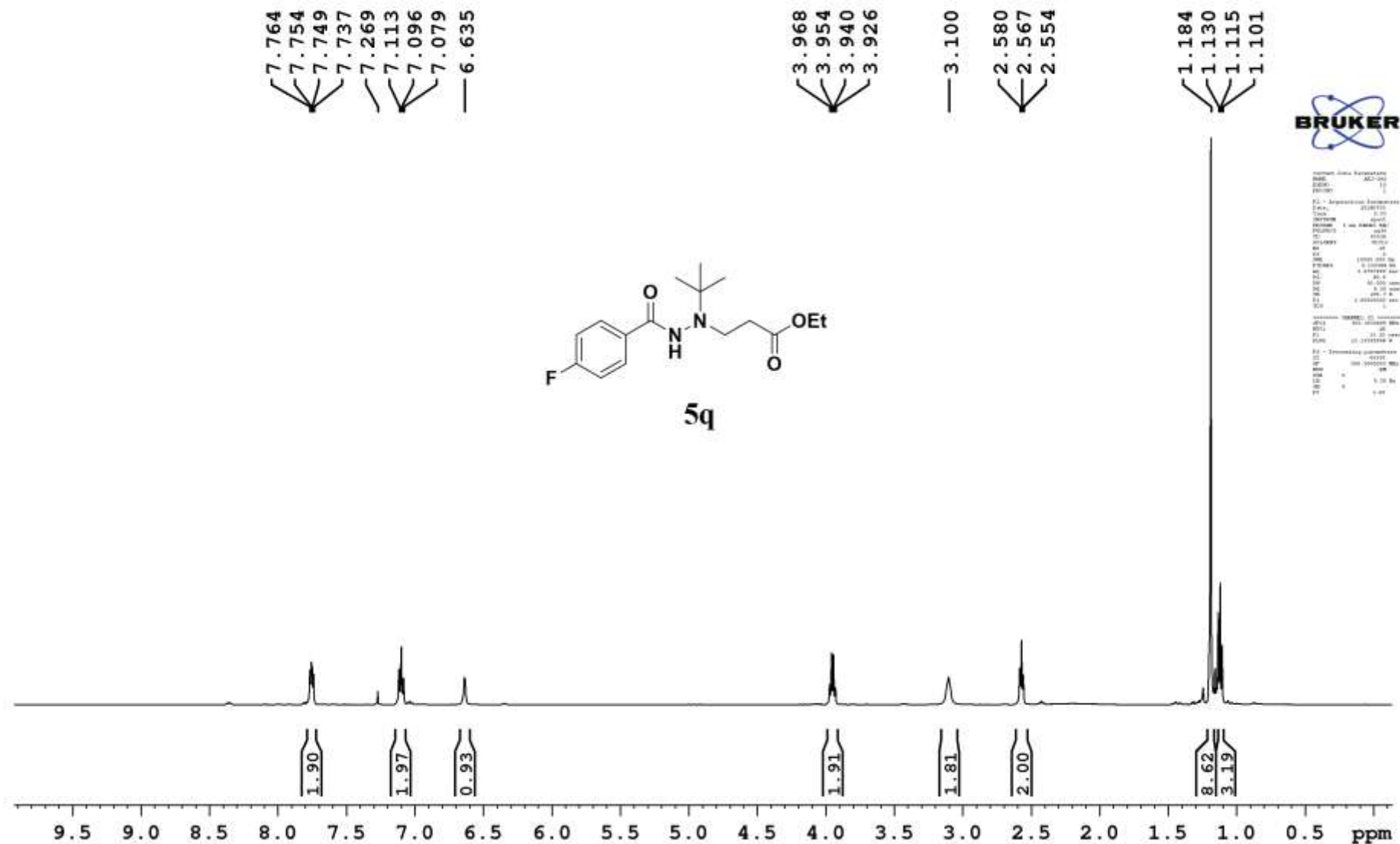


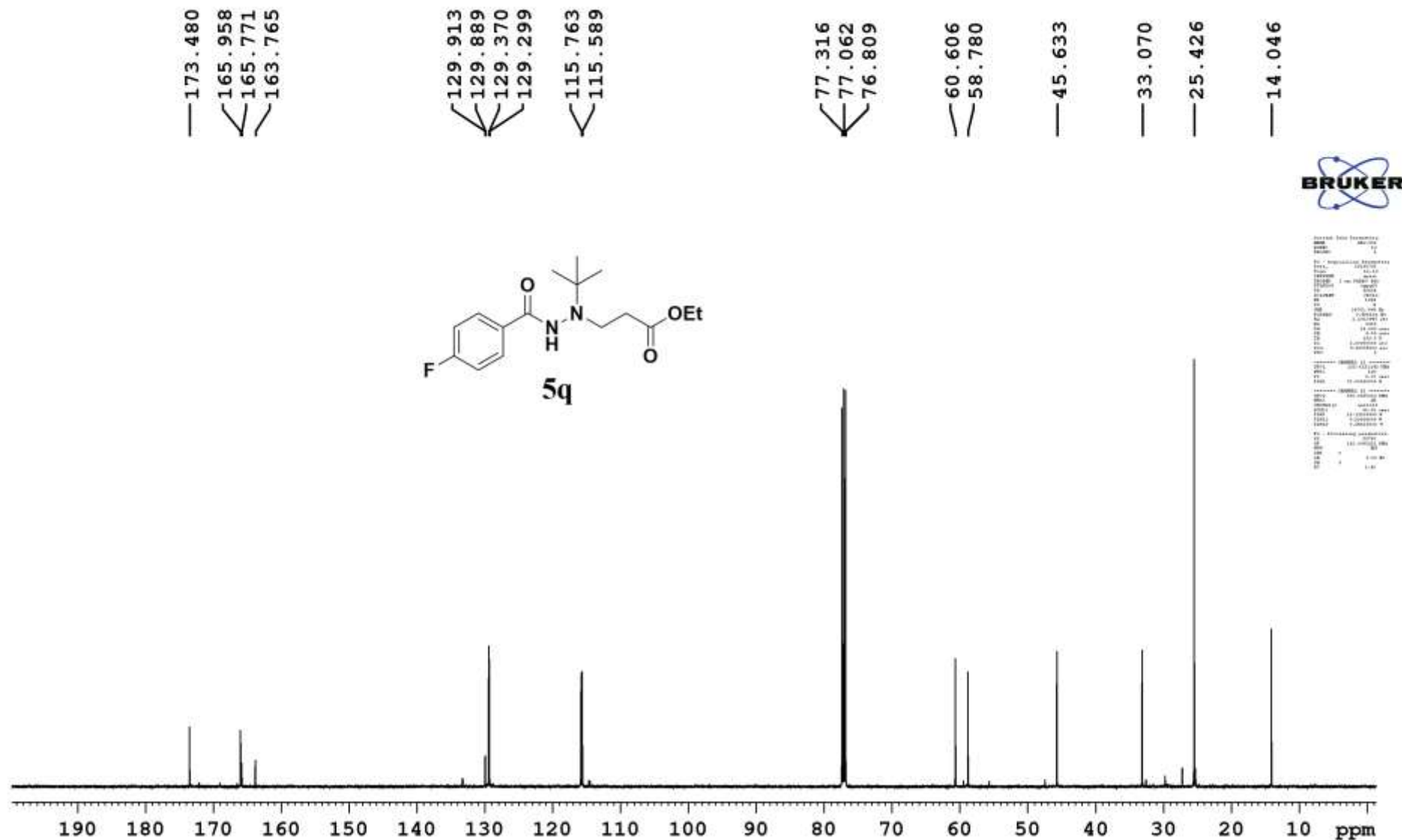
```

=====
NAME: 5p
EXPNO: 1
PROCNO: 1
PROCNAME: 5p
F2 - Acquisition Parameters
Date_ : 20170710
Time: 10.10
INSTRUM: spect
PROBHD: 5 mm QNP 1H/13
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NUC1: 13C
NUC2: 1H
=====
=====
NAME: 5p
EXPNO: 1
PROCNO: 1
PROCNAME: 5p
F2 - Processing parameters
Date_ : 20170710
Time: 10.10
INSTRUM: spect
PROBHD: 5 mm QNP 1H/13
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NUC1: 13C
NUC2: 1H
=====
=====
NAME: 5p
EXPNO: 1
PROCNO: 1
PROCNAME: 5p
F2 - Processing parameters
Date_ : 20170710
Time: 10.10
INSTRUM: spect
PROBHD: 5 mm QNP 1H/13
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NUC1: 13C
NUC2: 1H
=====

