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

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SUPPORTING INFORMATION

Contents

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.[1] Et_3N was procured from local suppliers. Solvents were distilled prior to use. IBX was synthesised from 2-iodobenzoic acid using a literature protocol.[2] 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 Kα) instrument.

Experimental Section:

General procedure for the synthesis of Morita-Baylis-Hillman (MBH) adducts:[3]

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_2O (10 mL); the reaction mixture was extracted with EtOAc (3 × 15 mL), the combined organic layer dried over anhydrous Na_2SO_4 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:[4]

The MBH adduct (1.0 mmol) and IBX (1.5 equiv.) were dissolved in CH_3CN (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.

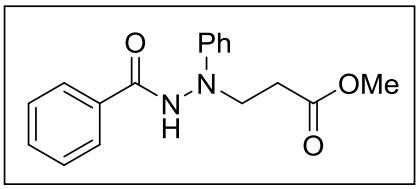
General procedure for the synthesis of the benzohydrazides:

Method A: The MBH ketone **1** (0.5 mmol) was dissolved in CH_3CN (500 μL). Phenylhydrazine (**2a**, 0.75 mmol) was then added to the solution followed by the addition of Et_3N (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_2O (5 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was dried over Na_2SO_4 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 tabluation below*).

Method B: The MBH ketone **1** (0.5 mmol) was dissolved in CH_3CN (500 µL). The hydrazine hydrochloride derivative (0.75 mmol) was then added to the solution followed by H_2O (50 µL) and Et_3N (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_2O (5 mL) and extracted with EtOAc (3 × 8 mL). The combined organic layer was dried over Na_2SO_4 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 tabluation below*).

Representative example:

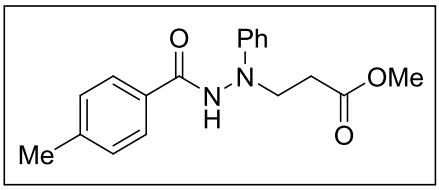
Synthesis of Methyl 3-(2-benzoyl-1-phenylhydrazinyl)propanoate (3a):



The MBH ketone **1a** (190 mg, 1.0 mmol) was dissolved in CH_3CN (1 mL). Phenylhydrazine (147.5 µL, 1.5 mmol) was then added to the solution followed by the addition of Et_3N (70 µL, 0.5 mmol). The reaction mixture was further stirred at room temperature for 15 h. The reaction mixture was then diluted with H_2O (8 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was dried over Na_2SO_4 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 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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]$^+$ calculated for $C_{17}H_{18}N_2O_3Na$: 321.1210; found: 321.1210.

<u>Tabulated Data of the synthesized products</u>:

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

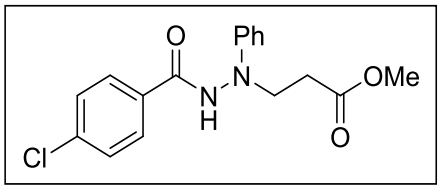


Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 136 mg (87%); Off white solid; mp 145-147 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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

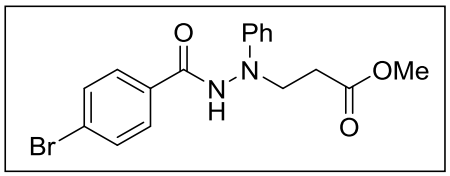
Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 8.27 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.54, 32.00, 48.05, 51.91, 113.07, 119.83, 127.26, 129.33, 129.45, 129.76, 142.73, 147.77, 166.51, 173.35; Anal. calculated for $C_{18}H_{20}N_2O_3$: C, 69.21; 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):



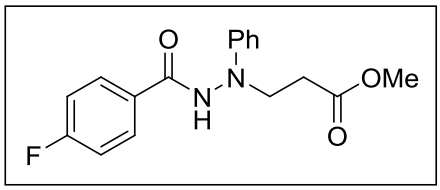
Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 131 mg (79%); Off white solid; mp 163-165 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.76 (t, *J* = 6.5 Hz, 2H), 3.65 (s, 3H), 3.93 (t, *J* = 6.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.88 (masked t, *J* = 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}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{17}H_{17}ClN_2O_3$: 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 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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, 2H), 8.64 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + Na]^+$ calculated for $C_{17}H_{17}BrN_2O_3Na$: 399.0315; found: 399.0327.

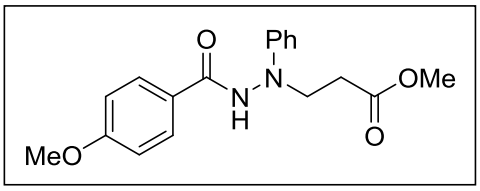
Methyl 3-(2-(4-fluorobenzoyl)-1-phenylhydrazinyl)propanoate (3e):



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 3:7)
Yield: 155 mg (98%); Off white solid; mp 112-115 ºC; ^{1}H NMR (500 MHz, CDCl3): δ 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}C NMR

(125 MHz, $CDCl_3$): δ 31.90, 48.02, 52.04, 113.06, 115.91 (d, $J_{C\text{-}F}$ = 22 Hz), 119.98, 128.73 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.40, 129.73 (d, $J_{C\text{-}F}$ = 9.0 Hz), 147.45, 165.14 (d, $J_{C\text{-}F}$ = 252.0 Hz), 165.60, 173.61; Anal. calculated for $C_{17}H_{17}FN_2O_3$: C, 64.55; H, 5.42; N, 8.86; found C, 65.10; H, 5.76; N, 8.45.

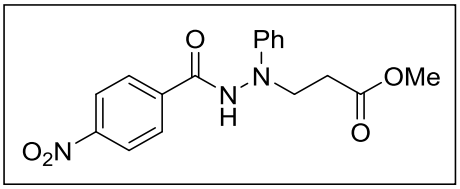
Methyl 3-(2-(4-methoxybenzoyl)-1-phenylhydrazinyl)propanoate (3f):[#]



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 103 mg (63%); Yellow solid; mp 157-160 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + H]^+$ calculated for $C_{18}H_{21}N_2O_4$: 329.1496; found: 329.1495.

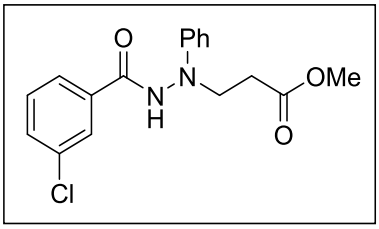
[#]Corresponding pyrazole obtained as the minor product; see end of this section for structure, yield and tabulated data.

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 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{17}H_{17}N_3O_5$: C, 59.47; H, 4.99; N, 12.24; found C, 59.70; H, 5.08; N, 11.60.

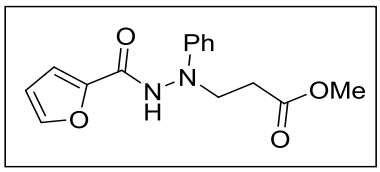
Methyl 3-(2-(3-chlorobenzoyl)-1-phenylhydrazinyl)propanoate (3h):



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

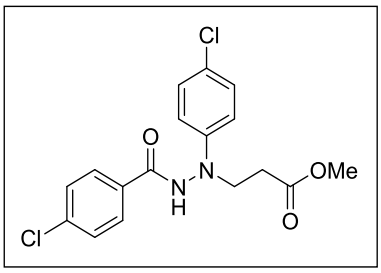
Yield: 125 mg (75%); Brown semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.78 (t, J = 6.5 Hz, 2H), 3.66 (s, 3H), 3.95 (t, J = 6.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 6.88 (masked t, J = 7.0 Hz, 1H), 7.27 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.90 (s, 1H), 8.47 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + H]^+$ calculated for $C_{17}H_{18}ClN_2O_3$: 333.1000; found: 333.1002.

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



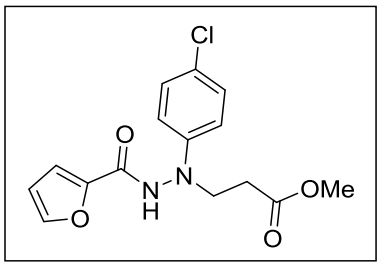
Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 114 mg (79%); Orange solid; mp 105-108 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.76 (t, J = 6.5 Hz, 2H), 3.64 (s, 3H), 3.93 (t, J = 6.5 Hz, 2H), 6.53-6.58 (m, 1H), 6.87 (masked t, J = 7.0 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 7.21-7.28 (m, 3H), 7.50-7.54 (unresolved m, 1H), 8.32 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{15}H_{16}N_2O_4$: 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):



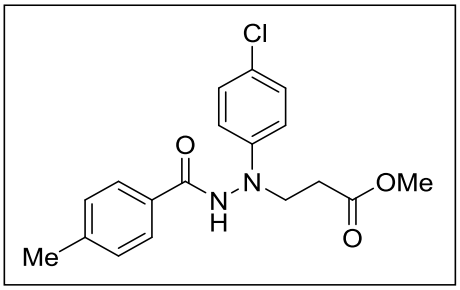
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield:110 mg (60%); White solid; mp 163-168 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.74 (t, J = 6.0 Hz, 2H), 3.66 (s, 3H), 3.91 (t, J = 6.0 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 9.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 8.66 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + Na]^+$ calculated for $C_{17}H_{16}Cl_2N_2O_3Na$: 389.0430; found: 389.0432.

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



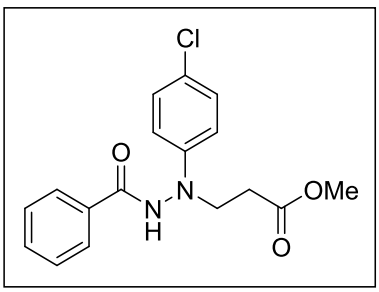
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 113 mg (70%); Mustard solid; mp 83-85 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.74 (t, J = 6.5 Hz, 2H), 3.66 (s, 3H), 3.91 (t, J = 6.5 Hz, 2H), 6.55-6.60 (m, 1H), 6.81 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 9.0 Hz, 2H), 7.23 (d, J = 3.5 Hz, 1H), 7.53 (s, 1H), 8.36 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{15}H_{15}ClN_2O_4$: 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):



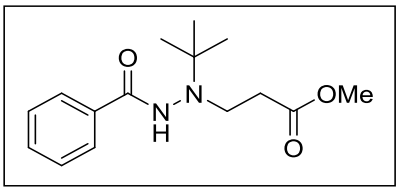
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 116 (67%); White solid; mp 179-182 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.74 (t, J = 6.5 Hz, 2H), 3.65 (s, 3H), 3.91 (t, J = 6.5 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 7.18 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 8.49 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{18}H_{19}ClN_2O_3$: 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):



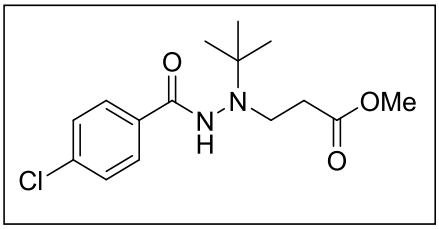
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 126 mg (76%); White solid; mp 135-137 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.75 (t, J = 6.5 Hz, 2H), 3.66 (s, 3H), 3.93 (t, J = 6.0 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 7.19 (d, J = 9.0 Hz, 2H), 7.49 (t, J = 2H), 7.58 (t, J = 6.5 Hz, 1H), 7.88 (d, J = 7.5 Hz, 2H), 8.50 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{17}H_{17}ClN_2O_3$: 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):



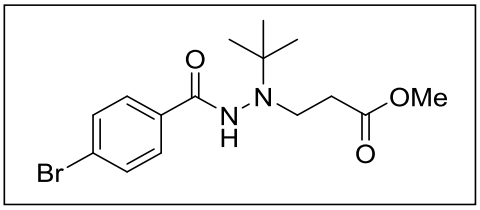
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 84 mg (60%); White solid; mp 123-125 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.17 (s, 9H), 2.56 (t, J = 6.5 Hz, 2H), 3.08 (bs, 2H), 3.48 (s, 3H), 6.66 (bs, 1H), 7.35-7.42 (m, 2H), 7.43-7.50 (m, 1H), 7.70 (d, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 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]$^{+}$ calculated for $C_{15}H_{22}N_2O_3Na$: 301.1523; found: 301.1521.

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



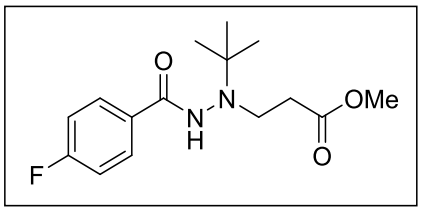
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 108 mg (69%); White solid; mp 114-116 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.17 (s, 9H), 2.57 (t, J = 7.0 Hz, 2H), 3.10 (t, J = 6.5 Hz, 2H), 3.50 (s, 3H), 6.64 (bs, 1H), 7.38 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{15}H_{21}ClN_2O_3$: 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):



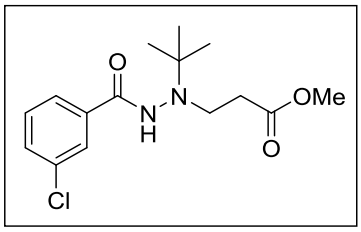
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield:134 mg (75%); White solid; mp 108-112 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 9H), 2.58 (t, J = 6.5 Hz, 2H), 3.10 (bs, 2H), 3.51 (s, 3H), 6.64 (bs, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 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]$^{+}$ calculated for $C_{15}H_{21}BrN_2O_3Na$: 379.0628; found: 379.0627.

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



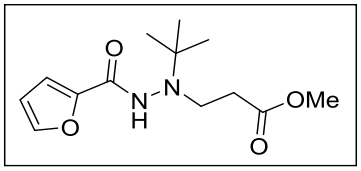
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 101 mg (68%); White solid; mp 117-120 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (s, 9H), 2.59 (t, J = 7.0 Hz, 2H), 3.11 (bs, 2H), 3.51 (s, 3H), 6.58 (bs, 1H), 7.11 (t, J = 9.0 Hz, 2H), 7.75 (dd, J = 5.5 & 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.42, 32.90, 45.81, 51.69, 58.78, 115.73 (d, $J_{C\text{-}F}$ = 22.0 Hz), 129.33 (d, $J_{C\text{-}F}$ = 9.0 Hz), 129.86 (d, $J_{C\text{-}F}$ = 3.0 Hz), 164.78 (d, $J_{C\text{-}F}$ = 251.0 Hz), 166.00, 173.92; HRMS (ESI-TOF): m/z $[M + Na]^+$ calculated for $C_{15}H_{21}FN_2O_3Na$: 319.1428; found: 319.1429.

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



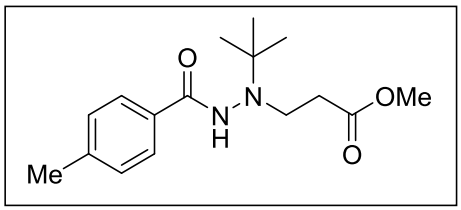
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 97 mg (62%); White solid; mp 121-123 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20 (s, 9H), 2.59 (t, J = 6.5 Hz, 2H), 3.12 (t, J = 6.0 Hz, 2H), 3.54 (s, 3H), 6.59 (bs, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.70-7.75 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{15}H_{21}ClN_2O_3$: 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):



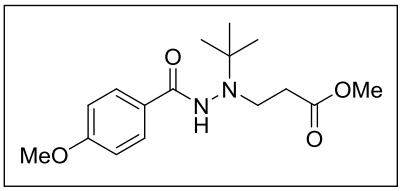
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 54 mg (40%); Light yellow solid; mp 113-115 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 9H), 2.57 (t, J = 6.5 Hz, 2H), 3.10 (t, J = 6.5 Hz, 2H), 3.54 (s, 3H), 6.49-6.53 (m, 1H), 6.84 (bs, 1H), 7.16 (d, J = 3.0 Hz, 1H), 7.45 (s, 1H);^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + Na]^+$ calculated for $C_{13}H_{20}N_2O_4Na$: 291.1315; found: 291.1317.

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



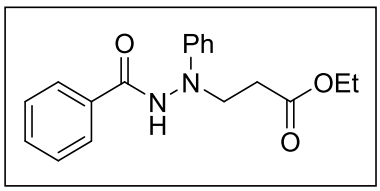
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 61 mg (42%); White solid; mp 114-116 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (s, 9H), 2.39 (s, 3H), 2.59 (t, *J* = 7.0 Hz, 2H), 3.07-3.13 (m, 2H), 3.50 (s, 3H), 6.57 (bs, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{16}H_{24}N_2O_3$: 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):



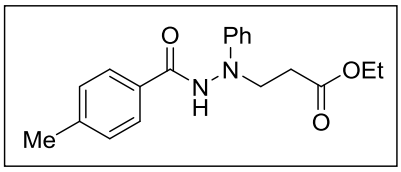
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 73 mg (47%); White solid; mp 124-126 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 9H), 2.58 (t, *J* = 6.5 Hz, 2H), 3.10 (bs, 2H), 3.49 (s, 3H), 3.84 (s, 3H), 6.55 (bs, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{16}H_{24}N_2O_4$: 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):



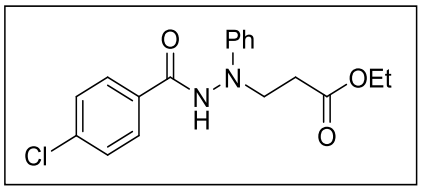
Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 120 mg (77%); Off white solid; mp 117-119 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (t, *J* = 7.5 Hz, 3H), 2.76 (t, *J* = 6.5 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 4.09 (q, *J* = 7.5 Hz, 2H), 6.87 (masked 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}C NMR (125 MHz, $CDCl_3$): δ 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 [M + Na]$^{+}$ calculated for $C_{18}H_{20}N_2O_3Na$: 335.1366; found: 335.1362.

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



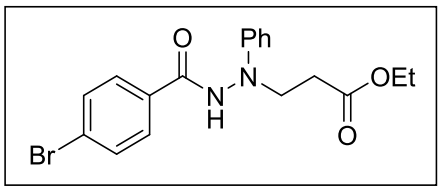
Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 98 mg (60%); Light orange solid; mp 123-126 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (t, J = 7.0 Hz, 3H), 2.43 (s, 3H), 2.75 (t, J = 6.5 Hz, 2H), 3.95 (t, J = 6.5 Hz, 2H), 4.09 (q, J = 7.0 Hz, 2H), 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); ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{19}H_{22}N_2O_3$: 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):



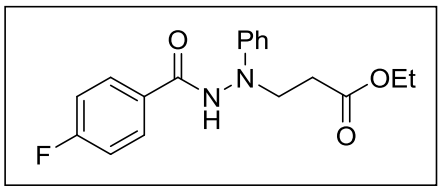
Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 156 mg (90%); Light orange solid; mp 117-119 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (t, J = 7.0 Hz, 3H), 2.73 (t, J = 6.5 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 4.09 (q, J = 7.5 Hz, 2H), 6.84 (d, J = 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); ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{18}H_{19}ClN_2O_3$: 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):



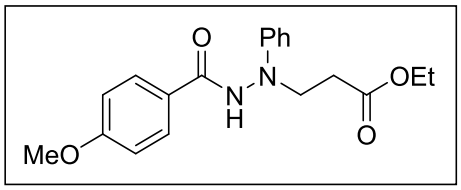
Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 150 mg (77%); Yellow solid; mp 132-136 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, J =7.0 Hz, 3H), 2.75 (t, J = 6.0 Hz, 2H), 3.94 (t, J = 6.0 Hz, 2H), 4.10 (q, J = 7.0 Hz, 2H), 6.85 (d, J = 7.5 Hz, 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); ^{13}C NMR (125 MHz, $CDCl_3$): 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 $[M + H]^+$ calculated for $C_{18}H_{20}BrN_2O_3$: 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 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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, 2 H), 8.62 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.11, 32.13, 47.99, 60.99, 113.07, 115.87 (d, $J_{C\text{-}F}$ = 22 Hz), 119.90, 128.79 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.37, 129.73 (d, $J_{C\text{-}F}$ = 9.0 Hz), 147.49, 165.12 (d, $J_{C\text{-}F}$ = 251.0 Hz), 165.53, 173.16; Anal. calculated for $C_{18}H_{19}FN_2O_3$: C, 65.44; H, 5.80; N, 8.48; found C, 65.79; H, 6.05; N, 8.08

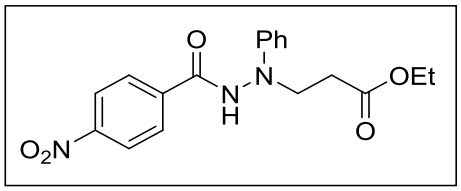
Ethyl 3-(2-(4-methoxybenzoyl)-1-phenylhydrazinyl)propanoate (5f):[#]



Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 103 mg (60%); Light yellow solid; mp 120-124 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + Na]^+$ calculated for $C_{19}H_{22}N_2O_4Na$: 365.1472; found: 365.1473.

[#]Corresponding regioisomeric pyrazoles obtained as the minor products; see end of this section for structures, yields and tabulated data.