```



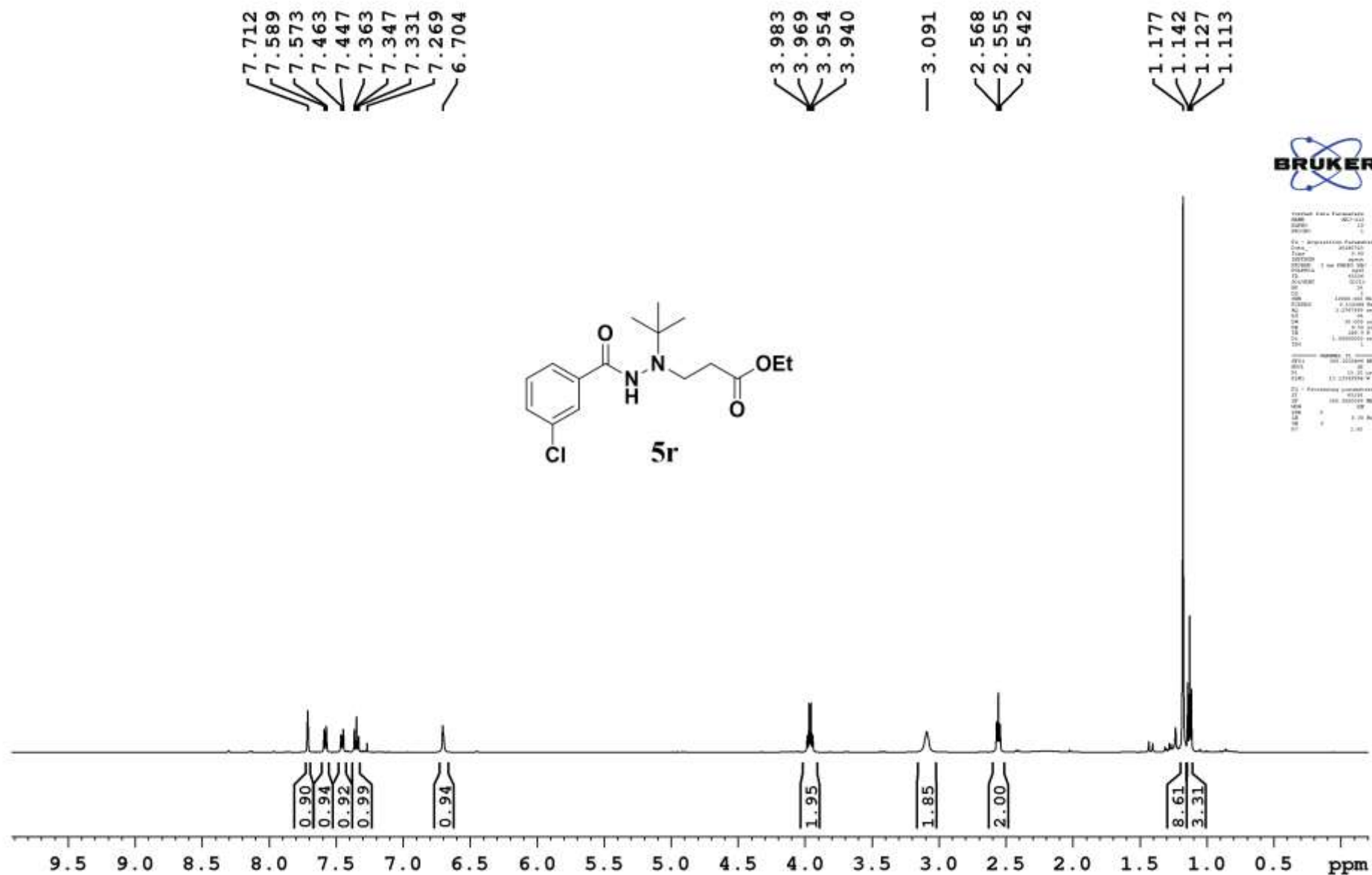




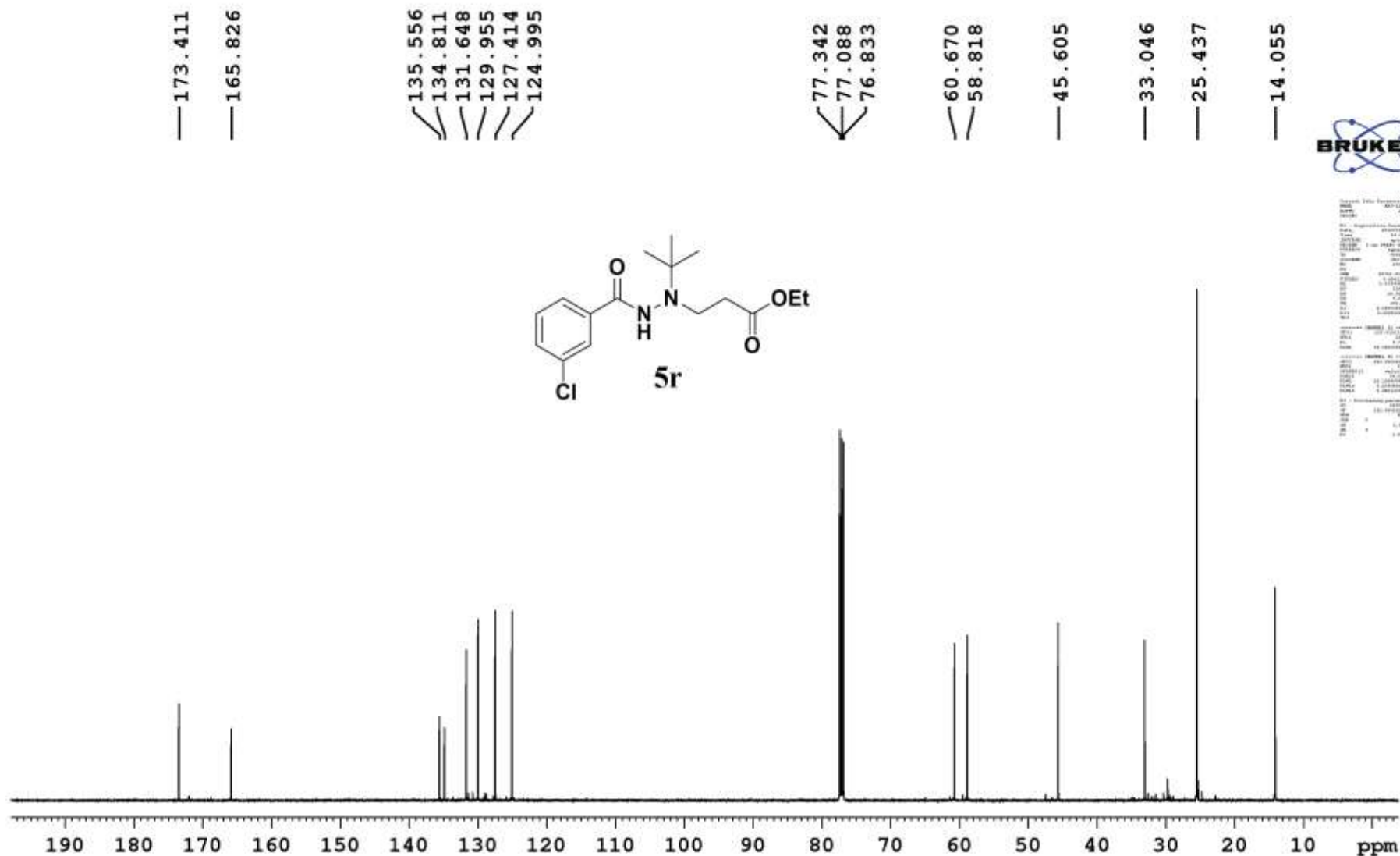
Acquired Data Summary  
 Date: 05/07/2018  
 Time: 10:45:10  
 File: 5q-13C-1D  
 Sample: 5q-13C-1D  
 Solvent: CDCl3  
 Concentration: 10.00 mg/mL  
 Volume: 0.50 mL  
 Weight: 0.50 g  
 Purity: 100.00%  
 MW: 274.34 g/mol  
 Formula: C16H21FNO4  
 SMILES: CCOC(=O)CCN(C(C)(C)C)C(=O)c1ccc(F)cc1  
 Acquisition Parameters  
 Name: 5q-13C-1D  
 Date: 05/07/2018  
 Time: 10:45:10  
 File: 5q-13C-1D  
 Sample: 5q-13C-1D  
 Solvent: CDCl3  
 Concentration: 10.00 mg/mL  
 Volume: 0.50 mL  
 Weight: 0.50 g  
 Purity: 100.00%  
 MW: 274.34 g/mol  
 Formula: C16H21FNO4  
 SMILES: CCOC(=O)CCN(C(C)(C)C)C(=O)c1ccc(F)cc1  
 Acquisition Parameters  
 Name: 5q-13C-1D  
 Date: 05/07/2018  
 Time: 10:45:10  
 File: 5q-13C-1D  
 Sample: 5q-13C-1D  
 Solvent: CDCl3  
 Concentration: 10.00 mg/mL  
 Volume: 0.50 mL  
 Weight: 0.50 g  
 Purity: 100.00%  
 MW: 274.34 g/mol  
 Formula: C16H21FNO4  
 SMILES: CCOC(=O)CCN(C(C)(C)C)C(=O)c1ccc(F)cc1



ES-AKJ-215-LB1; 23/07/2018

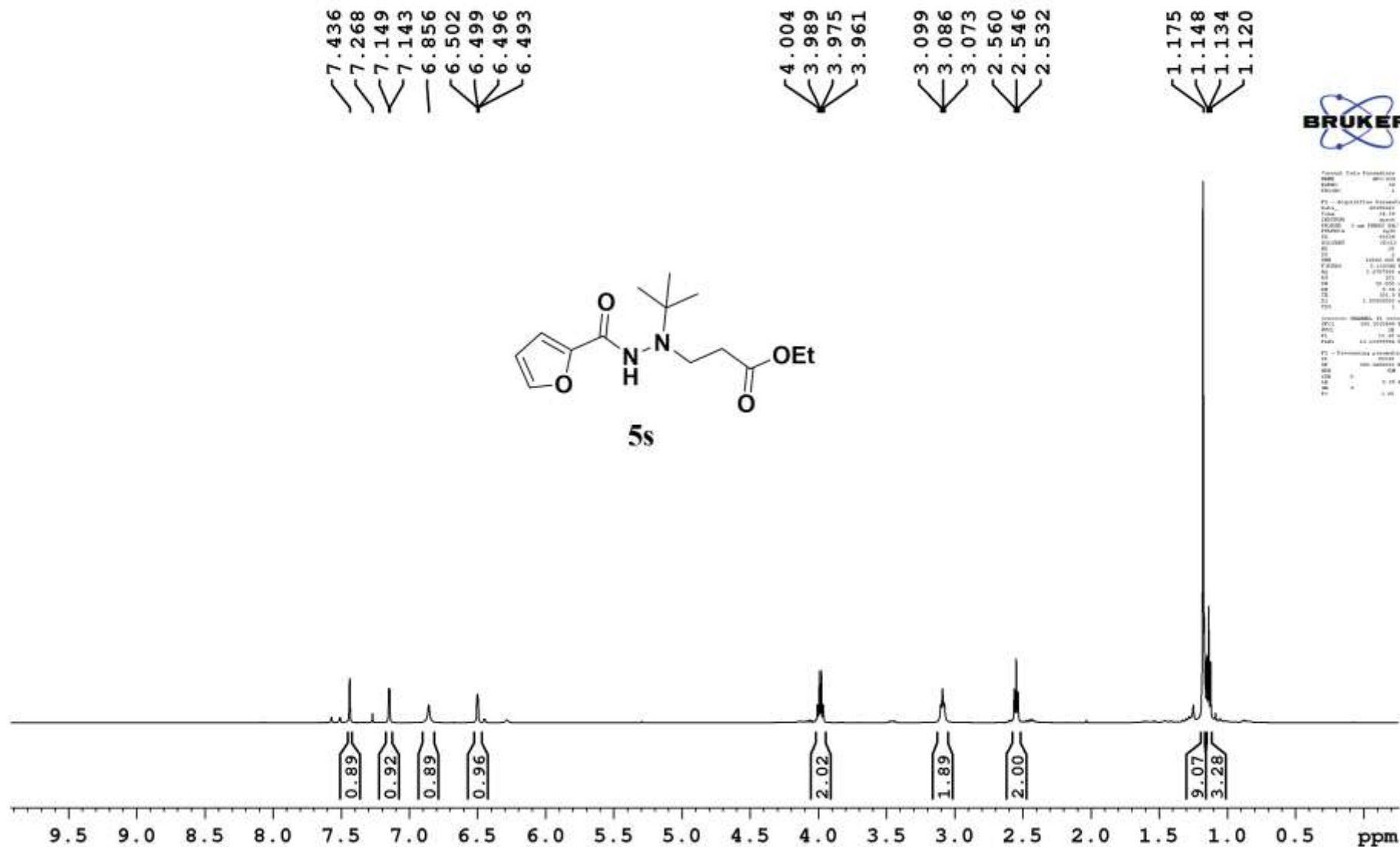


ES-AKJ-215-LB1; 23/07/2018



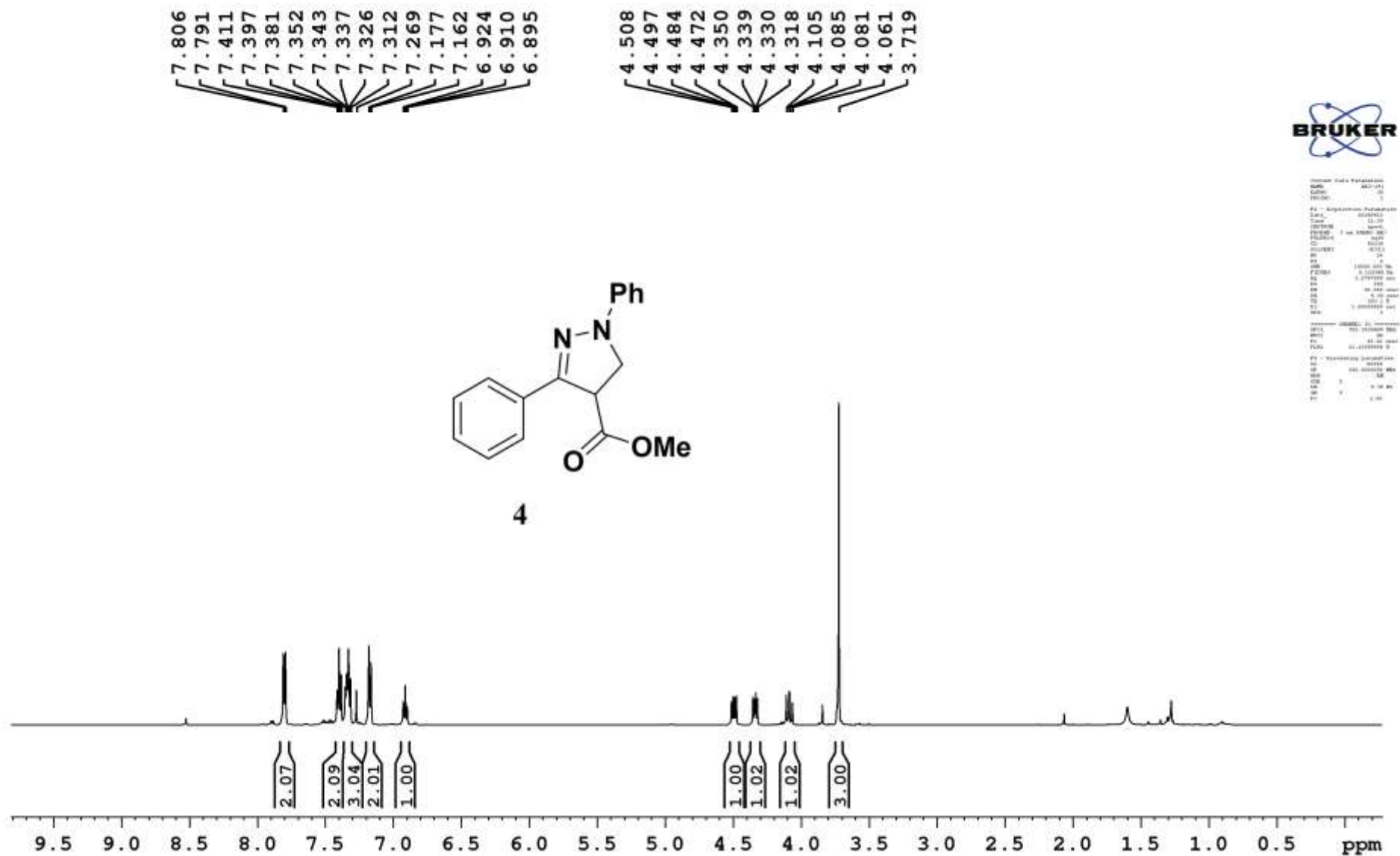
Sample: ES-AKJ-215-LB1  
Date: 23/07/2018  
Time: 14:14  
Operator: [illegible]  
Pulse: zgpg30  
Acq: 128000  
F2: 100.625  
SOLVENT: CDCl3  
NS: 1024  
DS: 4  
SWH: 19999.98 Hz  
FIDRES: 0.111111 Hz  
AQ: 0.357143 s  
RG: 655  
DQ: 0.000000 s  
DE: 1.900000 dB  
TE: 300.2 K  
T1: 1.500000 s  
T2: 0.100000 s  
T2RHO: 0.000000 s  
T2DELTA: 0.000000 s  
T2PHASE2: 0.000000 s  
T2PHASE3: 0.000000 s  
T2PHASE4: 0.000000 s  
T2PHASE5: 0.000000 s  
T2PHASE6: 0.000000 s  
T2PHASE7: 0.000000 s  
T2PHASE8: 0.000000 s  
T2PHASE9: 0.000000 s  
T2PHASE10: 0.000000 s  
T2PHASE11: 0.000000 s  
T2PHASE12: 0.000000 s  
T2PHASE13: 0.000000 s  
T2PHASE14: 0.000000 s  
T2PHASE15: 0.000000 s  
T2PHASE16: 0.000000 s  
T2PHASE17: 0.000000 s  
T2PHASE18: 0.000000 s  
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T2PHASE20: 0.000000 s  
T2PHASE21: 0.000000 s  
T2PHASE22: 0.000000 s  
T2PHASE23: 0.000000 s  
T2PHASE24: 0.000000 s  