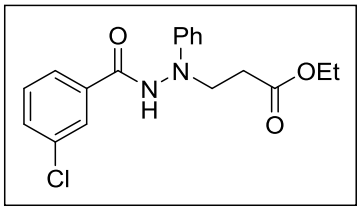
Ethyl 3-(2-(4-nitrobenzoyl)-1-phenylhydrazinyl)propanoate (5g):



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 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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,

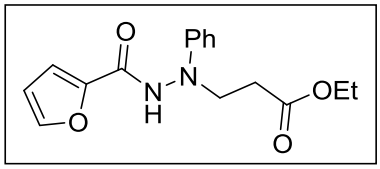
1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.11, 32.03, 48.09, 61.22, 113.23, 120.29, 123.97, 128.58, 129.49, 138.24, 146.89, 149.95, 164.54, 173.51; HRMS (ESI-TOF): m/z $[M + Na]^+$ calculated for $C_{18}H_{19}N_3O_5Na$: 380.1217; found: 380.1216.

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



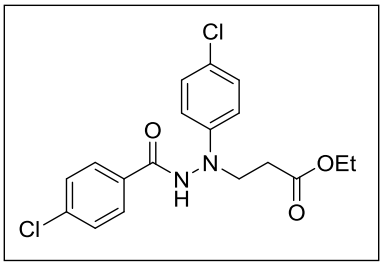
Synthesized using Method A; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 113 mg (65%); Orange red gum; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (t, J = 7.5 Hz, 3H), 2.72 (t, J = 6.5 Hz, 2H), 3.89 (t, J = 6.5 Hz, 2H), 4.09 (q, J = 7.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.86 (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}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + H]^+$ calculated for $C_{18}H_{20}ClN_2O_3$: 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 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27; found C, 63.45; H, 6.08; N, 9.23.

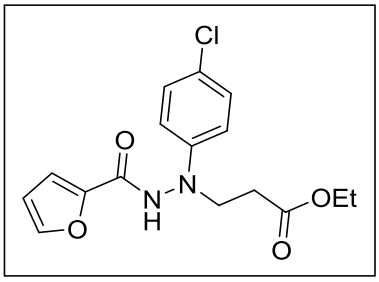
Ethyl 3-(2-(4-chlorobenzoyl)-1-(4-chlorophenyl)hydrazinyl)propanoate (5j):



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

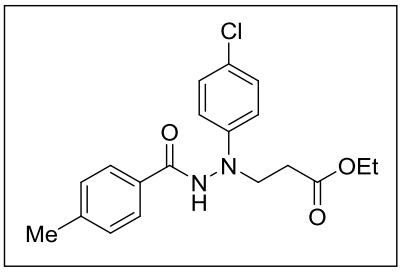
Yield: 116 mg (61%); Yellow solid; mp 110-112 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, J = 7.0 Hz, 3H), 2.71 (t, J = 6.0 Hz, 2H), 3.88 (t, J = 6.0 Hz, 2H), 4.10 (q, J = 7.0 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 8.78 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{18}H_{18}Cl_2N_2O_3$: 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):



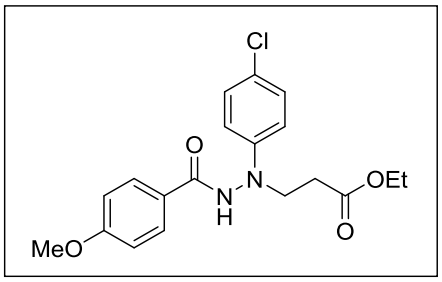
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 106 mg (63%); Orange solid; mp 78-81 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (t, J = 7.0 Hz, 3H), 2.72 (t, J = 6.5 Hz, 2H), 3.90 (t, J = 6.5 Hz, 2H), 4.10 (q, J = 7.0 Hz, 2H), 6.50-6.59 (m, 1H), 6.81 (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}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{16}H_{17}ClN_2O_4$: C, 57.06; H, 5.09; N, 8.32; found C, 57.12; H, 5.15; N, 8.26.

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



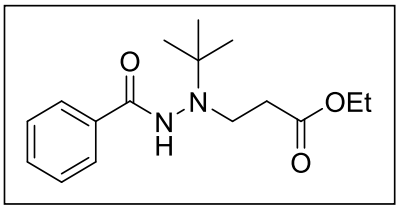
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 122 mg (67%); Light yellow solid; mp 154-157 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, J = 7.0 Hz, 3H), 2.43 (s, 3H), 2.73 (t, J = 6.0 Hz, 2H), 3.91 (t, J = 6.0 Hz, 2H), 4.10 (q, J = 7.0 Hz, 2H), 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}C NMR (125 MHz, $CDCl_3$): δ 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 $C_{19}H_{21}ClN_2O_3$: 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):



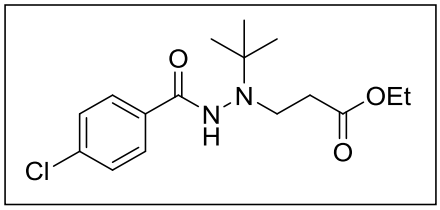
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 126 mg (67%); White solid; mp 143-145 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, J = 6.0 Hz, 3H), 2.73 (t, J = 6.0 Hz, 2H), 3.88 (s, 3H), 3.91 (t, J = 6.5 Hz, 2H), 4.11 (q, J = 7.0 Hz, 2H), 6.78 (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); ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{19}H_{21}ClN_2O_4$: 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 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): 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 = 7.5Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.74 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{16}H_{24}N_2O_3$: C, 65.73; H, 8.27; N, 9.58; found C, 65.63; H, 8.31; N, 9.52.

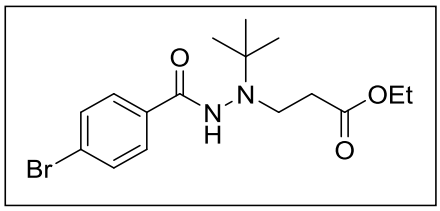
Ethyl 3-(1-(tert-butyl)-2-(4-chlorobenzoyl)hydrazinyl)propanoate (5o):



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 123 mg (75%); White solid; mp 115-117 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): 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); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.06,

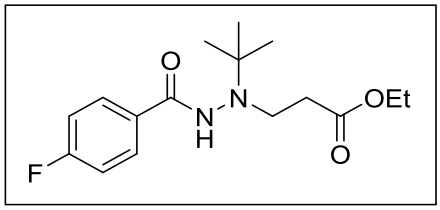
25.44, 33.09, 45.64, 58.80, 60.61, 128.44, 128.88, 132.16, 137.86, 165.92, 173.44; Anal. calculated for $C_{16}H_{23}ClN_2O_3$: C, 58.80; H, 7.09; N, 8.57; found C, 58.85; H, 7.18; N, 8.40.

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



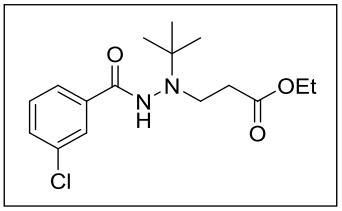
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 111 mg (60%); Light green solid; mp 112-115 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13 (t, J = 7.0 Hz, 3H), 1.19 (s, 9H), 2.57 (t, J = 6.5 Hz, 2H), 3.11 (t, J = 6.0 Hz, 2H), 3.97 (q, J = 7.0 Hz, 2H), 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, $CDCl_3$): δ 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 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 14.05, 25.43, 33.07, 45.63, 58.78, 60.61, 115.68 (d, $J_{C\text{-}F}$ = 22.0 Hz), 129.33 (d, $J_{C\text{-}F}$ = 9.0 Hz), 129.90 (d, $J_{C\text{-}F}$ = 3.0 Hz), 164.77 (d, $J_{C\text{-}F}$ = 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.

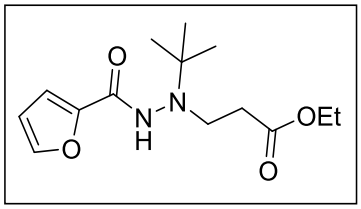
Ethyl 3-(1-(tert-butyl)-2-(3-chlorobenzoyl)hydrazinyl)propanoate(5r):



Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 88 mg (54%); White solid; mp 100-103 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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,

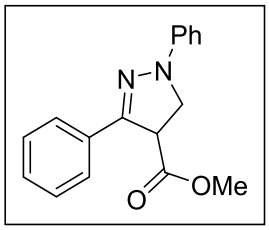
$CDCl_3$): δ 14.06, 25.44, 33.05, 45.61, 58.82, 60.67, 124.99, 127.41, 129.96, 131.65, 134.81, 135.56, 165.83, 173.41; Anal. calculated for $C_{16}H_{23}ClN_2O_3$: C, 58.80; H, 7.09; N, 8.57; found C, 59.39; H, 7.30; N, 8.22.

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



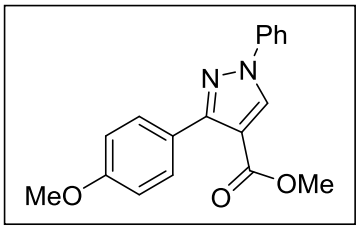
Synthesized using Method B; Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)
Yield: 47 mg (33%); Red gum; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13 (t, J = 7.0 Hz, 3H), 1.18 (s, 9H), 2.55 (t, J = 7.0 Hz, 2H), 3.09 (t, J = 6.5 Hz, 2H), 3.98 (q, J = 7.5 Hz, 2H), 6.48-6.52 (m, 1H), 6.80 (bs, 1H), 7.14 (d, J = 3.0 Hz, 1H), 7.44 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + H]^+$ calculated for $C_{14}H_{23}N_2O_4$: 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 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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); ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + H]^+$ calculated for $C_{17}H_{17}N_2O_2$: 281.1285; found: 281.1286.

Methyl 3-(4-methoxyphenyl)-1-phenyl-1H-pyrazole-4-carboxylate (6):[#]

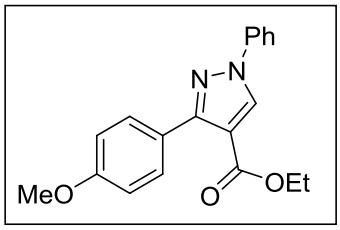


Purified by silica gel chromatography (EtOAc: petroleum ether, 1:9)

Yield: 20 mg (13%); Brown solid; mp 115-118 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + H]^+$ calculated for $C_{18}H_{17}N_2O_3$: 309.1234; found: 309.1235.

[#]Formed alongside the benzohydrazide **3f**.

Ethyl 3-(4-methoxyphenyl)-1-phenyl-1H-pyrazole-4-carboxylate (7a):[#]

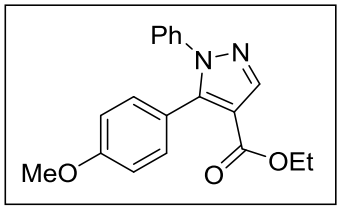


Purified by silica gel chromatography (EtOAc: petroleum ether, 1:9)

Yield: 19 mg (12%); Brown semi solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + H]^+$ calculated for $C_{19}H_{19}N_2O_3$: 323.1390; found: 323.1389.

[#]Formed alongside the benzohydrazide **5f**.

Ethyl 5-(4-methoxyphenyl)-1-phenyl-1H-pyrazole-4-carboxylate (7b):[#]

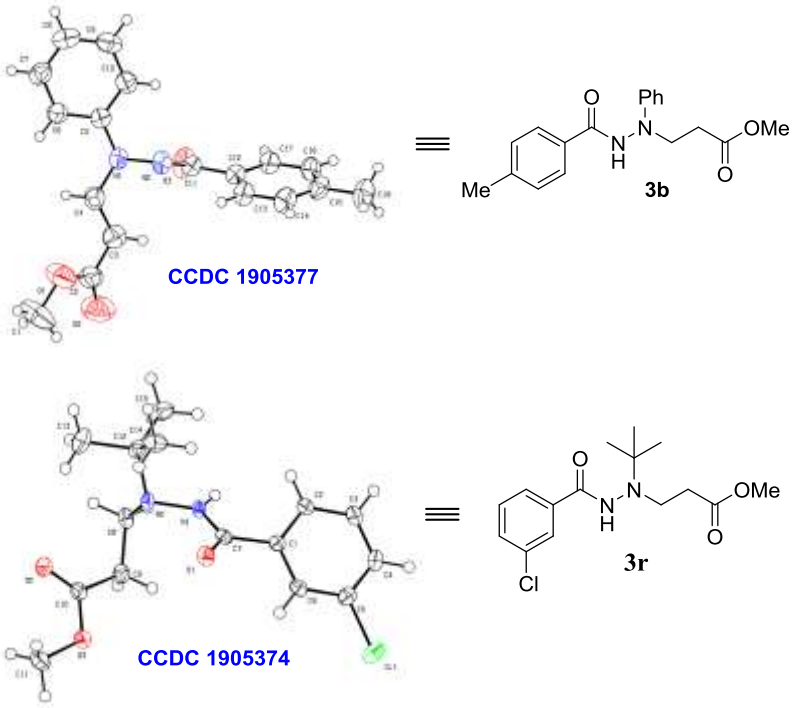


Purified by silica gel chromatography (EtOAc: petroleum ether, 1:9)

Yield: 24 mg (15%); Brown solid; mp 124-127 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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}C NMR (125 MHz, $CDCl_3$): δ 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 $[M + H]^+$ calculated for $C_{19}H_{19}N_2O_3$: 323.1390; found: 323.1391.

[#]Formed alongside the benzohydrazide **5f**.

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



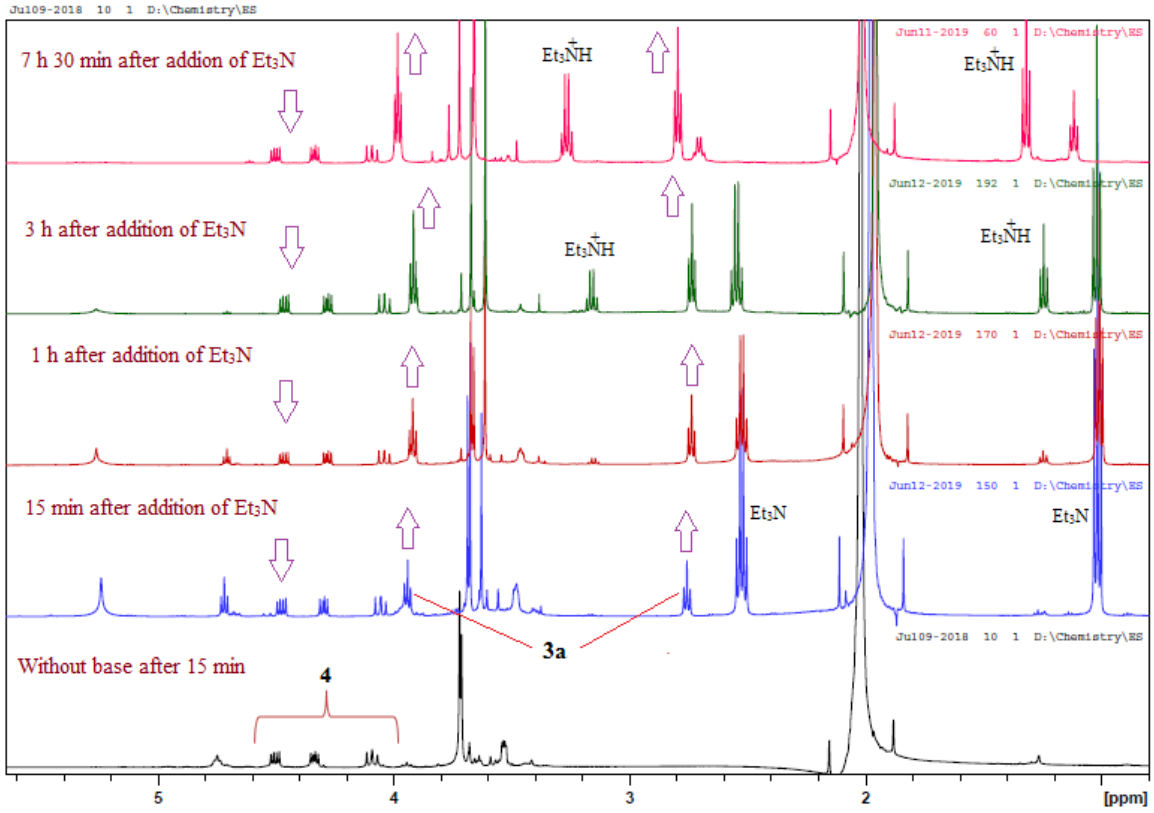
Crystal data and structure refinement for **3b** & **3r**

Compound	**3b**	**3r**
Identification code (CCDC Number)	1905377	1905374
Empirical formula	$C_{18}H_{20}N_2O_3$	$C_{15}H_{21}ClN_2O_3$
Formula weight	312.36	312.79
Temperature/K	293.15	100
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	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/$Å^3$	1694(5)	1585(2)
Z	4	4
$\rho_{calc}mg/mm^3$	1.225	1.311
m/mm^{-1}	0.084	0.252

F(000)	664	664
Crystal size/mm^3	0.230 × 0.220 × 0.200	0.150 × 0.130 × 0.090
2ɵTheta 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, -11 ≤ 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^2	1.135	1.043
Final R indexes [I>2σ (I)]	R_1 = 0.0571, wR_2 = 0.1658	R_1 = 0.0275, wR_2 = 0.0675
Final R indexes [all data]	R_1 = 0.0775, wR_2 = 0.1781	R_1 = 0.0299, wR_2 = 0.0687
Largest diff. peak/hole / e Å^{-3}	0.287/-0.315	0.120/-0.238

Studies on the Reaction Mechanism:

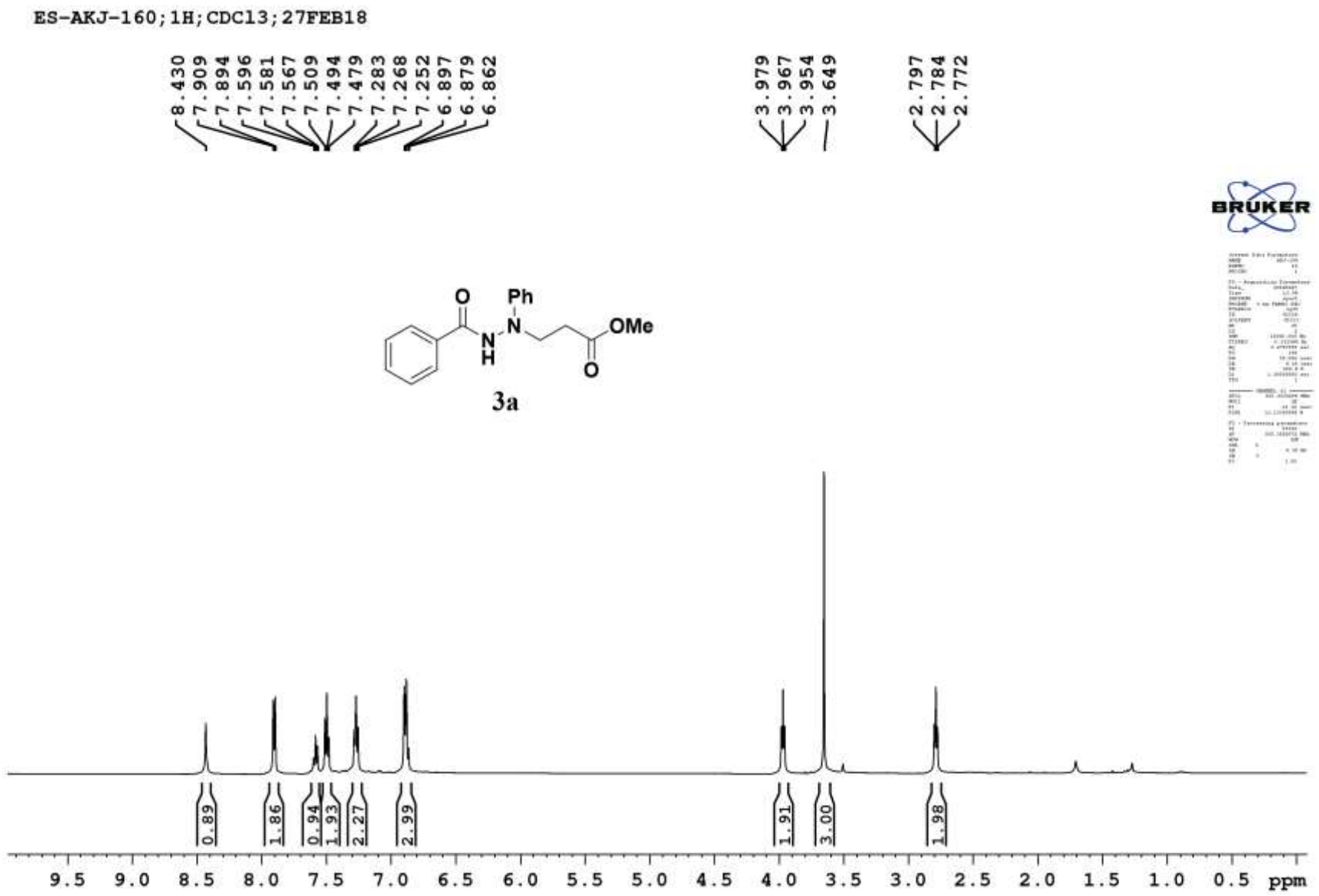
^{1}H NMR spectra recorded at various stages of the reaction of MBH ketone 1a with phenylhydrazine (2a)