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T2PHASE27: 0.000000 s  
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T2PHASE29: 0.000000 s  
T2PHASE30: 0.000000 s  
T2PHASE31: 0.000000 s  
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T2PHASE33: 0.000000 s  
T2PHASE34: 0.000000 s  
T2PHASE35: 0.000000 s  
T2PHASE36: 0.000000 s  
T2PHASE37: 0.000000 s  
T2PHASE38: 0.000000 s  
T2PHASE39: 0.000000 s  
T2PHASE40: 0.000000 s  
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T2PHASE66: 0.000000 s  
T2PHASE67: 0.000000 s  
T2PHASE68: 0.000000 s  
T2PHASE69: 0.000000 s  
T2PHASE70: 0.000000 s  
T2PHASE71: 0.000000 s  
T2PHASE72: 0.000000 s  
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T2PHASE76: 0.000000 s  
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T2PHASE88: 0.000000 s  
T2PHASE89: 0.000000 s  
T2PHASE90: 0.000000 s  
T2PHASE91: 0.000000 s  
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T2PHASE93: 0.000000 s  
T2PHASE94: 0.000000 s  
T2PHASE95: 0.000000 s  
T2PHASE96: 0.000000 s  
T2PHASE97: 0.000000 s  
T2PHASE98: 0.000000 s  
T2PHASE99: 0.000000 s  
T2PHASE100: 0.000000 s