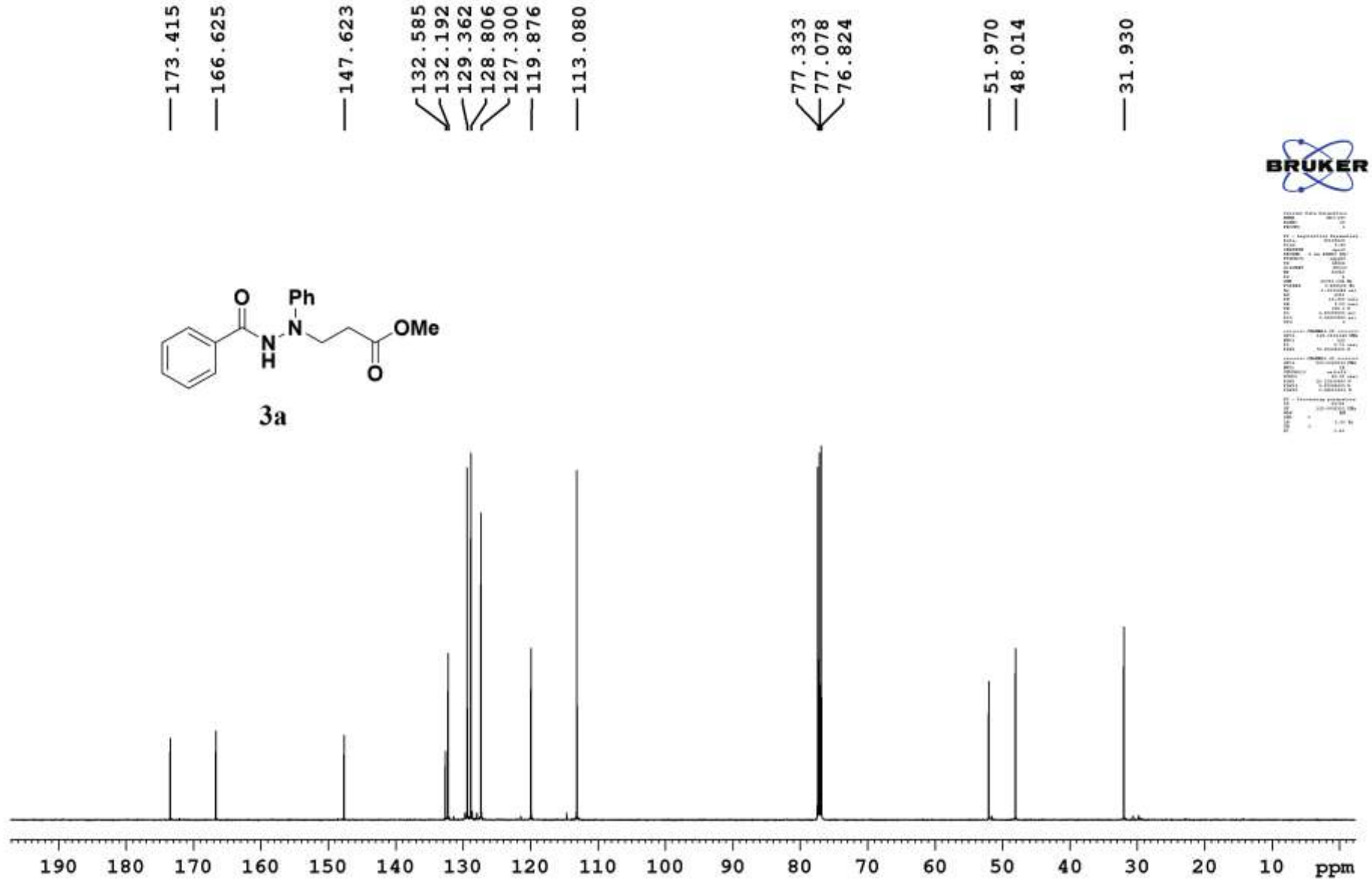
References:

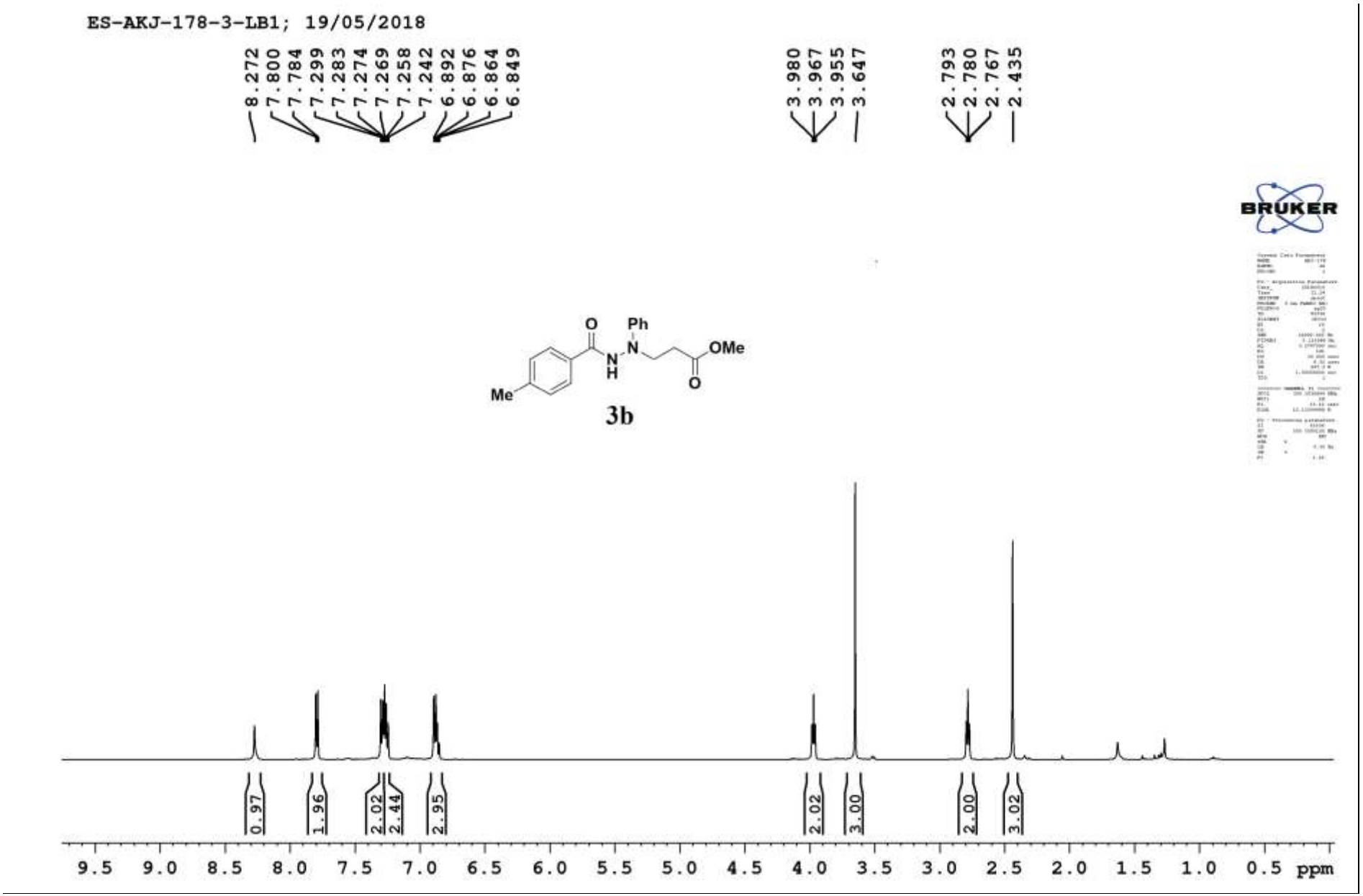
1. Zhao, D.; Shi, Z.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 12426.
2. Frigerio, M.; Santagostina, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537.
3. Latorre, A.; Saez. J, A.; Rodríguez, S.; Gonzalez, V. F. *Tetrahedron Lett.* **2014**, *70*, 97.
4. Santos, S. M.; Coelho, F. *RSC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

^{1}H and ^{13}C NMR spectra of the synthesized products

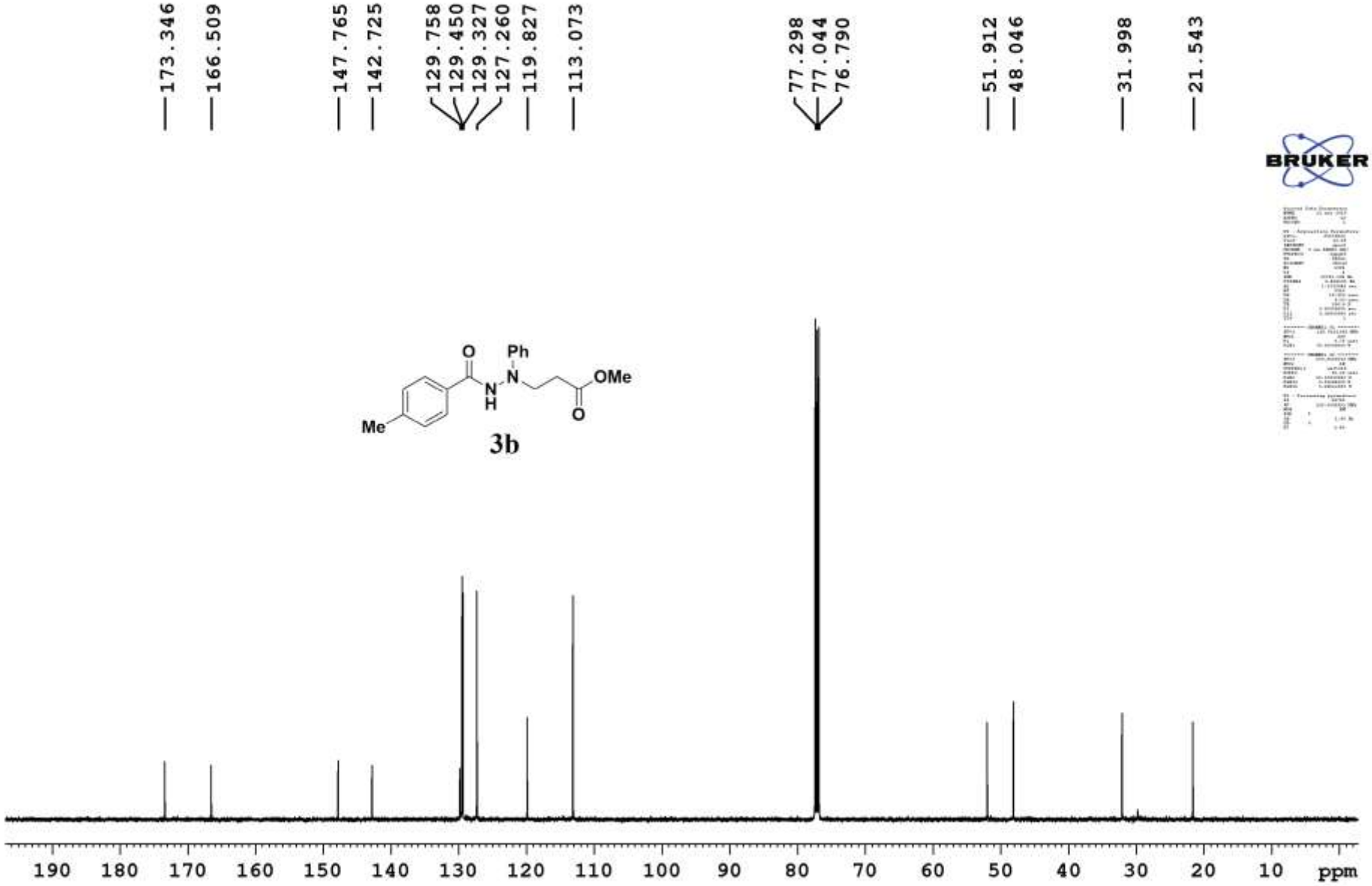


ES-AKJ-160, CDCl3; 27 FEB 18

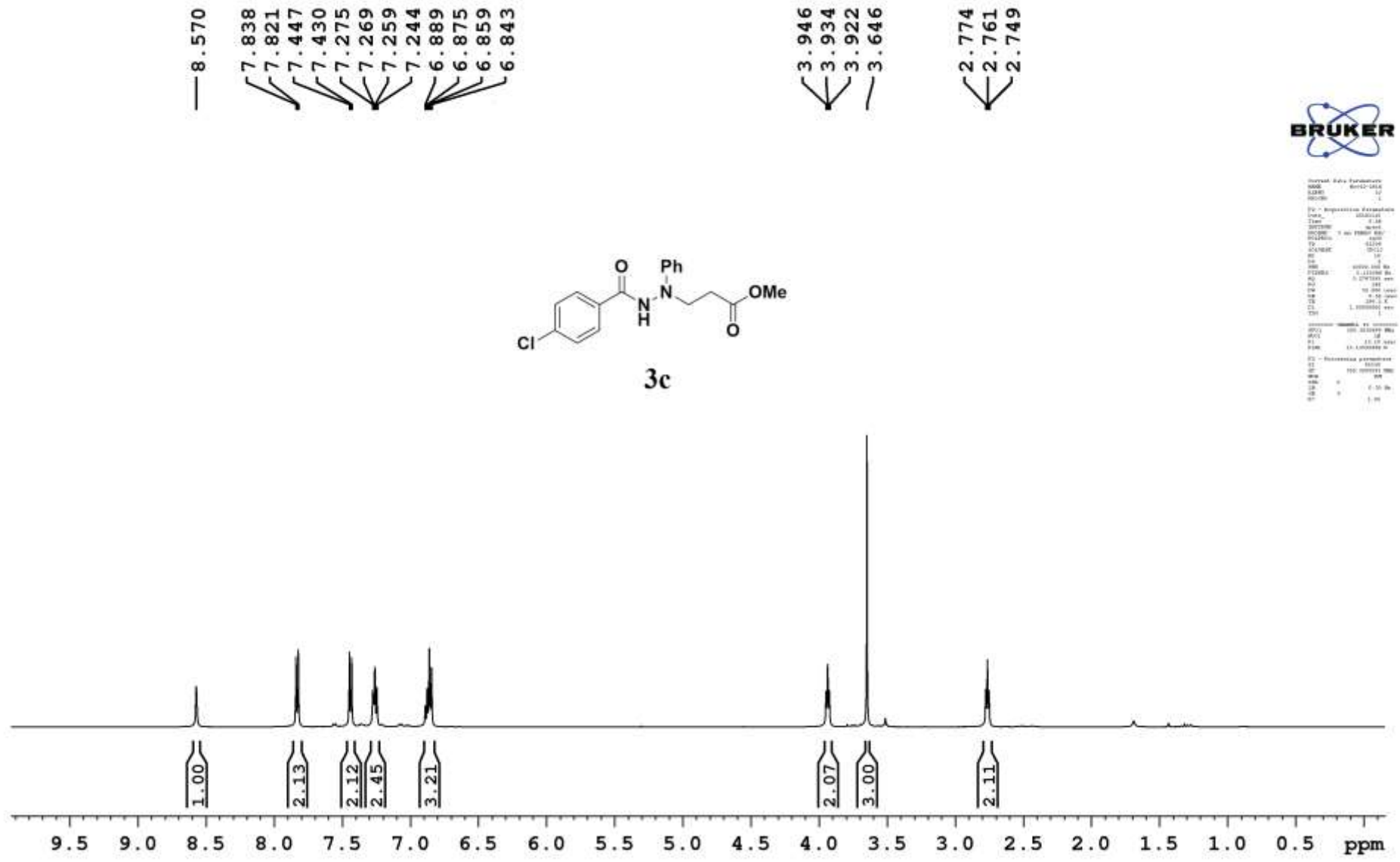



ES-AKJ-178-3-LB1; 19/05/2018
8.272
7.800
7.784
7.299
7.283
7.274
7.269
7.258
7.242
6.892
6.876
6.864
6.849
3.980
3.967
3.955
3.647
2.793
2.780
2.767
2.435
BRUKER
O
Ph
N
N
H
OMe
O
Me
3b
0.97
1.96
2.02
2.44
2.95
2.02
3.00
2.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

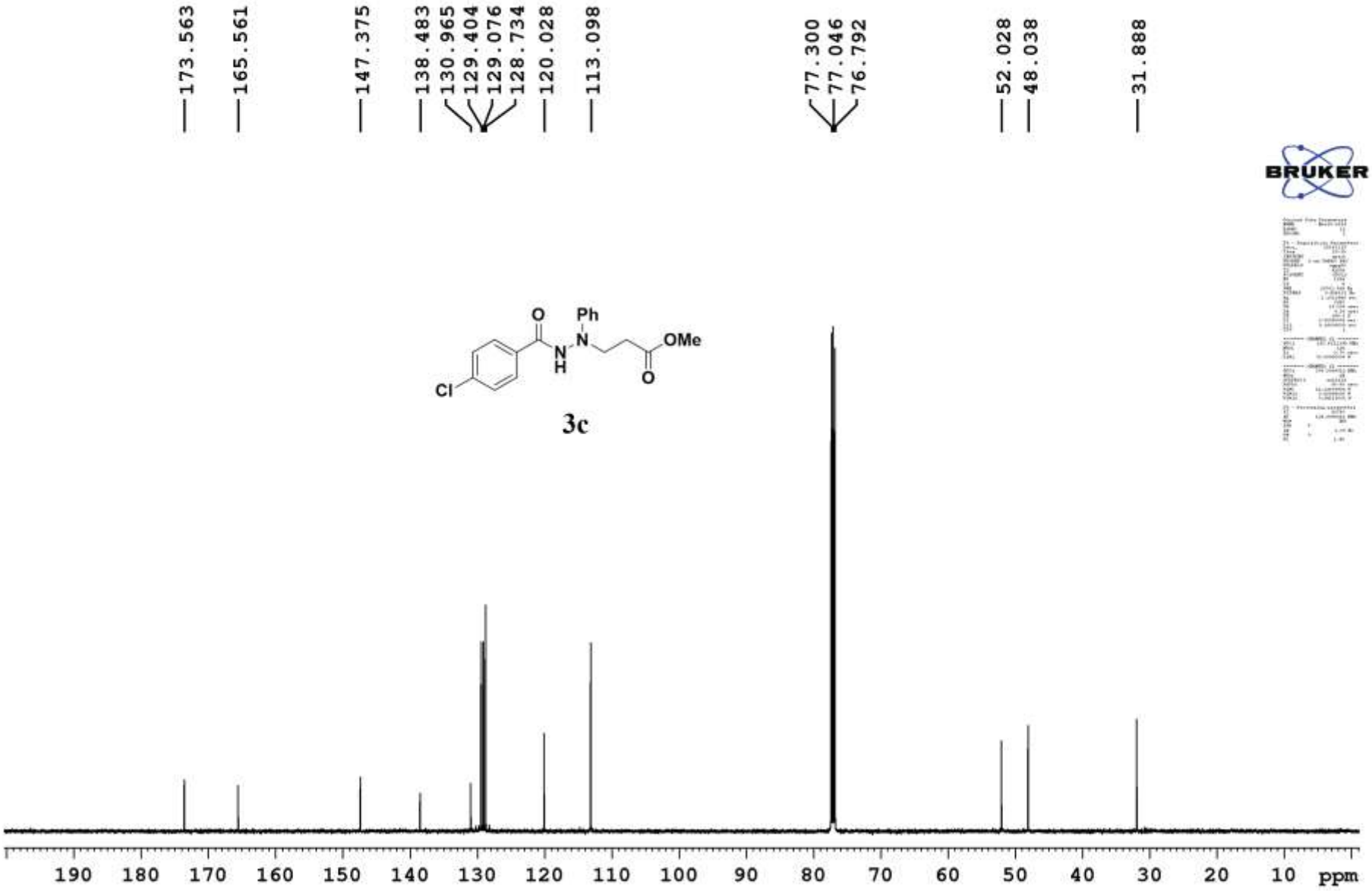
ES-AKJ-178-3-LB1; 21/05/2018

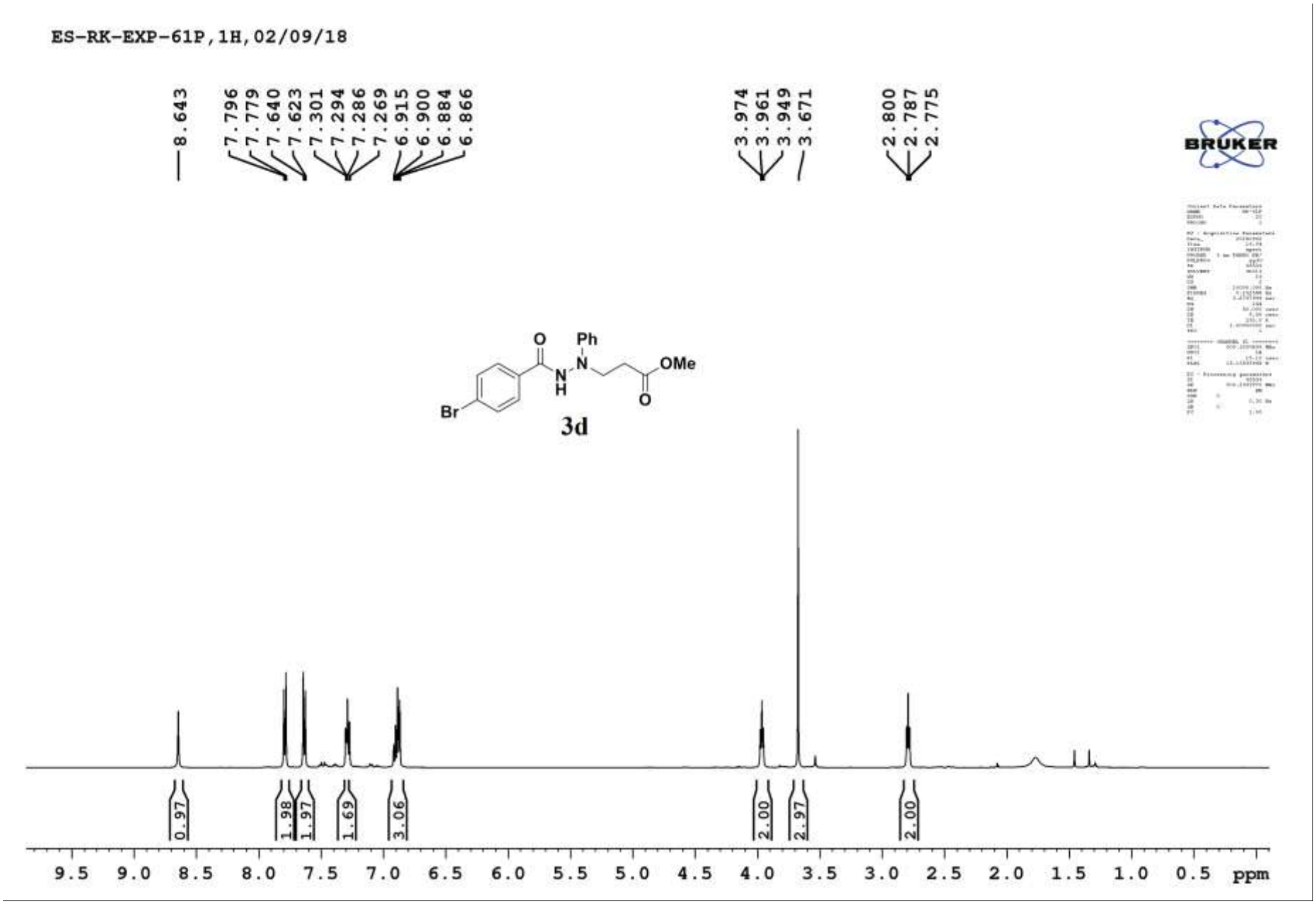


ES-AKJ-MC-50; 10/11/2018

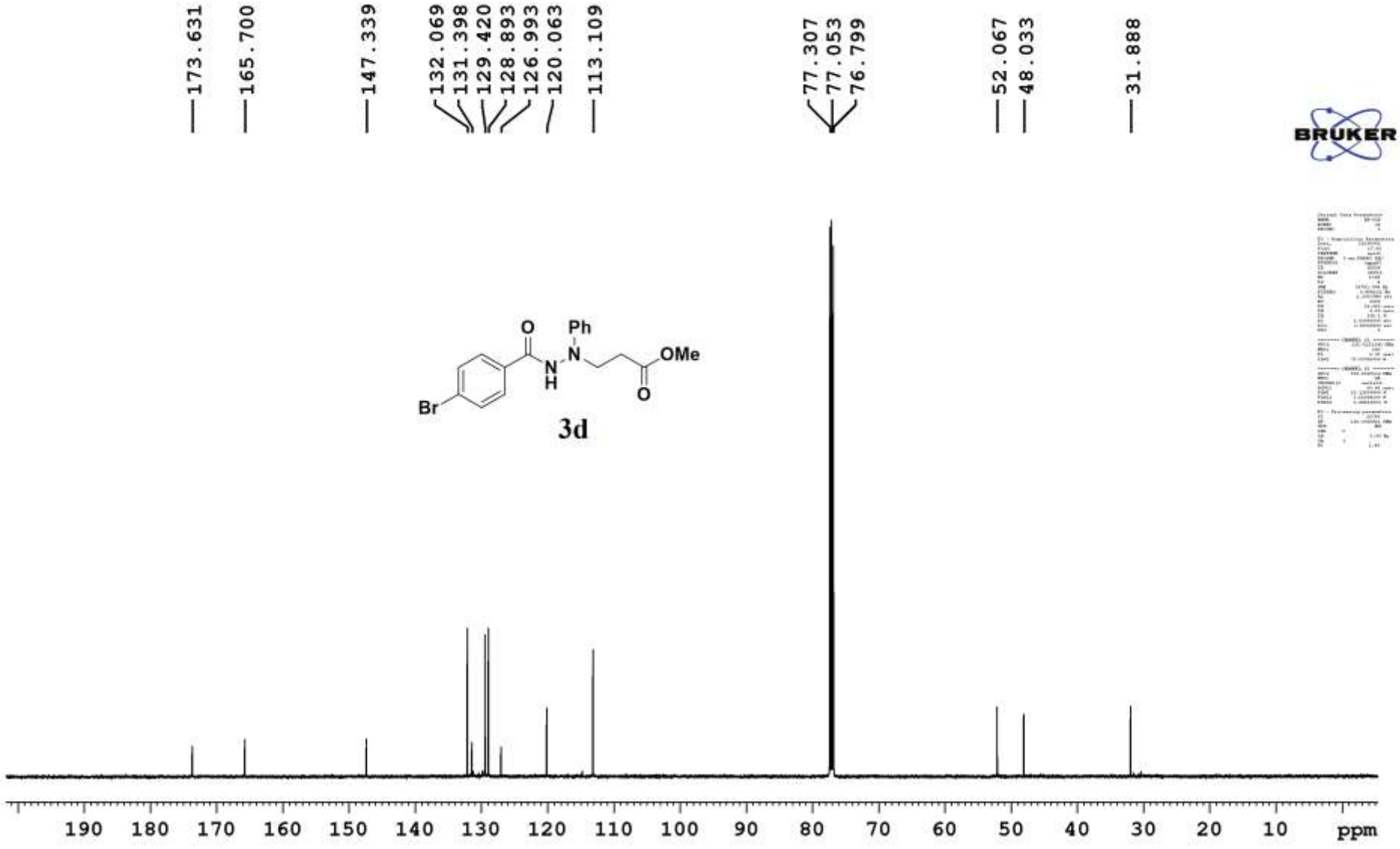


ES-AKJ-MC-50; 10/11/2018

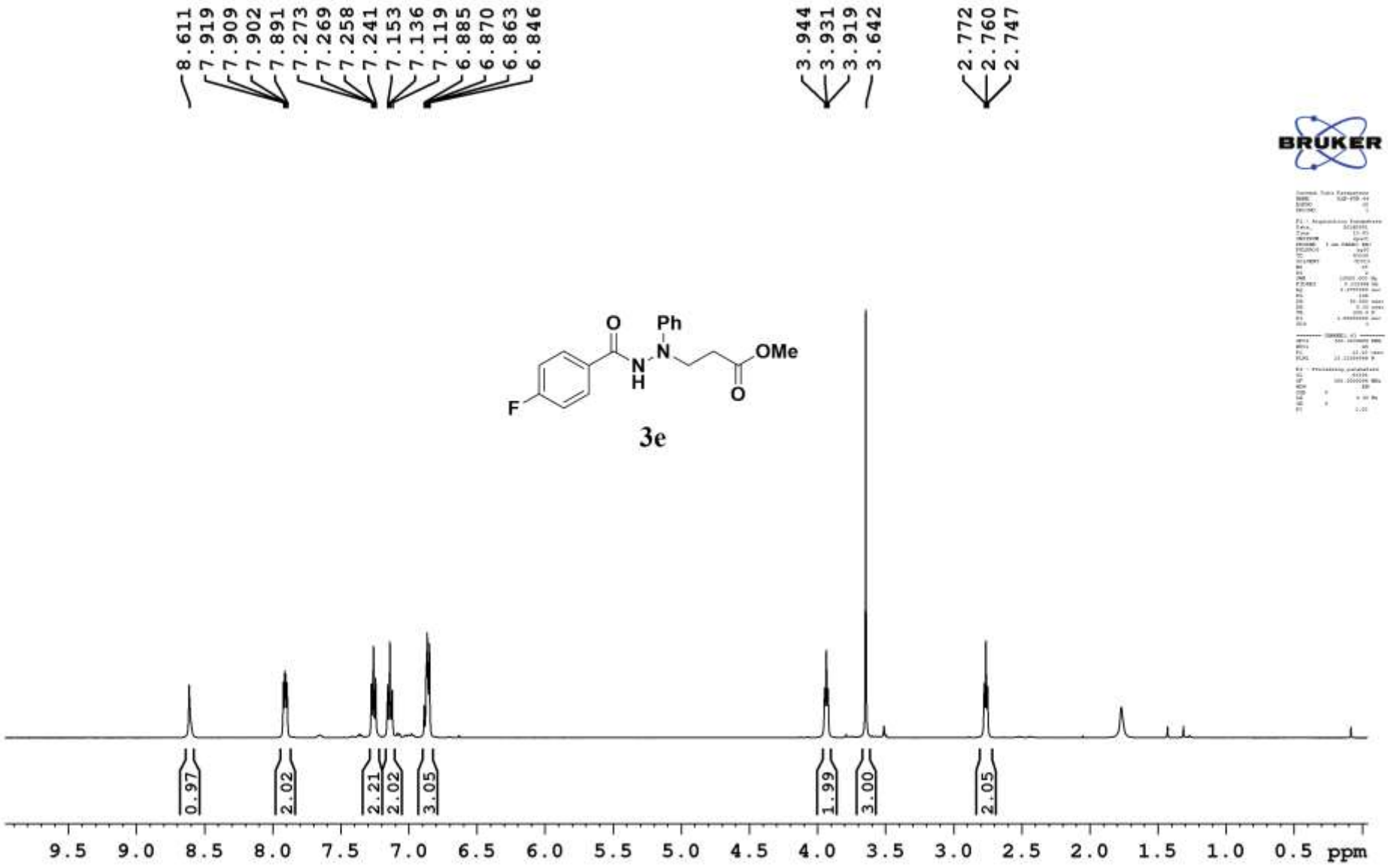



ES-RK-EXP-61P,1H,02/09/18
8.643
7.796
7.779
7.640
7.623
7.301
7.294
7.286
7.269
6.915
6.900
6.884
6.866
3.974
3.961
3.949
3.671
2.800
2.787
2.775
BRUKER
O
Ph
N
N
H
OMe
O
Br
3d
0.97
1.98
1.97
1.69
3.06
2.00
2.97
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