ES-AKJ-234; CDC13; 23/02/2019





ES-AKJ-191-1LB1; 15/06/2018

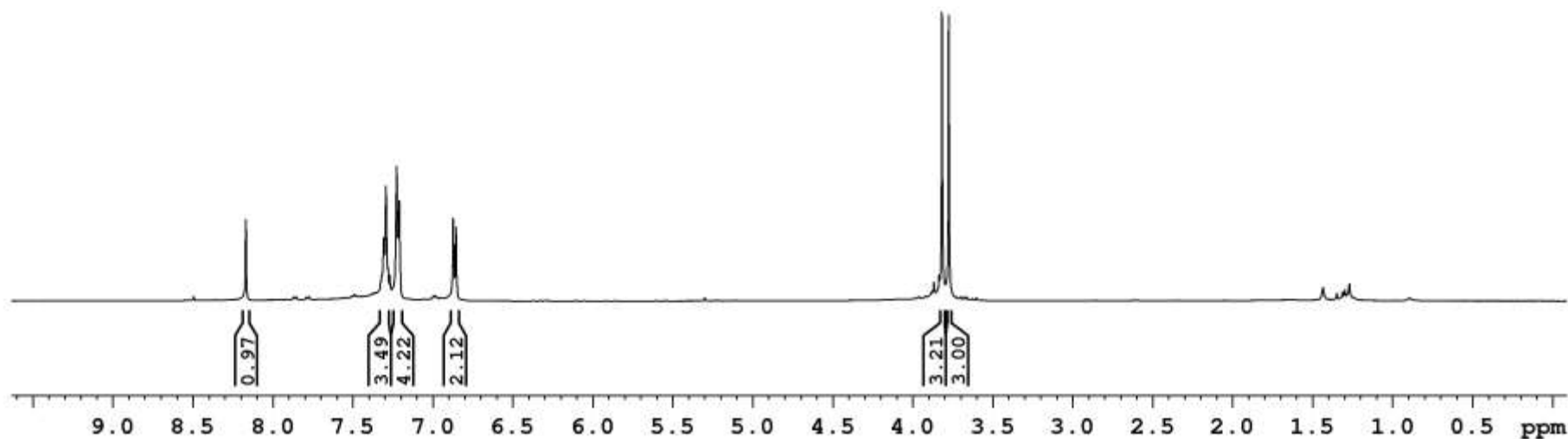
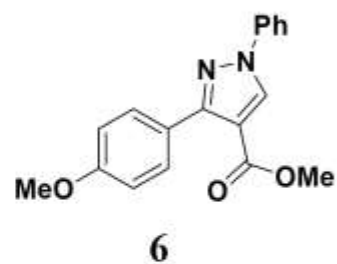




ES-RK-67 (3) , 1H.CDC13, 19/2/19

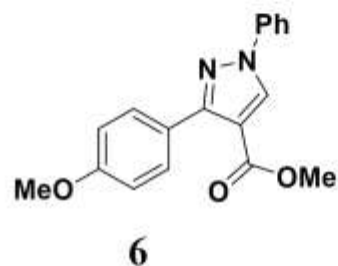
— 8.169  
7.319  
7.308  
7.293  
7.281  
7.269  
7.226  
7.209  
6.872  
6.855

3.816  
3.774



Current Date/Time: 19/02/19  
Date: 19/02/19  
Time: 11:14  
User: [illegible]  
Sample: [illegible]  
Solvent: CDCl3  
Conc: 100 mg/mL  
Temp: 25.00  
P1: 12.00  
P2: 12.00  
P3: 12.00  
P4: 12.00  
P5: 12.00  
P6: 12.00  
P7: 12.00  
P8: 12.00  
P9: 12.00  
P10: 12.00  
P11: 12.00  
P12: 12.00  
P13: 12.00  
P14: 12.00  
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P16: 12.00  
P17: 12.00  
P18: 12.00  
P19: 12.00  
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P92: 12.00  
P93: 12.00  
P94: 12.00  
P95: 12.00  
P96: 12.00  
P97: 12.00  
P98: 12.00  
P99: 12.00  
P100: 12.00

ES-RK-67 (3) -DEPT, 19/219



—163.507  
—160.190

—145.525  
—142.457  
—139.384

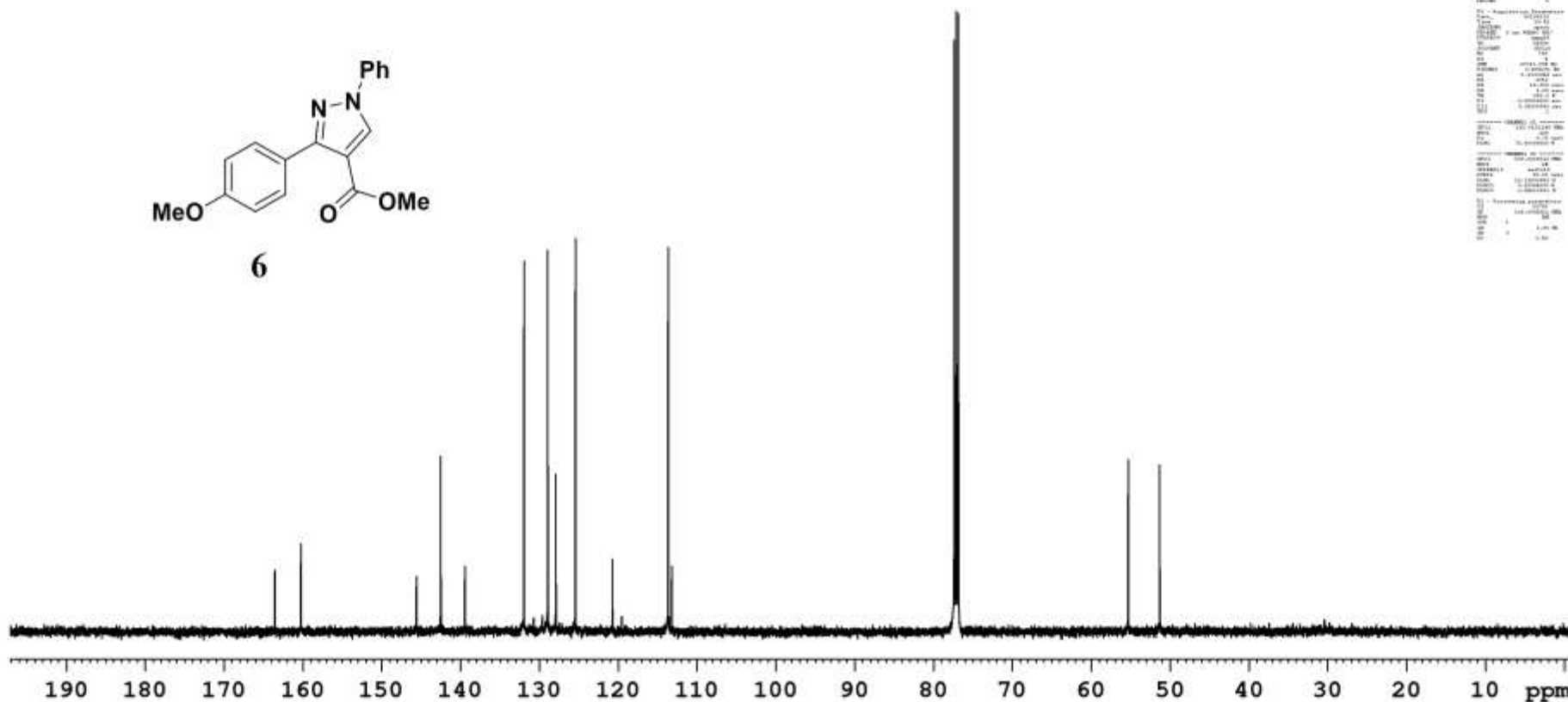
—131.890  
—128.870  
—127.849  
—125.369  
—120.675  
—113.593  
—113.145