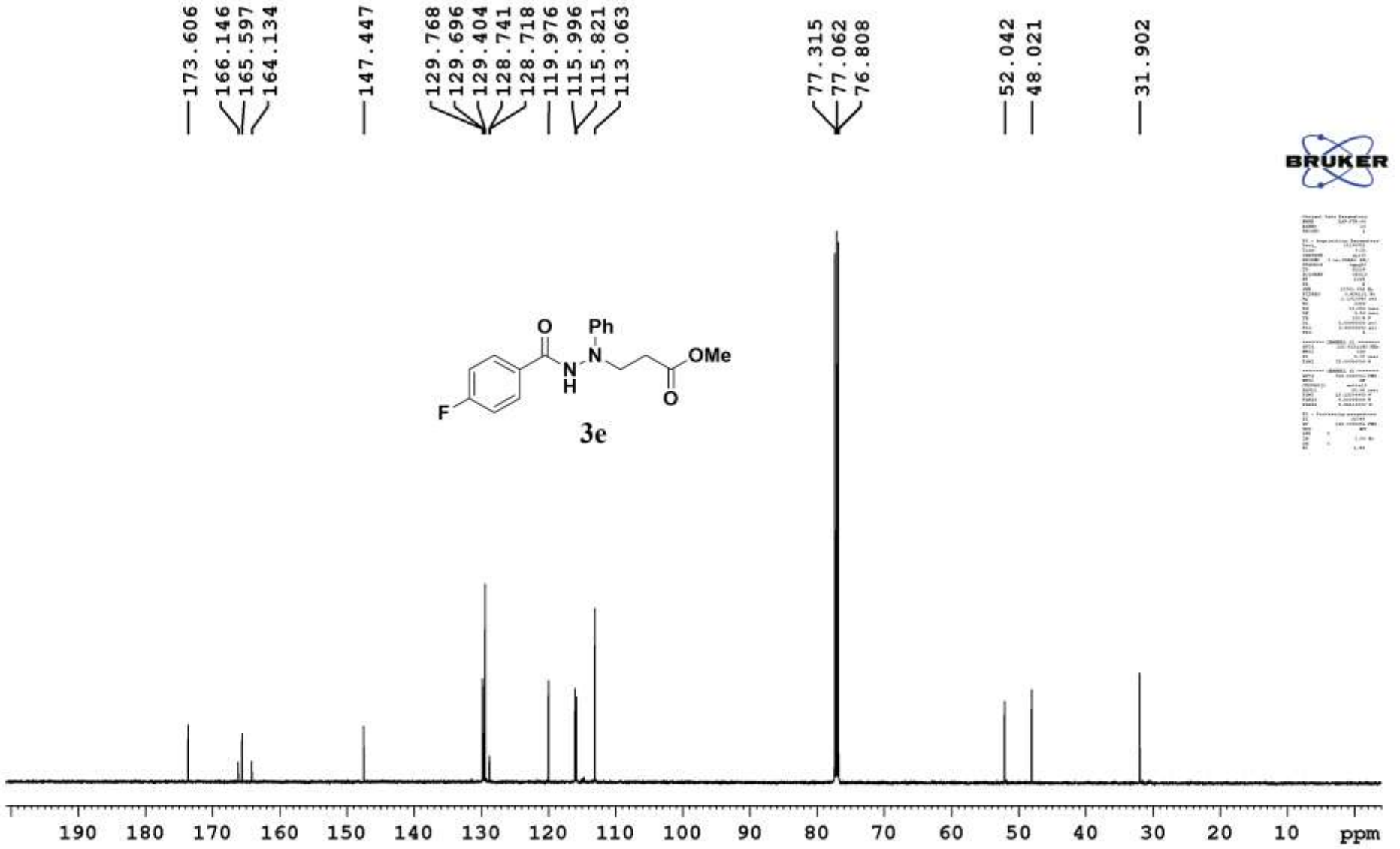
ES-RK-EXP-61P,13C,02/09/18



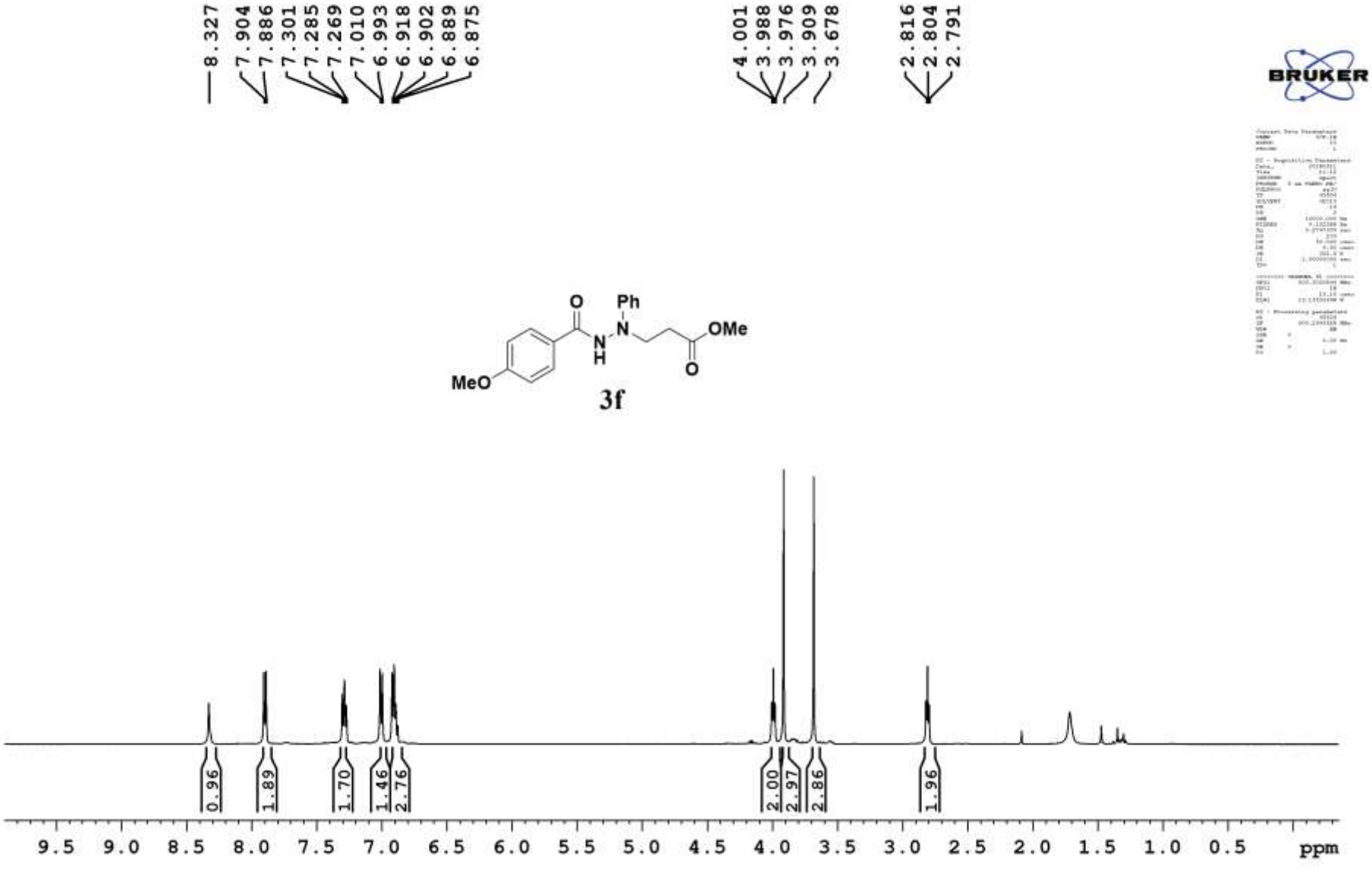
ES-RK-EXP-64P,1H,CDCL3,01/09/18

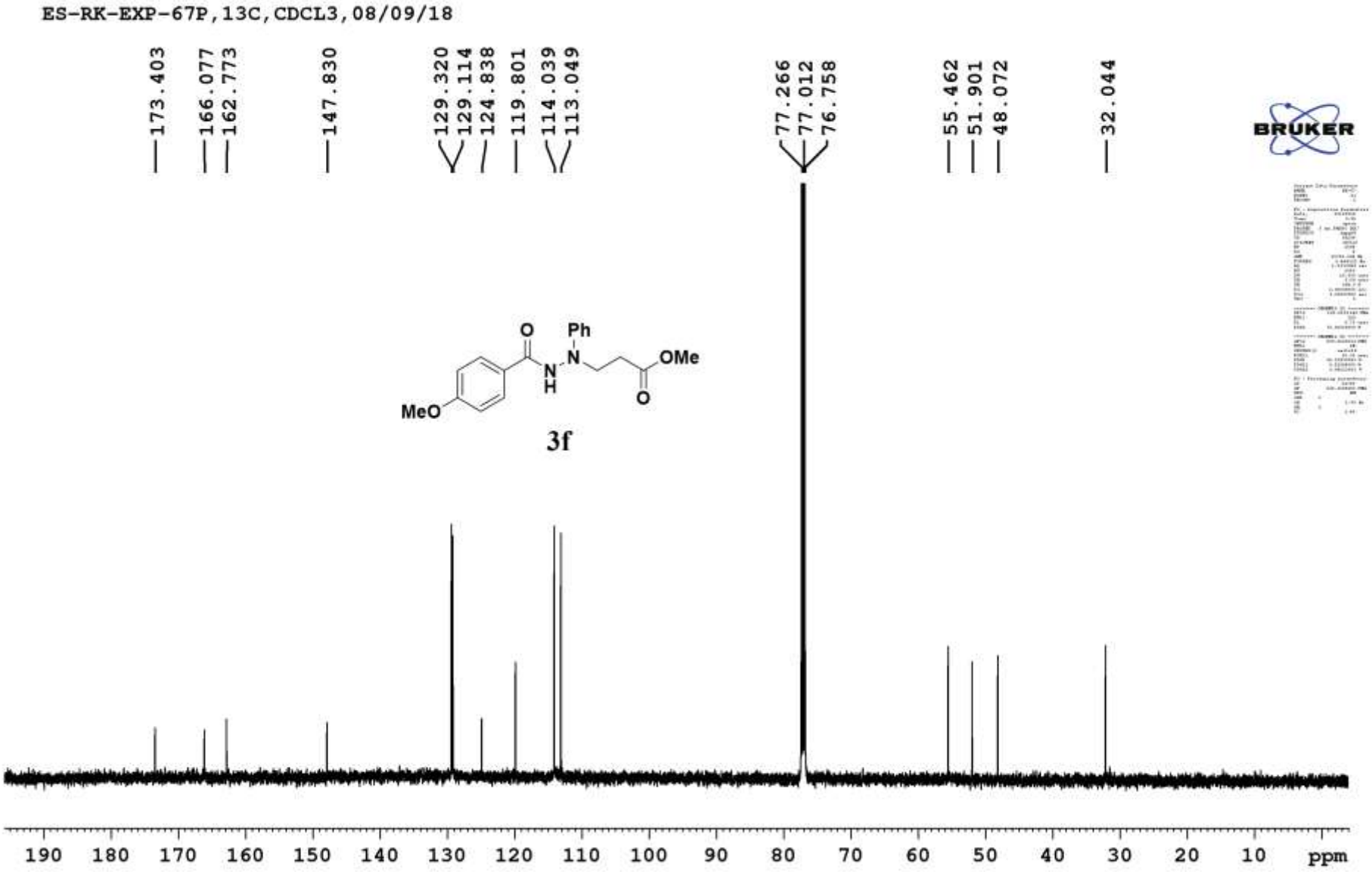


ES-RK-EXP-64,13C,02/09/18

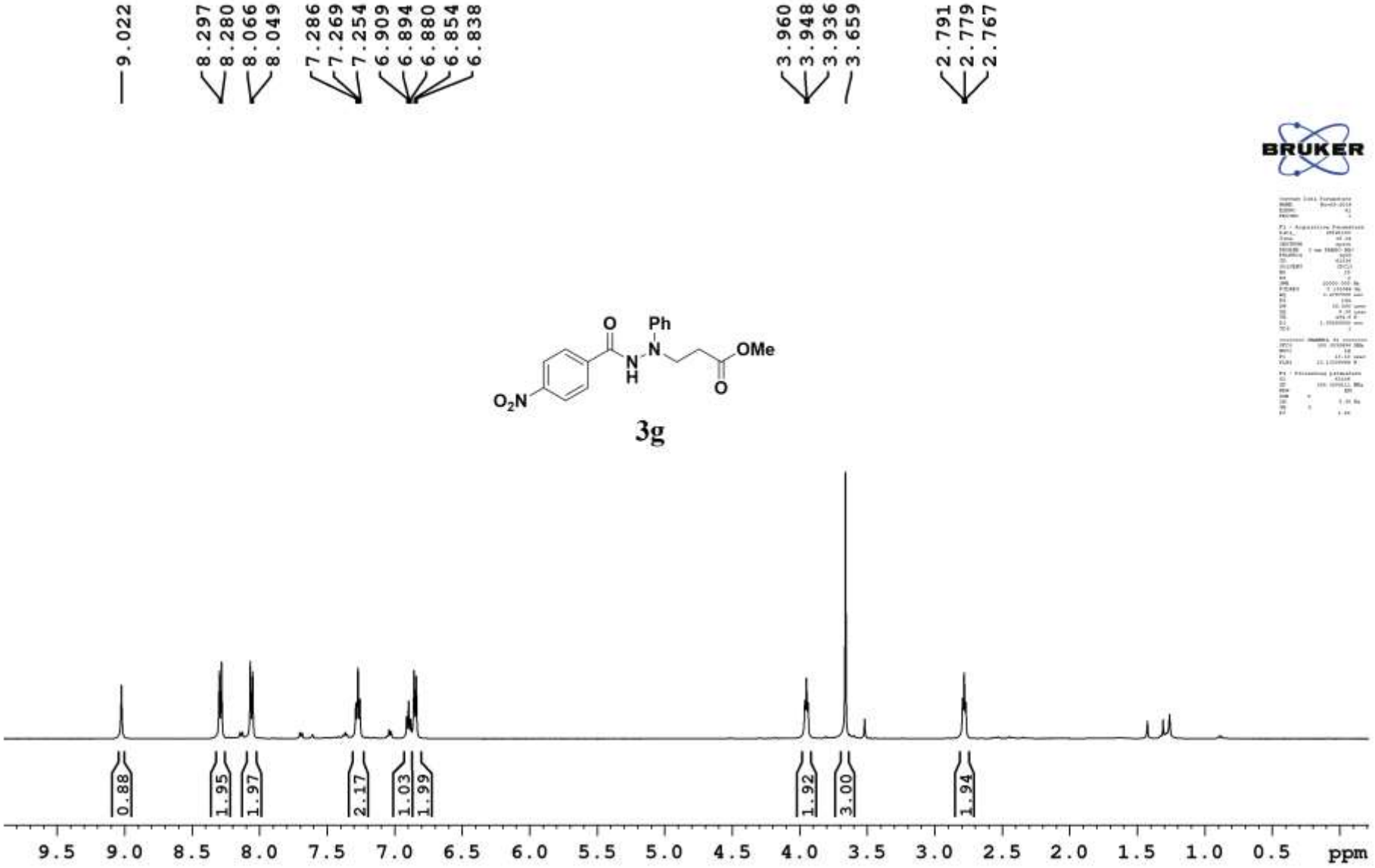


ES-RK-EXP-67P,1H,11/09/18

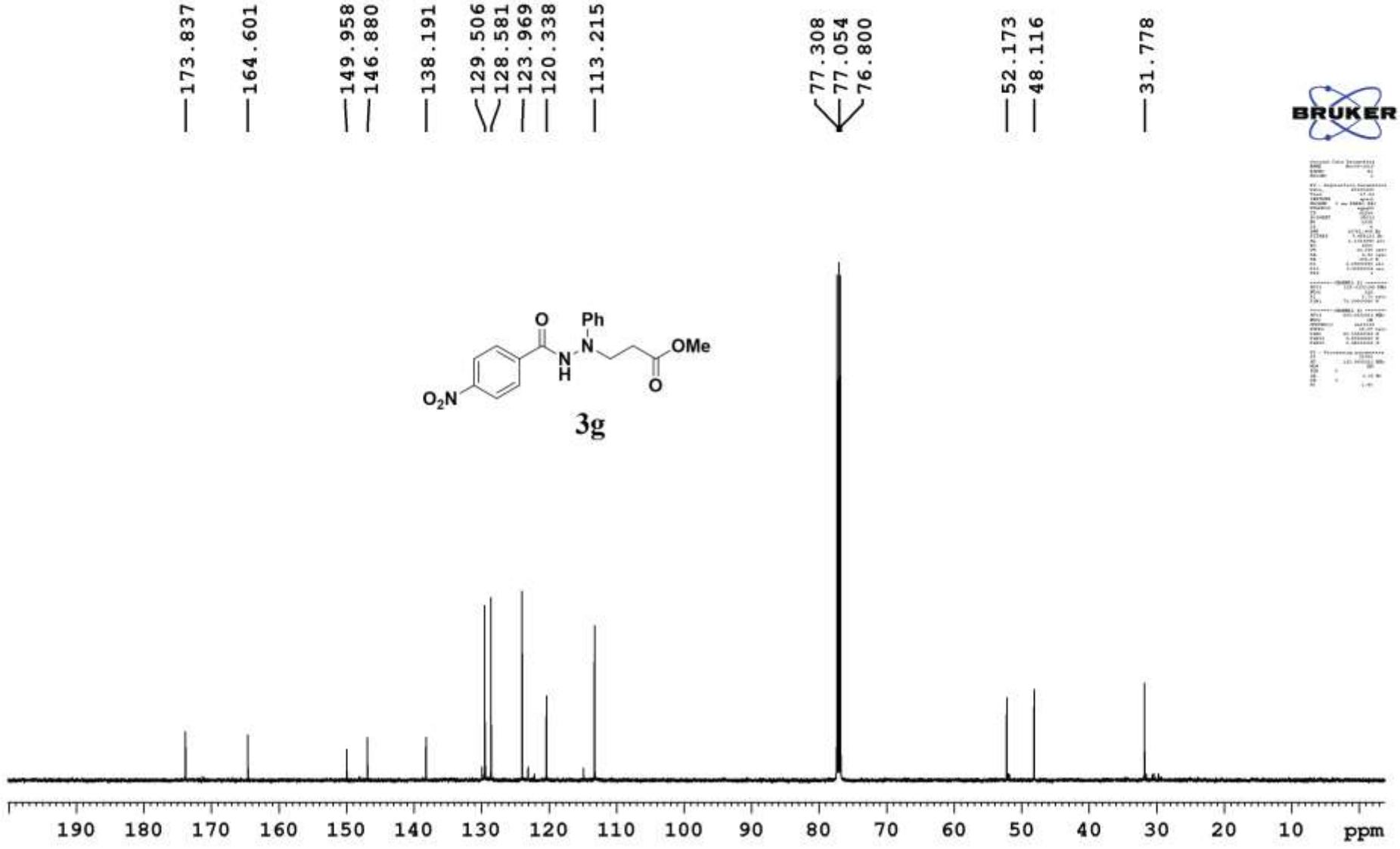



ES-RK-EXP-67P,13C,CDCL3,08/09/18
173.403
166.077
162.773
147.830
129.320
129.114
124.838
119.801
114.039
113.049
77.266
77.012
76.758
55.462
51.901
48.072
32.044
BRUKER
O
Ph
N
N
H
OMe
O
MeO
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

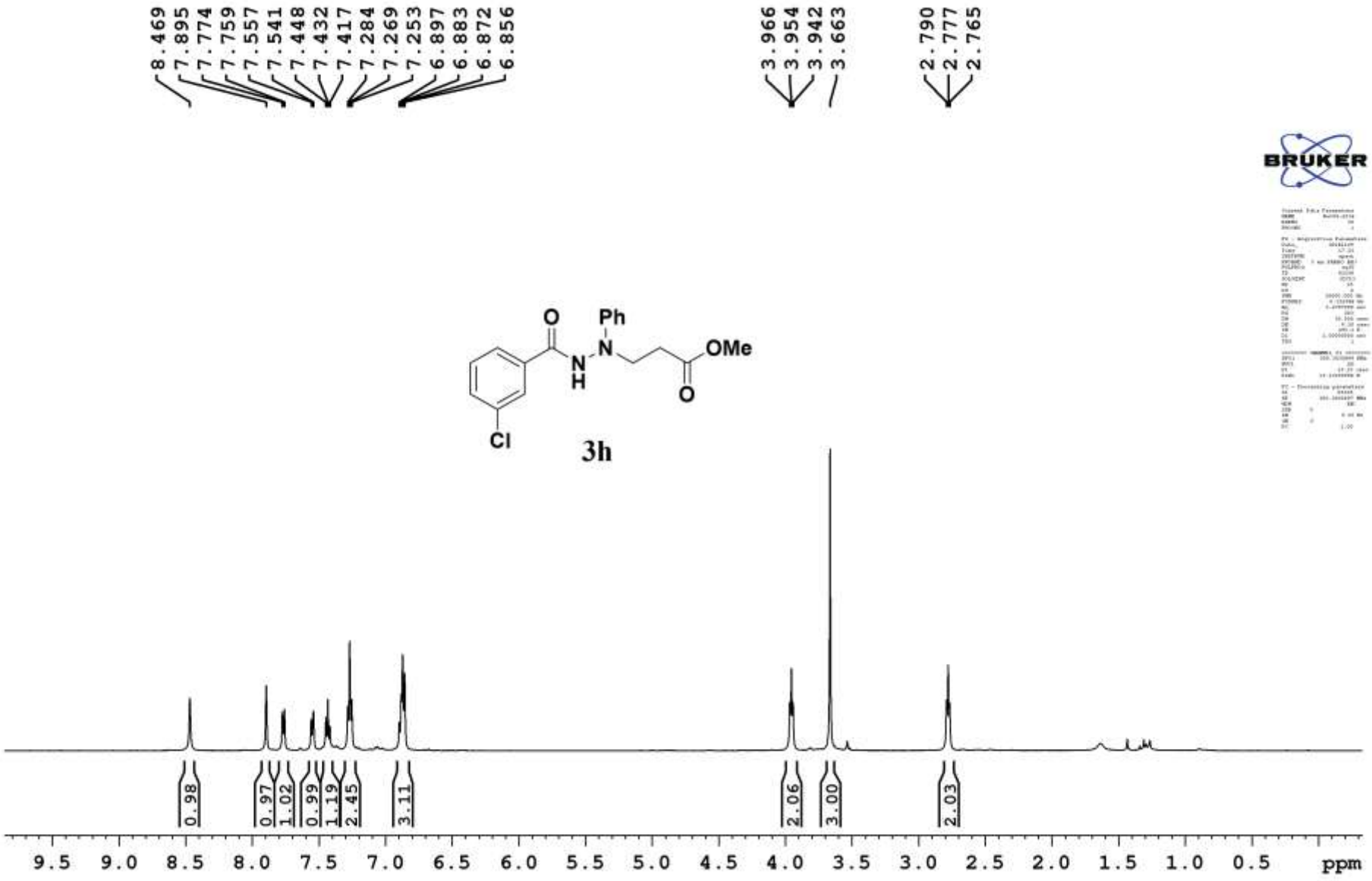
ES-AKJ-219; 09/11/2018



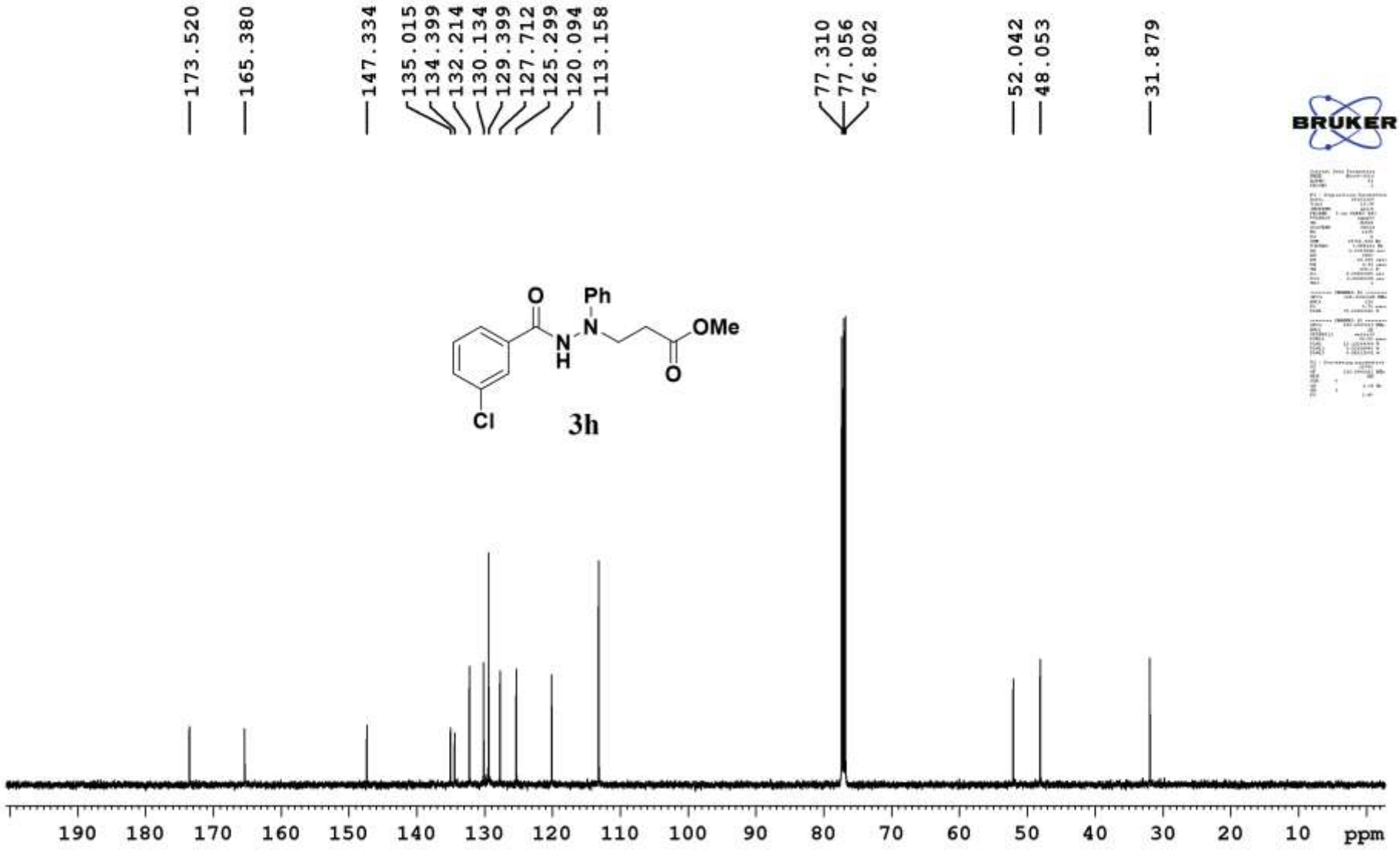
ES-AKJ-219; 09/11/2018



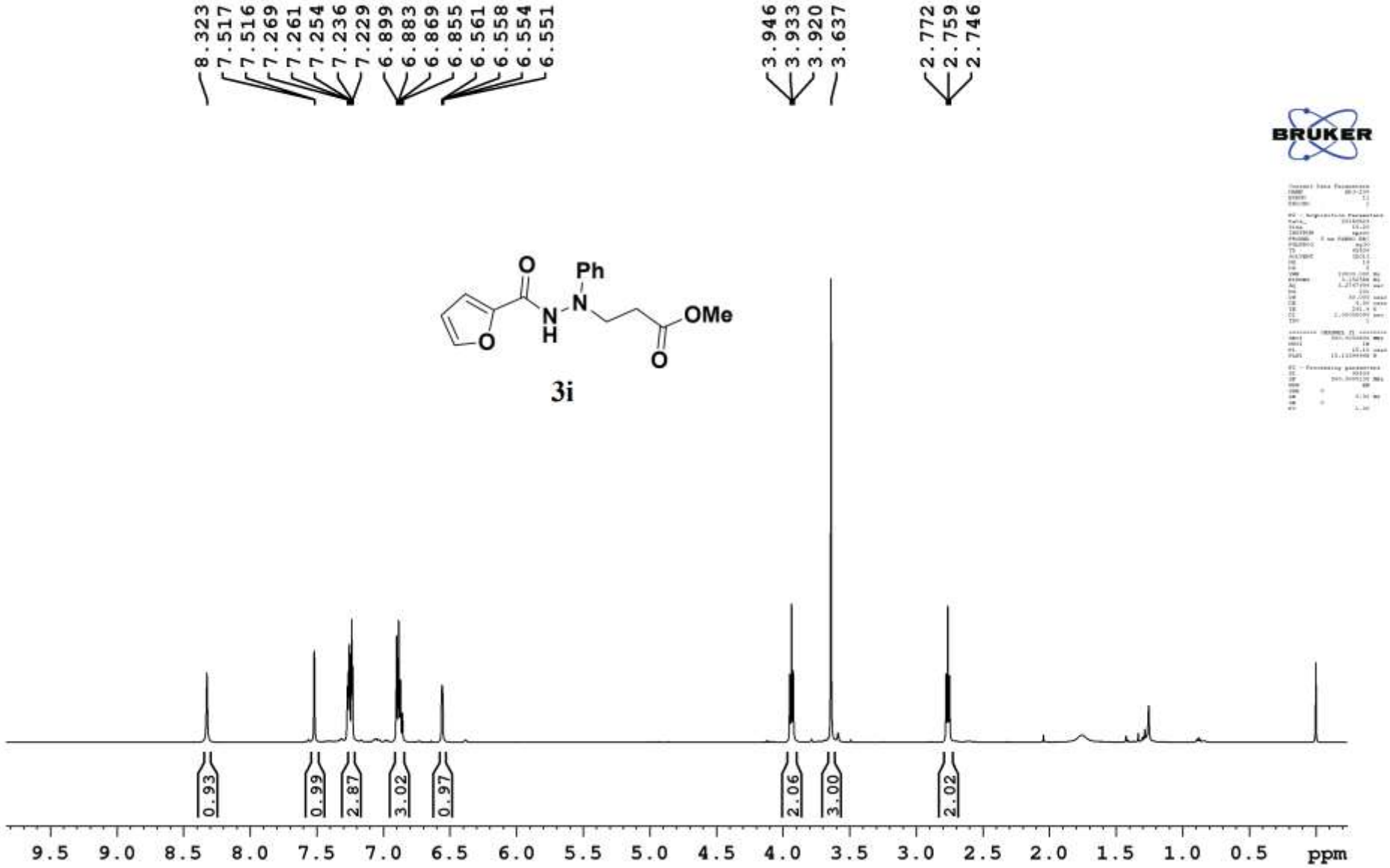
ES-AKJ-198-3; 09/11/2018



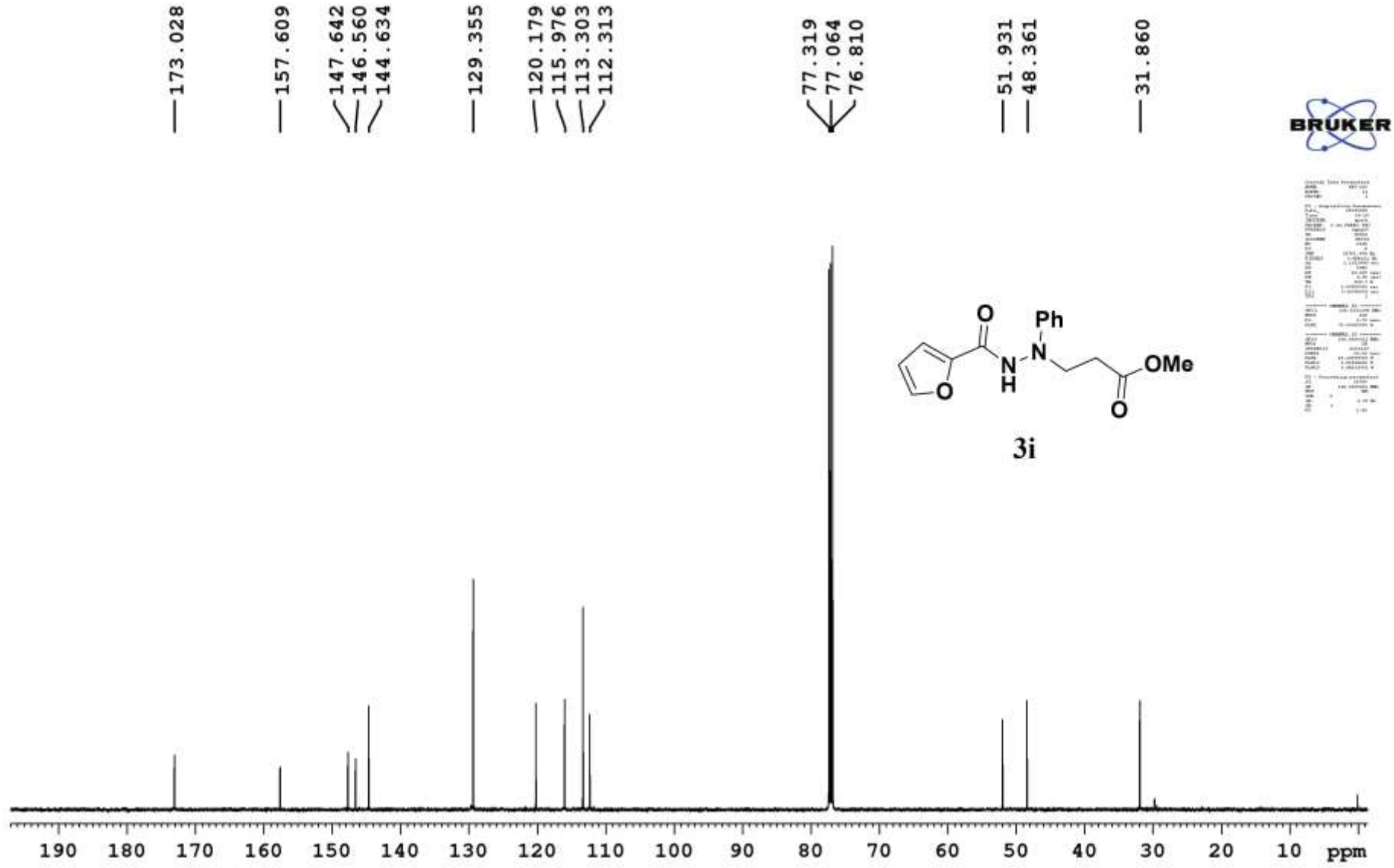
ES-AKJ-198-3; 09/11/2018



ES-AKJ-230; 23/08/2018

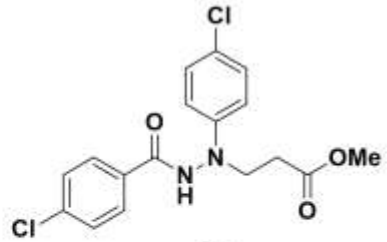


ES-AKJ-230; 23/08/2018

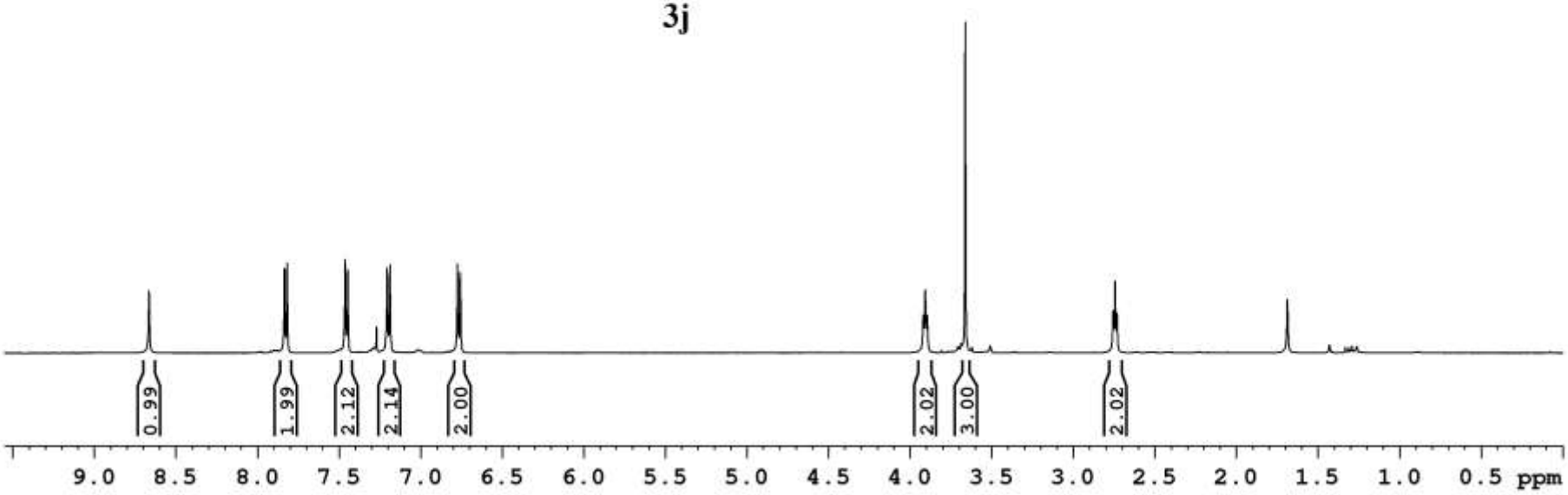


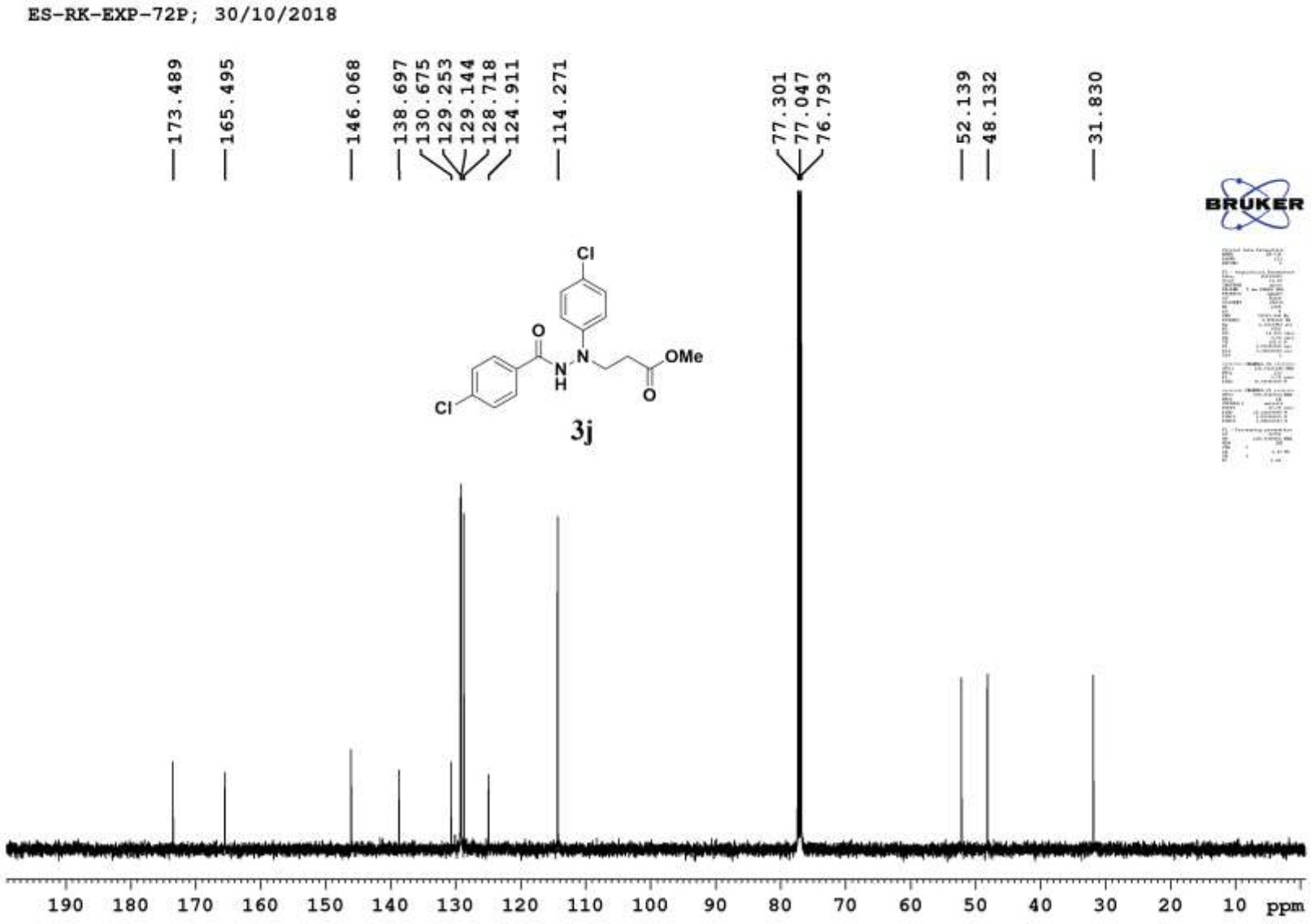
ES-RK-EXP-72P; 30/10/2018

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

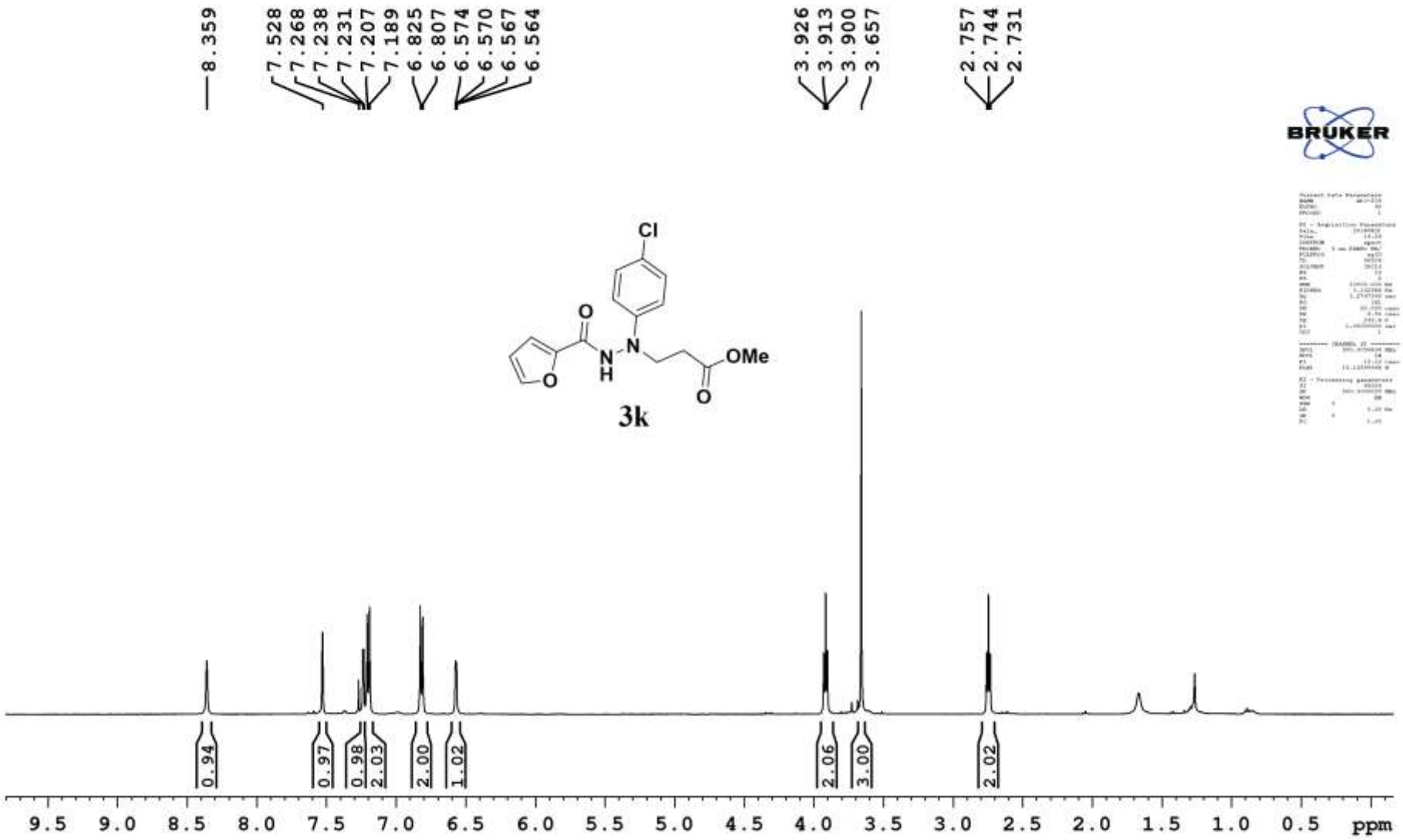


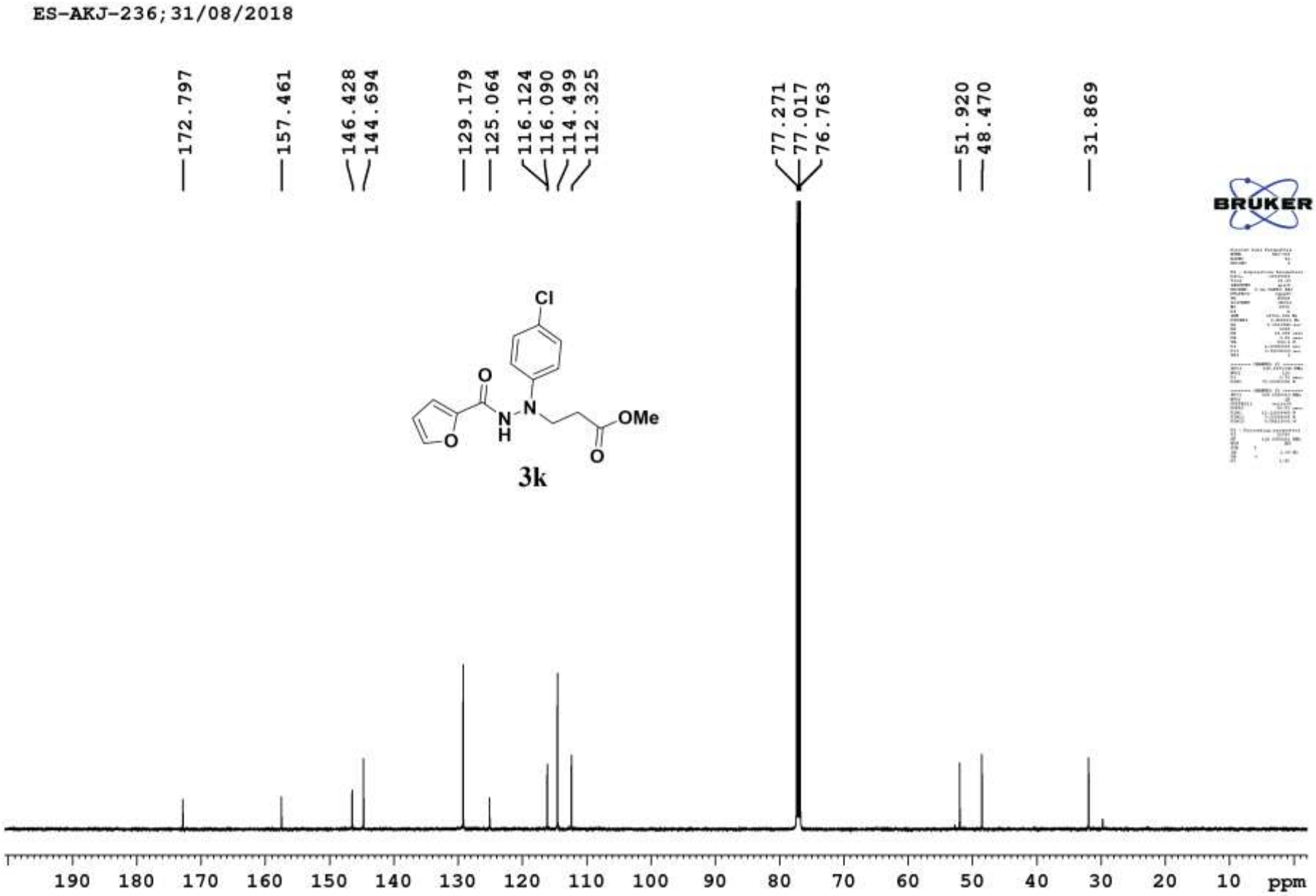
3j



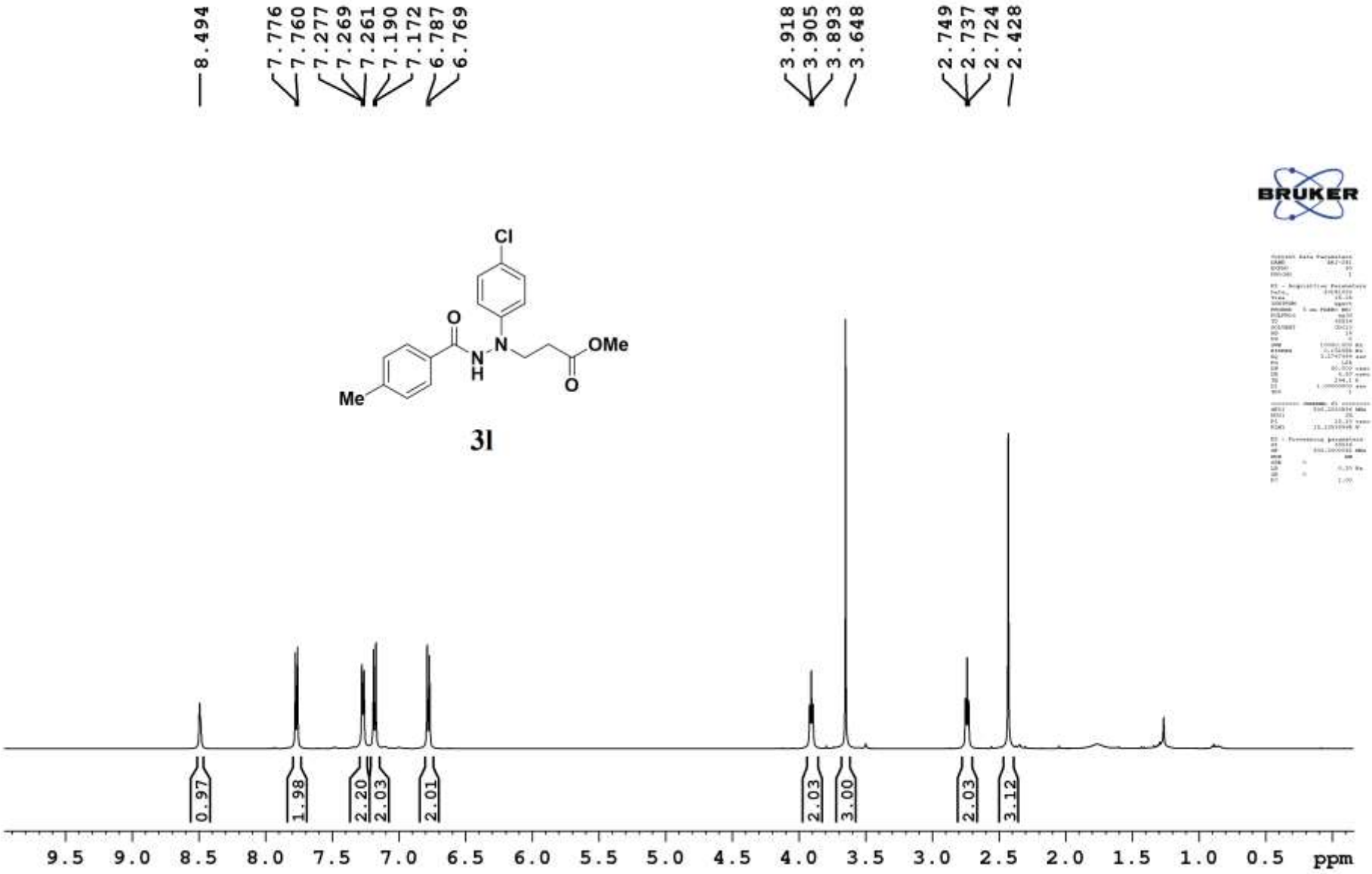

ES-RK-EXP-72P; 30/10/2018
173.489
165.495
146.068
138.697
130.675
129.253
129.144
128.718
124.911
114.271
77.301
77.047
76.793
52.139
48.132
31.830
BRUKER
Cl
O
N
N
H
OMe
O
Cl
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