77.296  
77.041  
76.788

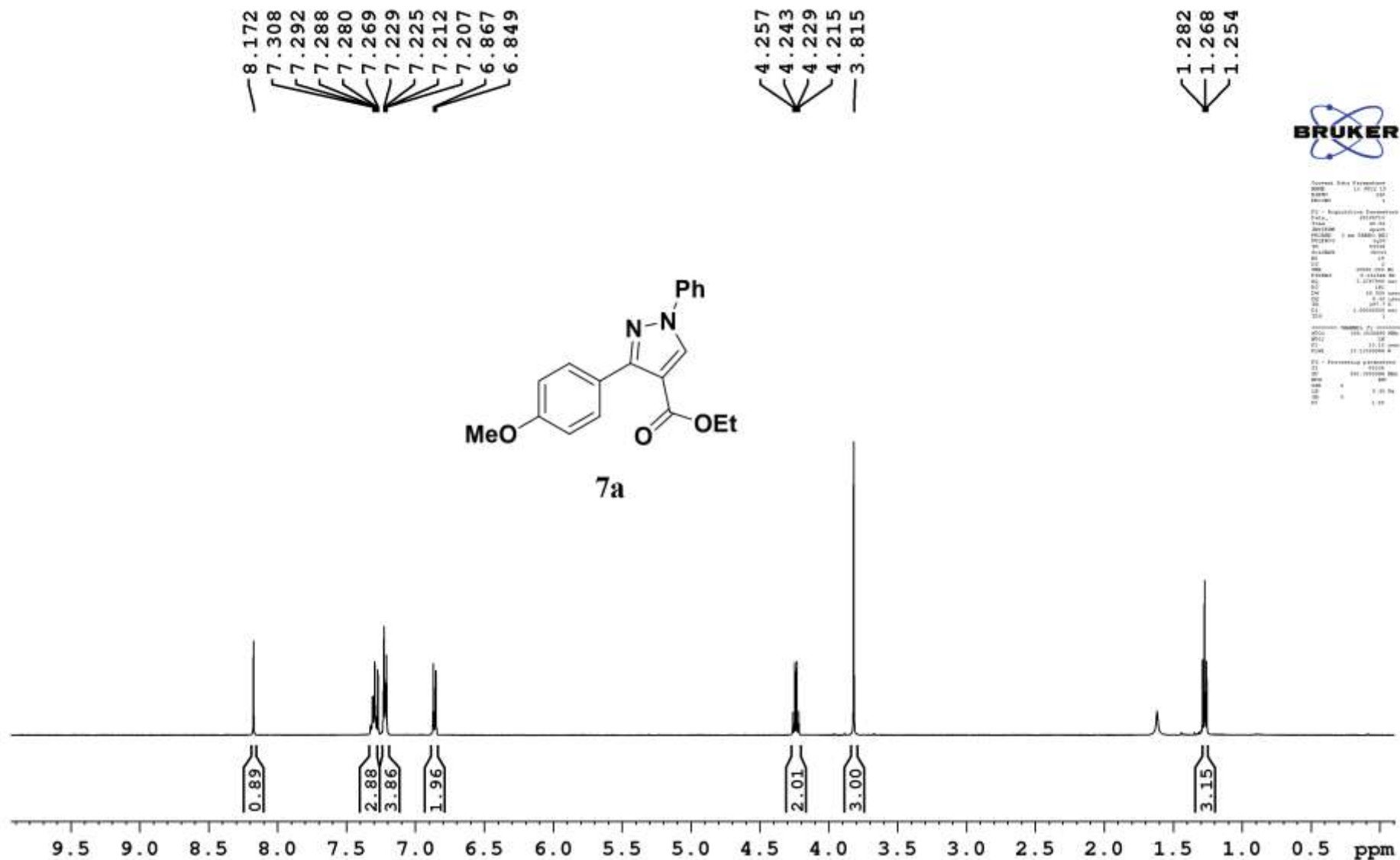
—55.218  
—51.241



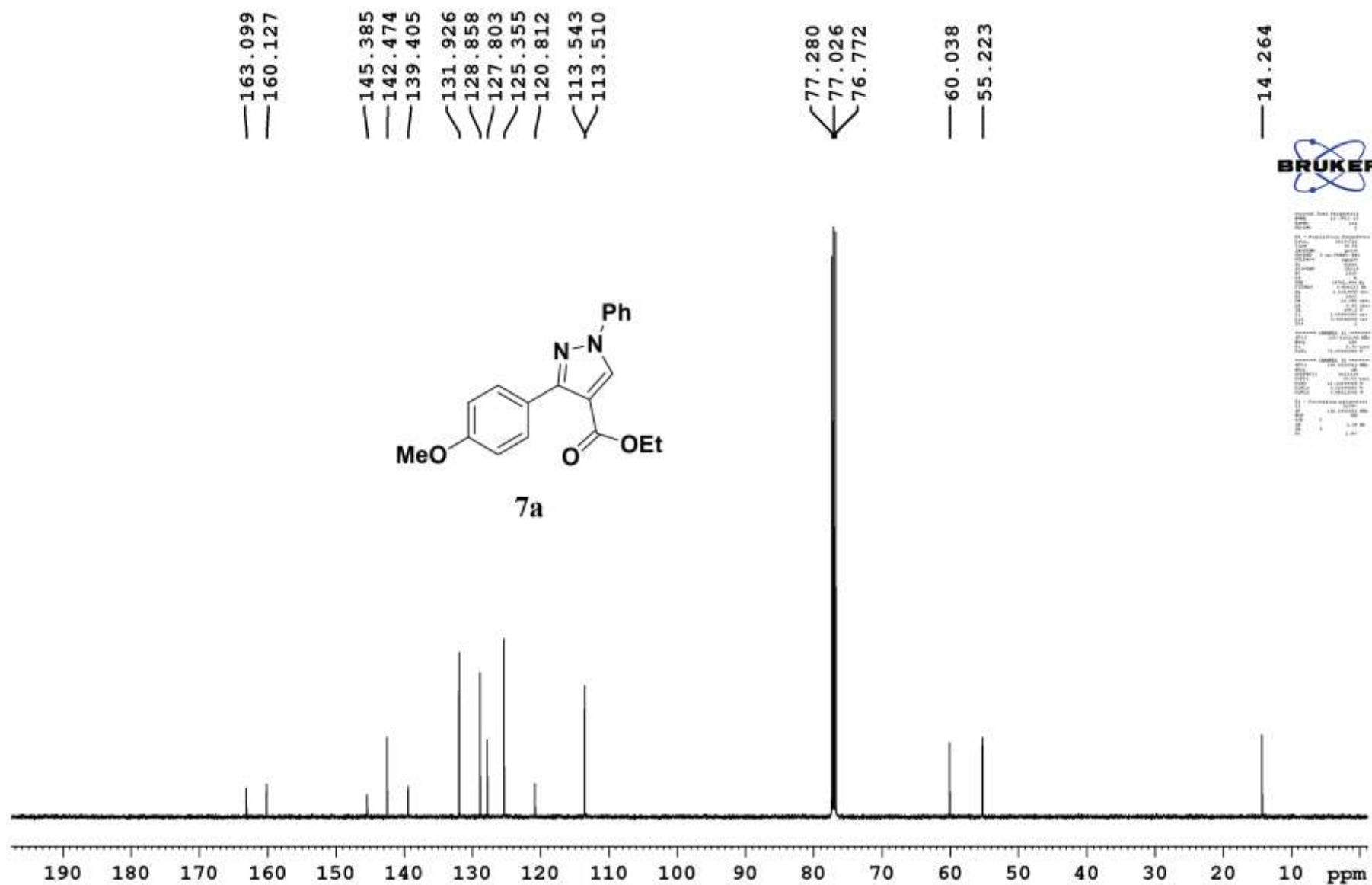
===== DEPT-135 =====  
Date: 10/11/2019 10:00:00  
Time: 10:00:00  
F1: 100 MHz  
F2: 400 MHz  
P1: 12.00  
P2: 12.00  
SFO: 400.1464000  
AQ: 1.00  
RG: 655.36  
WDW: EM  
SSB: 0  
GB: 0  
PC: 1.00  
===== DEPT-135 =====  
Date: 10/11/2019 10:00:00  
Time: 10:00:00  
F1: 100 MHz  
F2: 400 MHz  
P1: 12.00  
P2: 12.00  
SFO: 400.1464000  
AQ: 1.00  
RG: 655.36  
WDW: EM  
SSB: 0  
GB: 0  
PC: 1.00



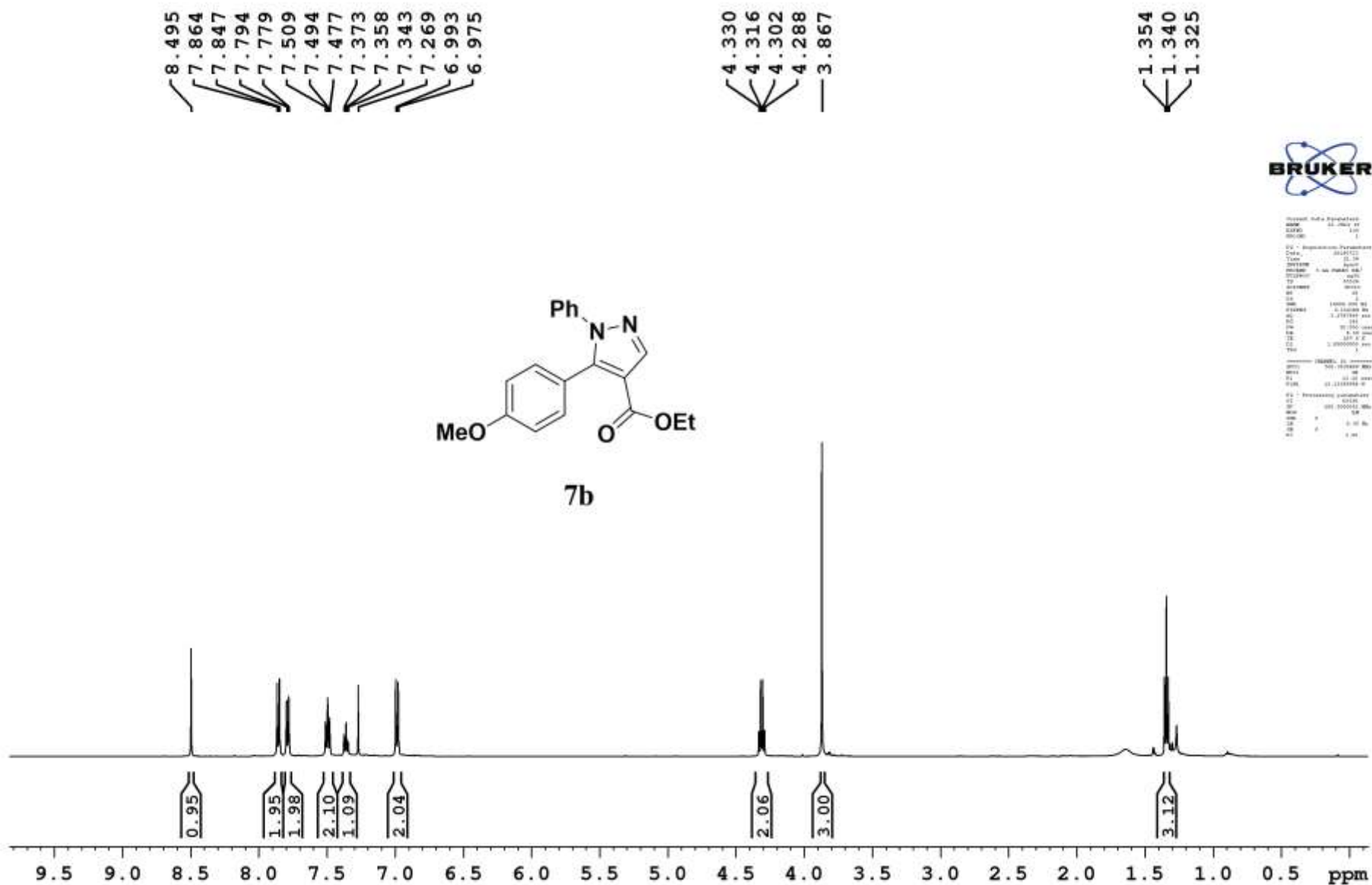




ES-AKJ-MC-49-2; CDC13; 13/07/2019



ES-AKJ-MC-49-1; CDC13; 13/07/2019



ES-AKJ-MC-49-1; CDC13; 13/07/2019

—163.074  
—160.093

—153.803.

—139.341—

132.232

130.727

— 129.536  
— 127.360

121.369  
124.677

— 119.491

✓ 113.463

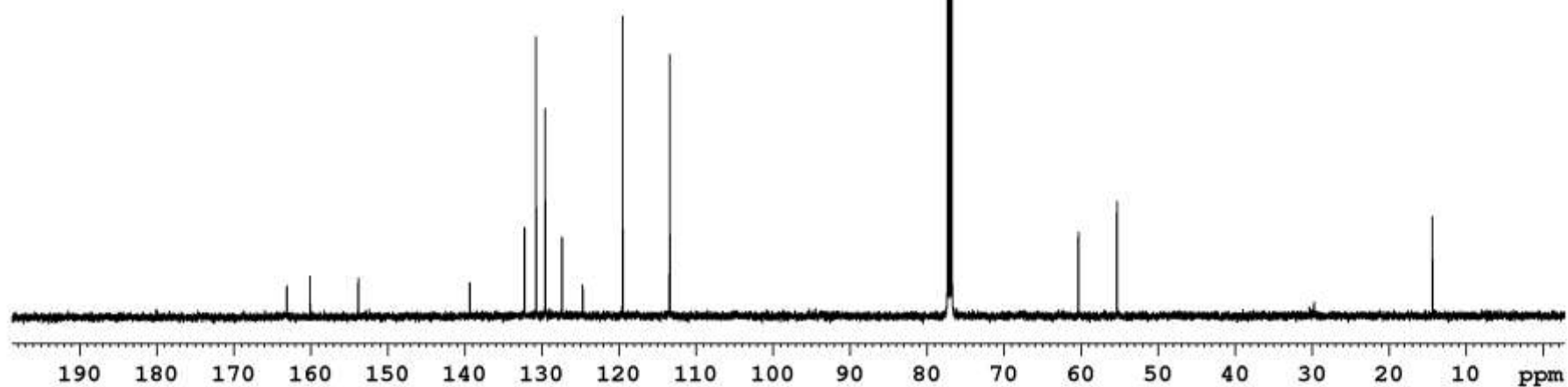
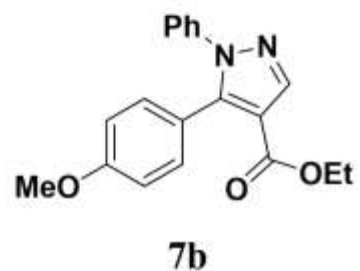
113.365

77.272  
77.018  
76.762

— 60.298

—55.310

—14.330

[illegible]