ES-AKJ-236;31/08/2018

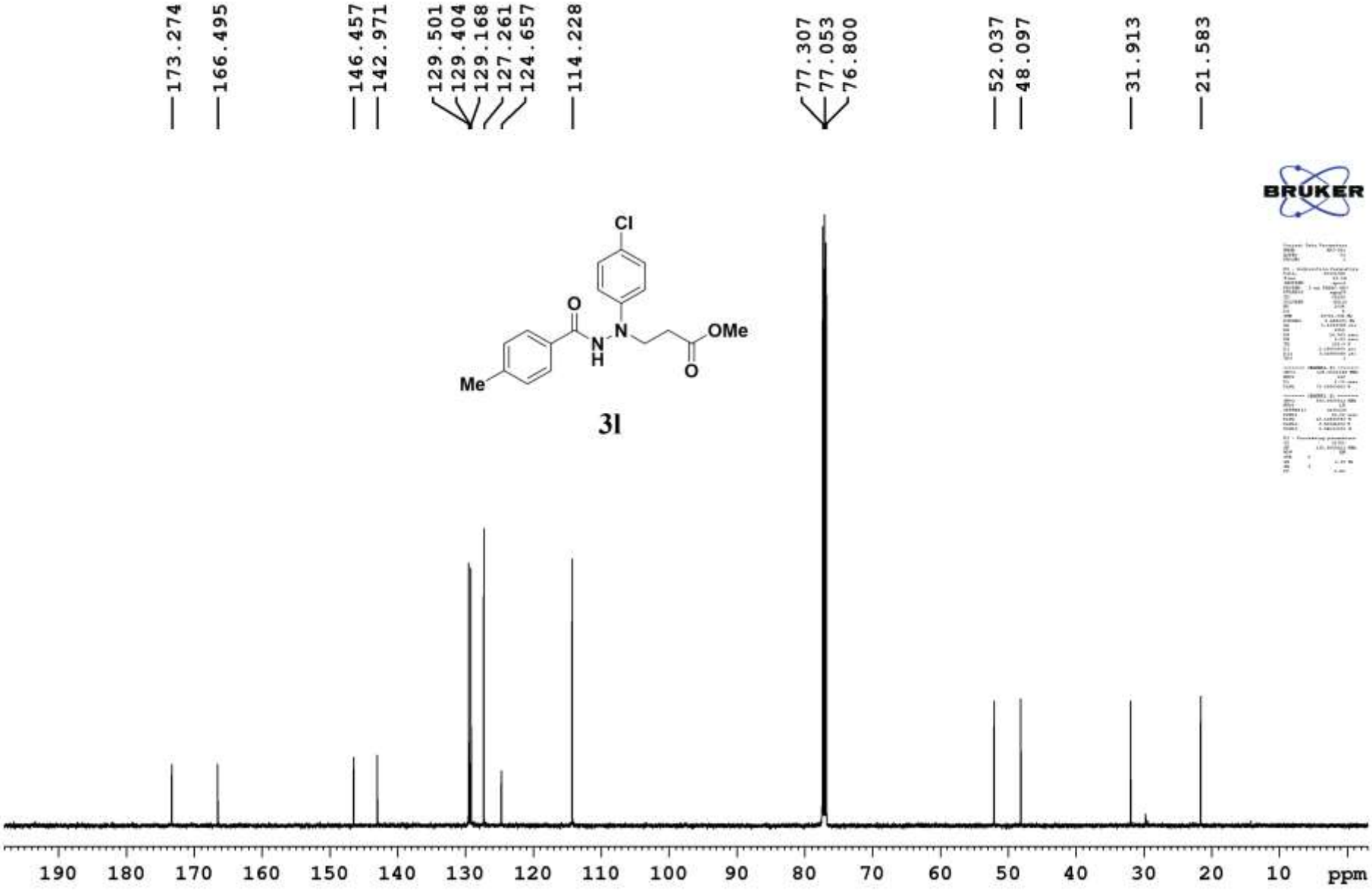



ES-AKJ-236;31/08/2018
172.797
157.461
146.428
144.694
129.179
125.064
116.124
116.090
114.499
112.325
77.271
77.017
76.763
51.920
48.470
31.869
BRUKER
Cl
O
N
N
H
O
OMe
O
3k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

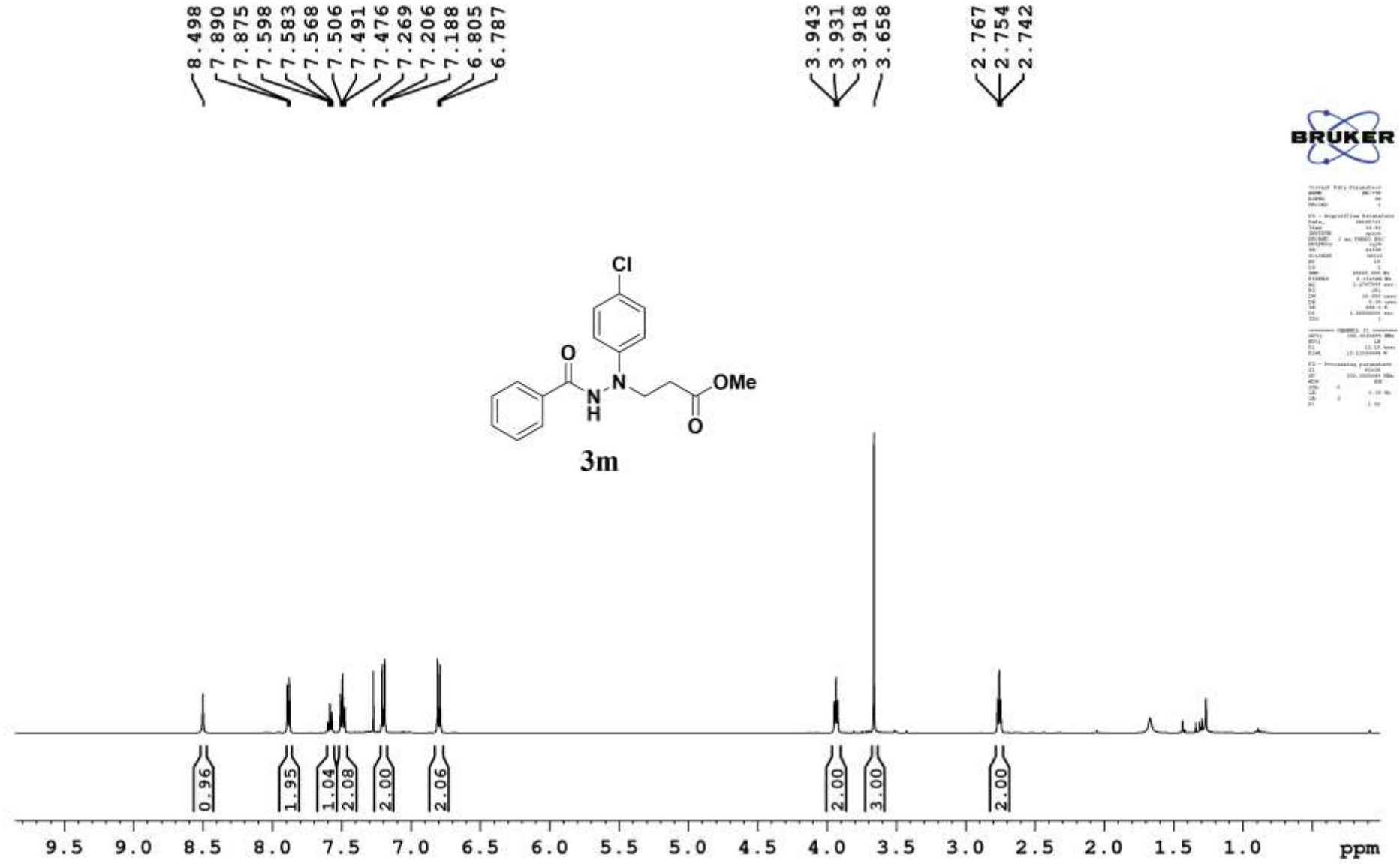
ES-AKJ-241; 30/10/2018



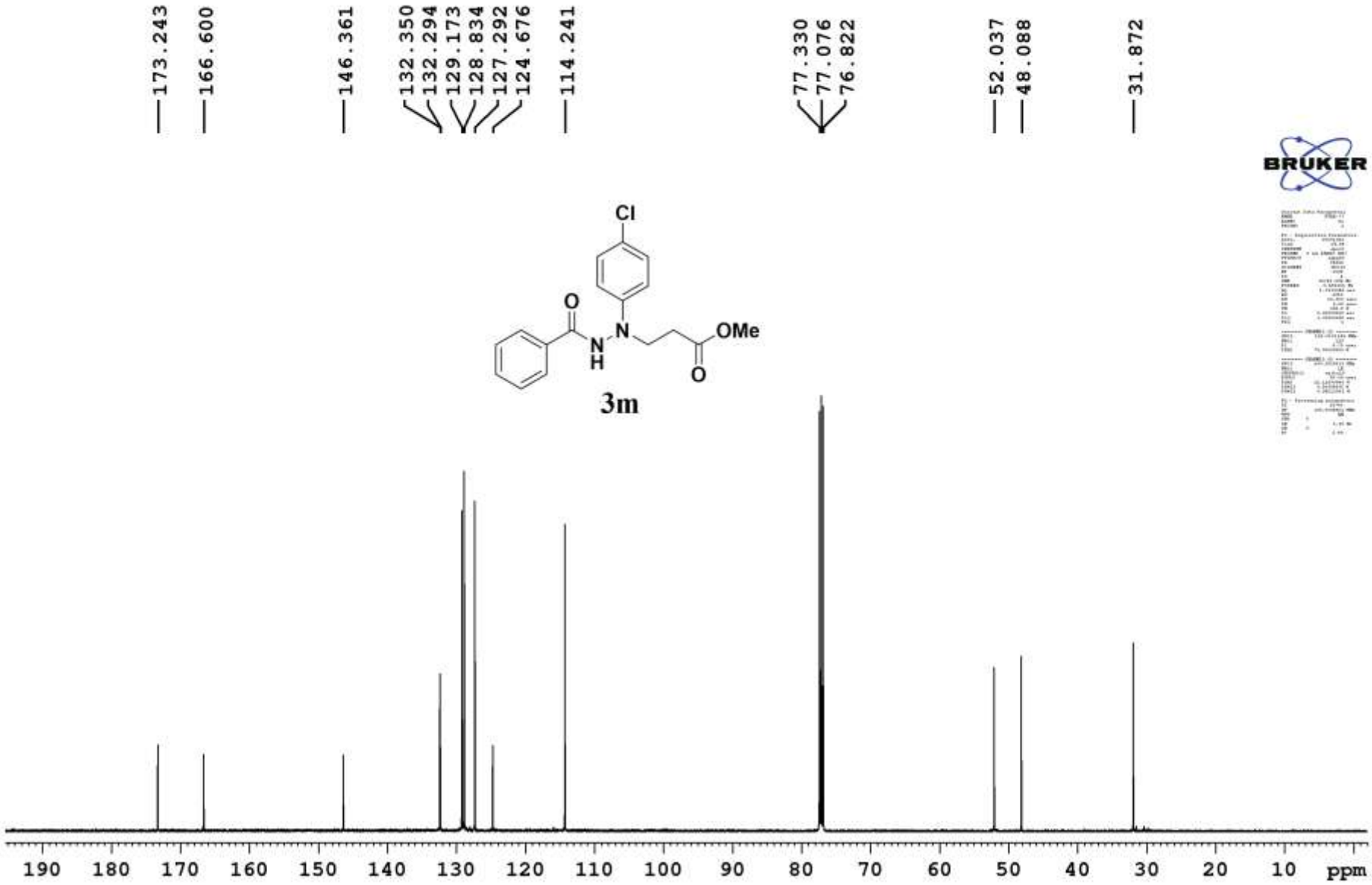
ES-AKJ-241; 30/10/2018



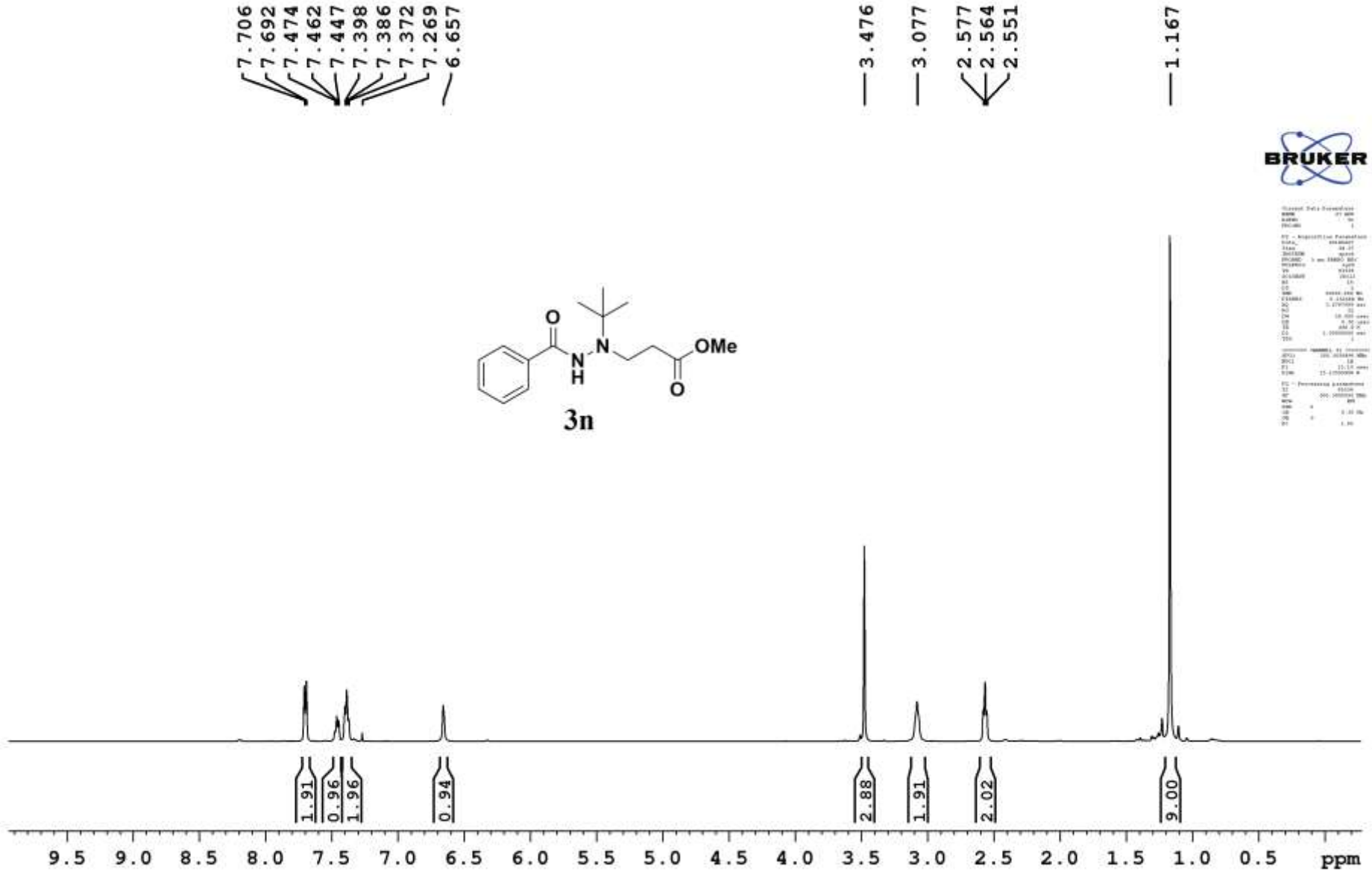
ES-RK-77P,1H,CDCl3,13/7/19



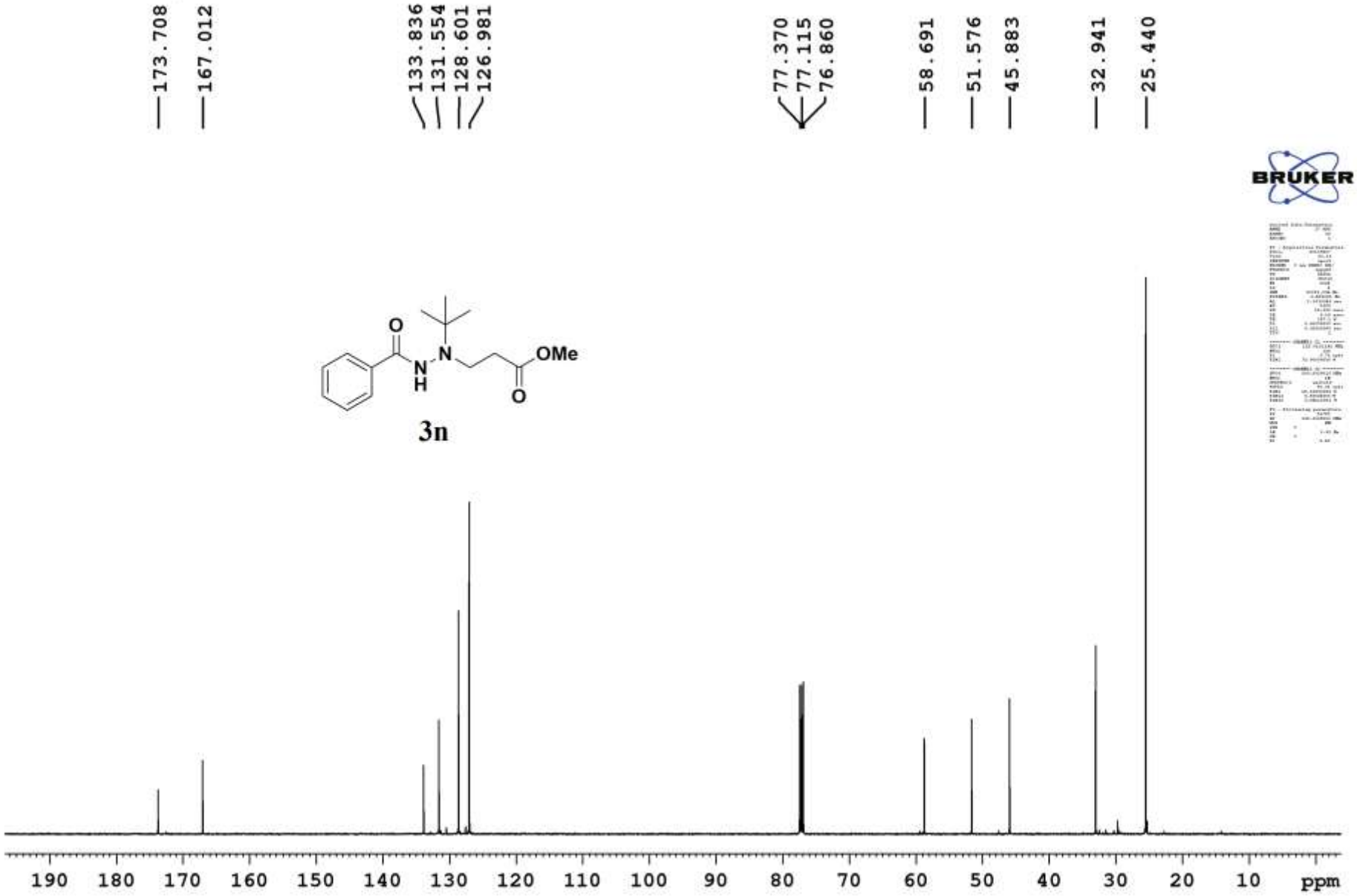
ES-RK-EXP-77P; 31/10/2018



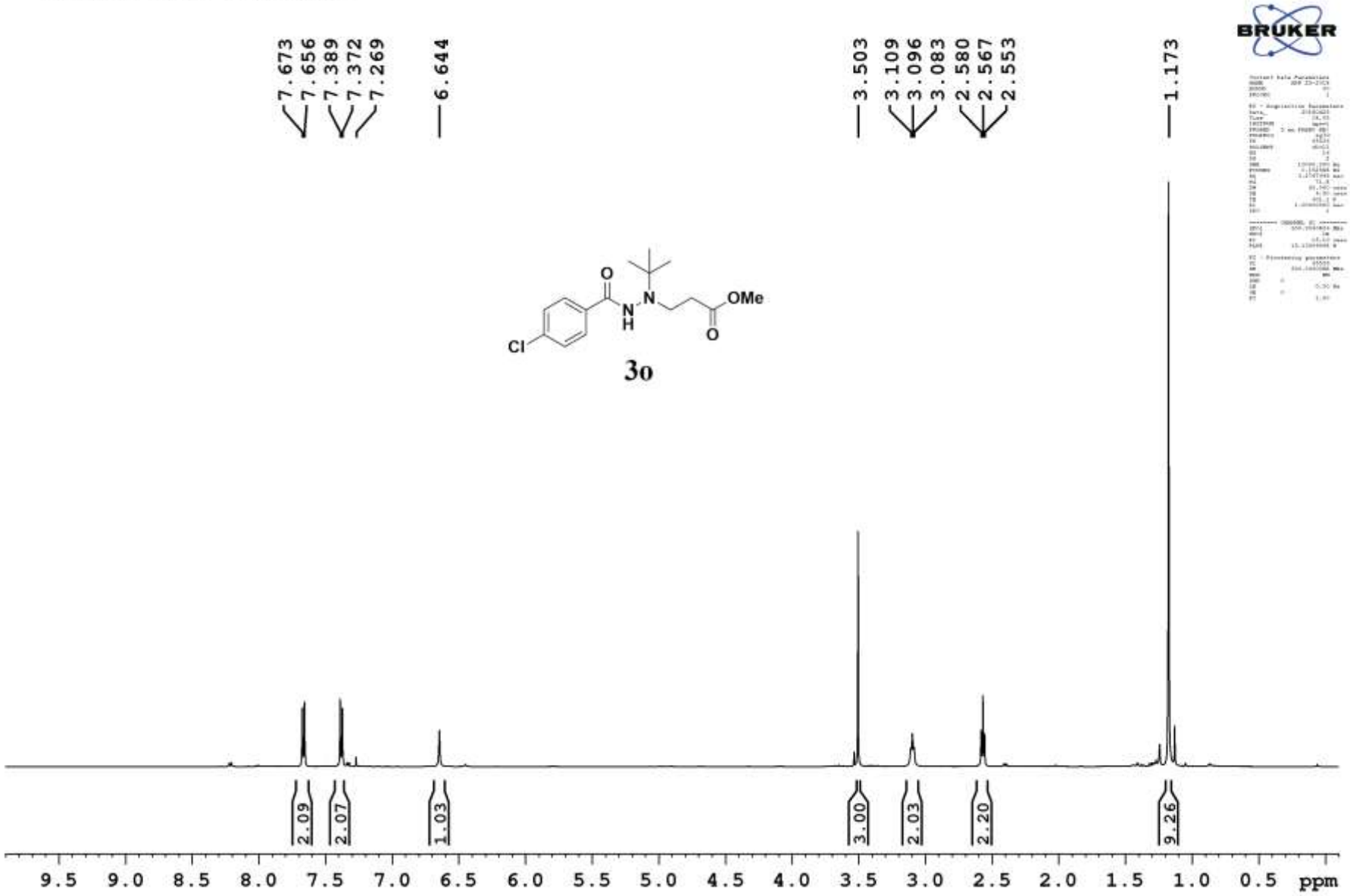
ES-MC-58-3; 27/04/2018



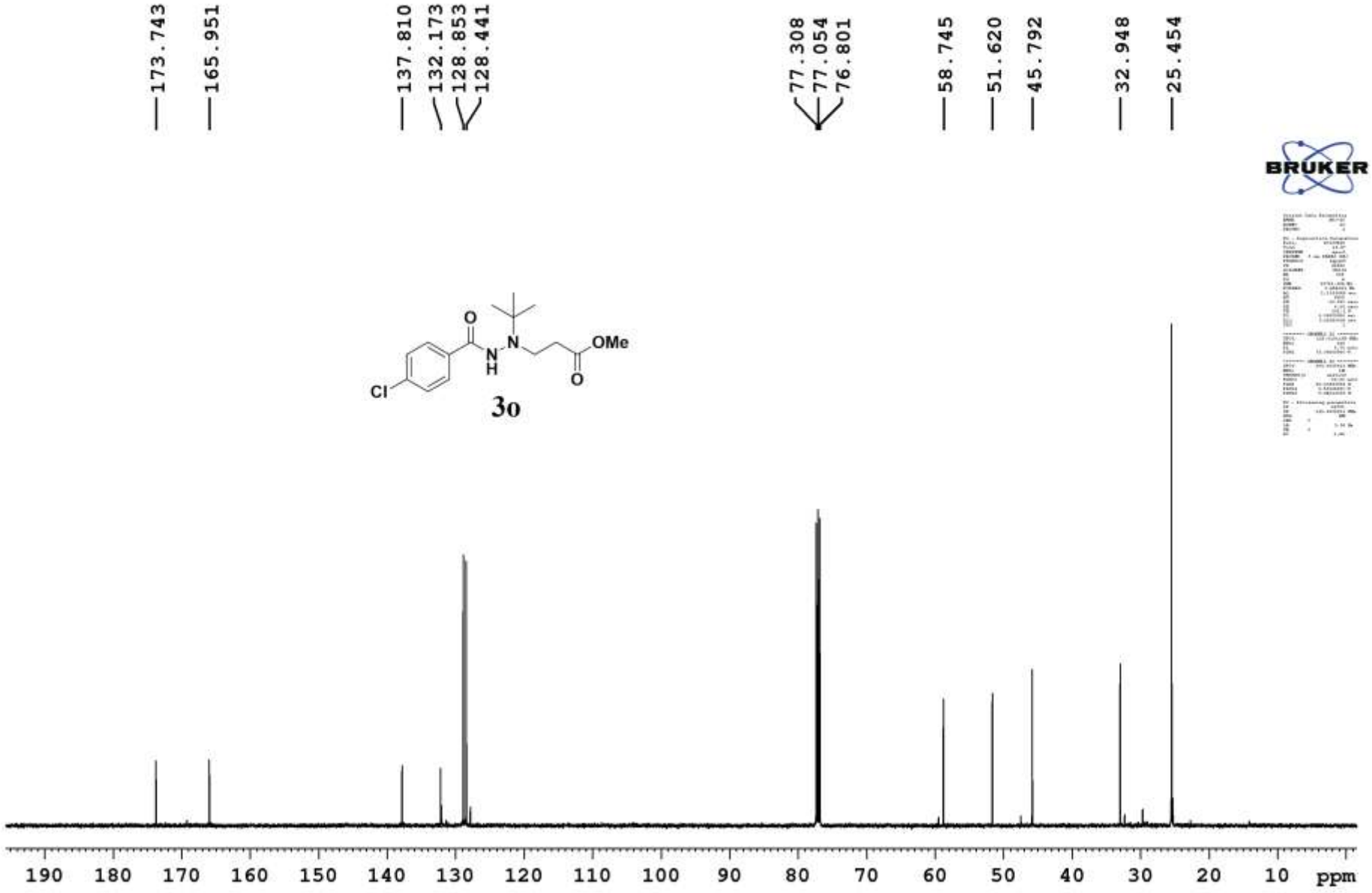
ES-MC-58-3; 27/04/2018



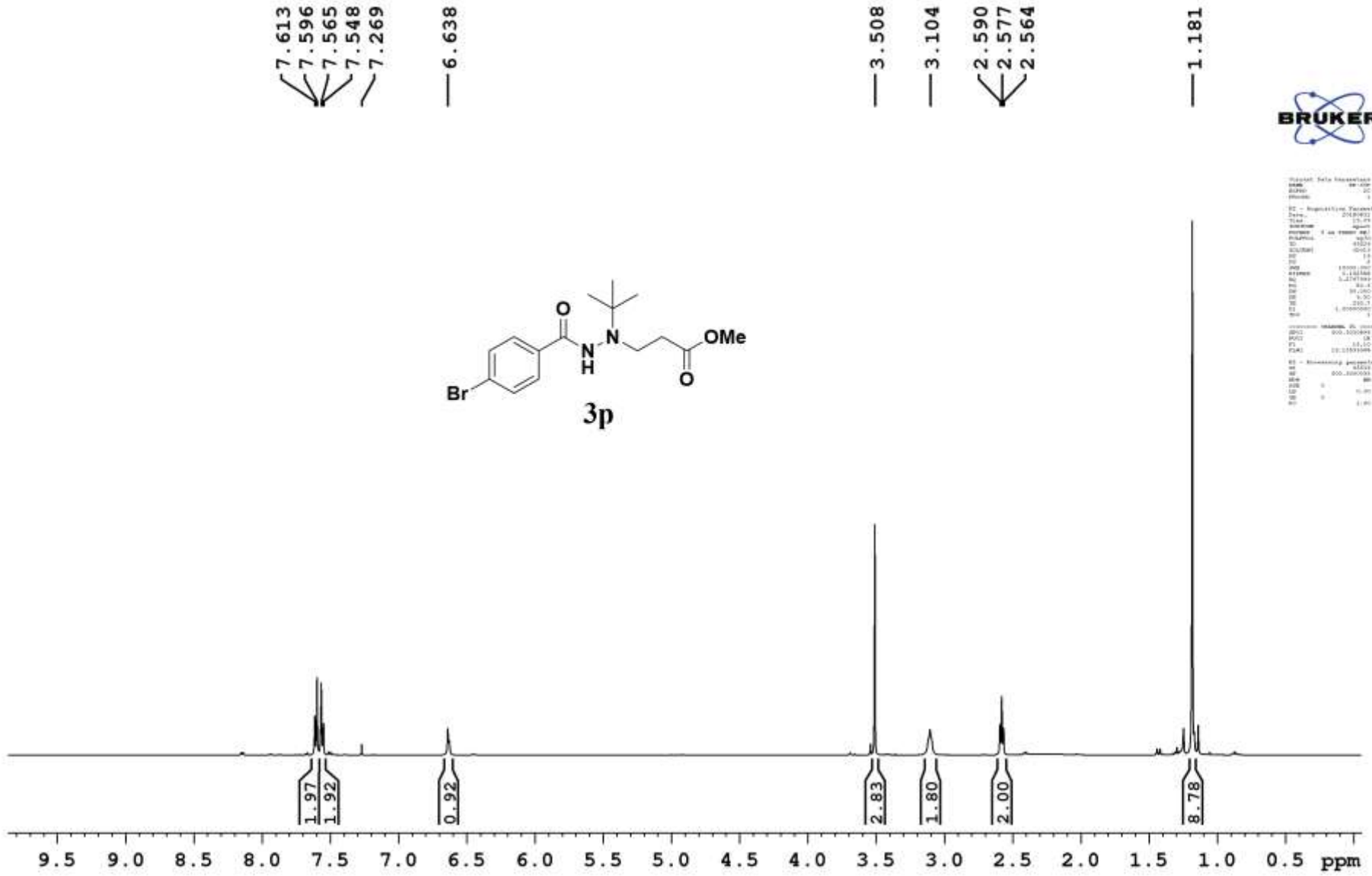
ES-AKJ-MC-55; 24/04/2018

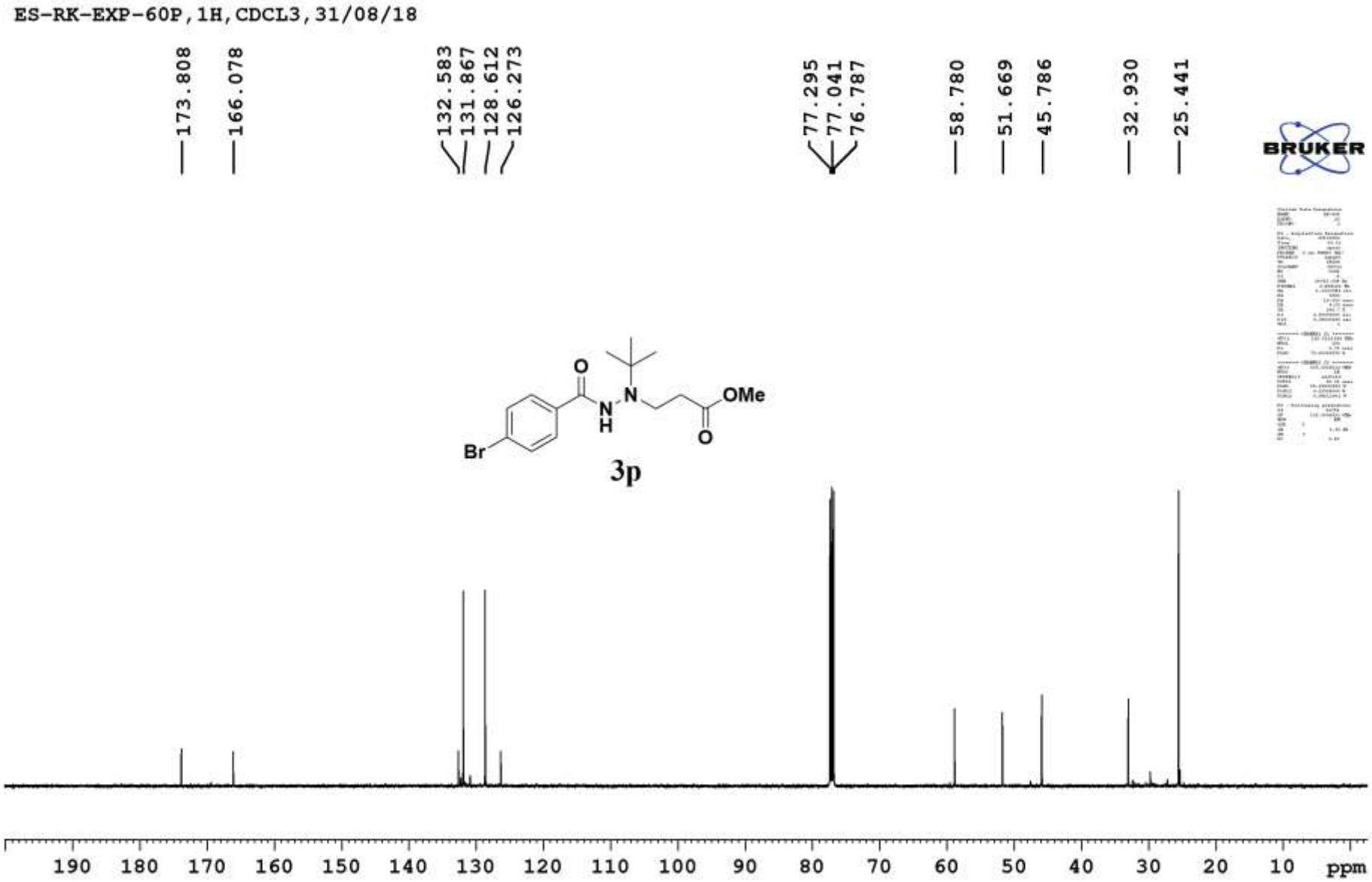


ES-AKJ-MC-55; 24/04/2018

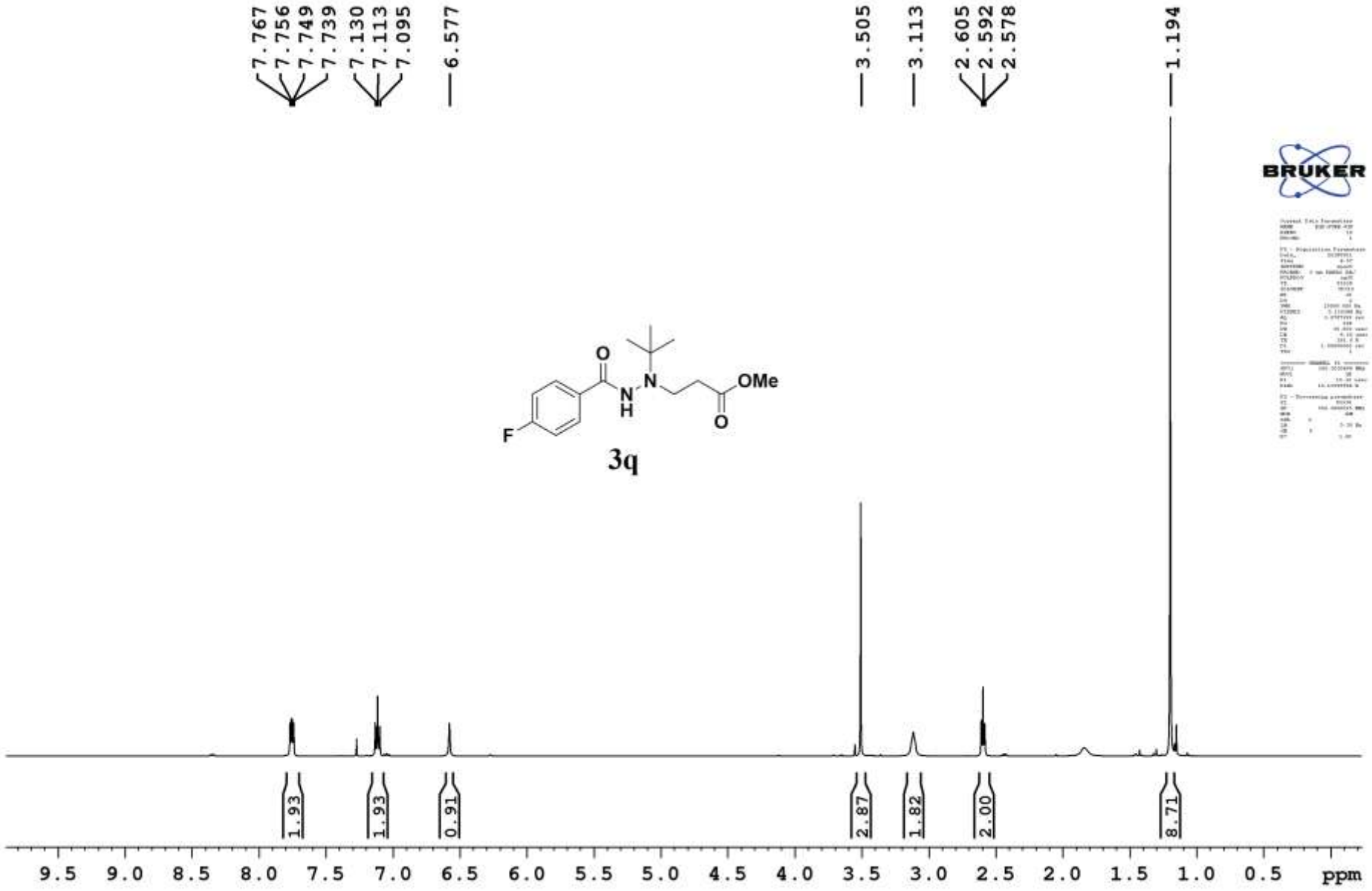


ES-RK-EXP-60P,1H,CDCL3,31/08/18

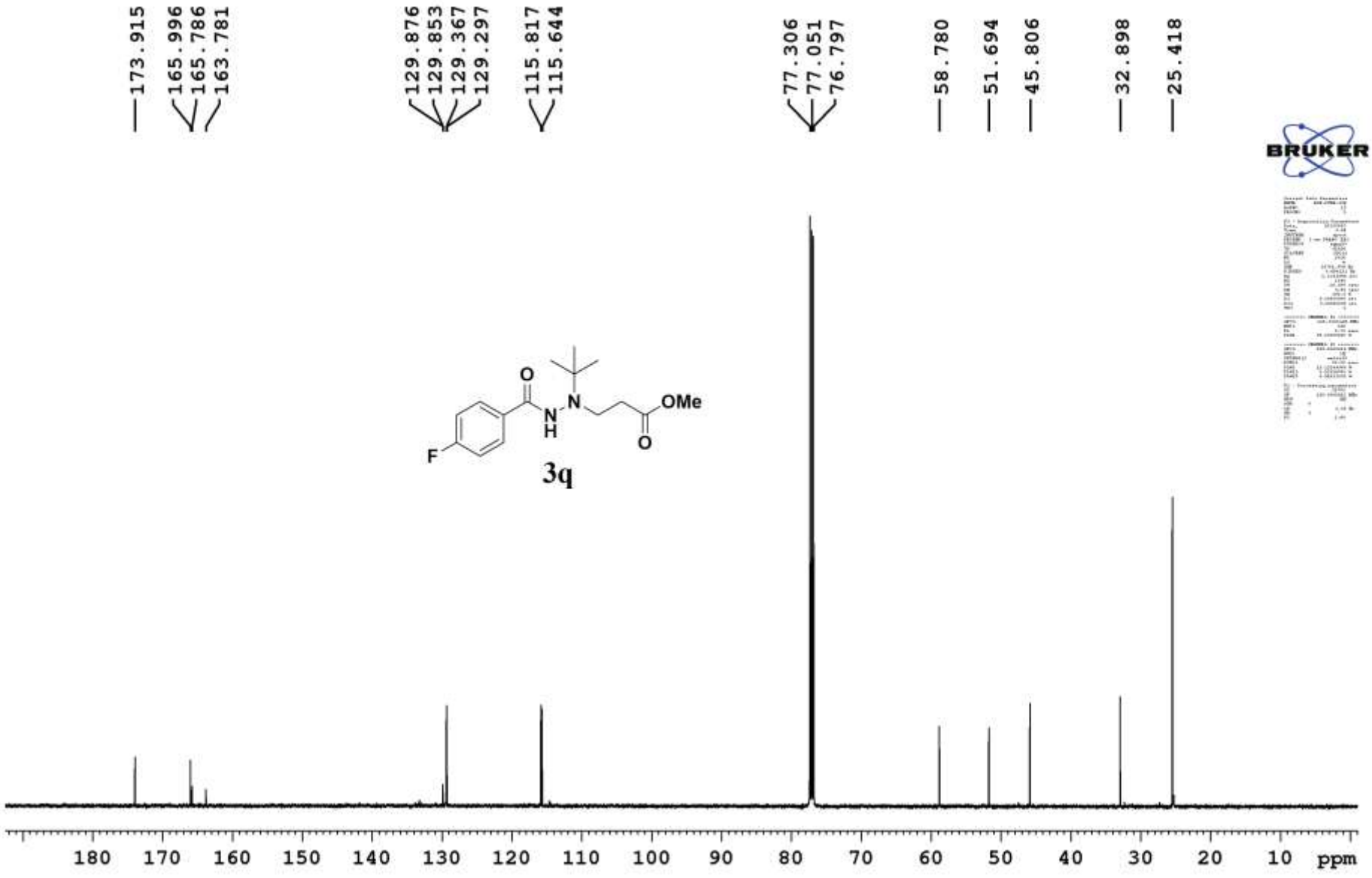



ES-RK-EXP-60P,1H,CDCL3,31/08/18
173.808
166.078
132.583
131.867
128.612
126.273
77.295
77.041
76.787
58.780
51.669
45.786
32.930
25.441
BRUKER
O
N
N
H
OMe
O
Br
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

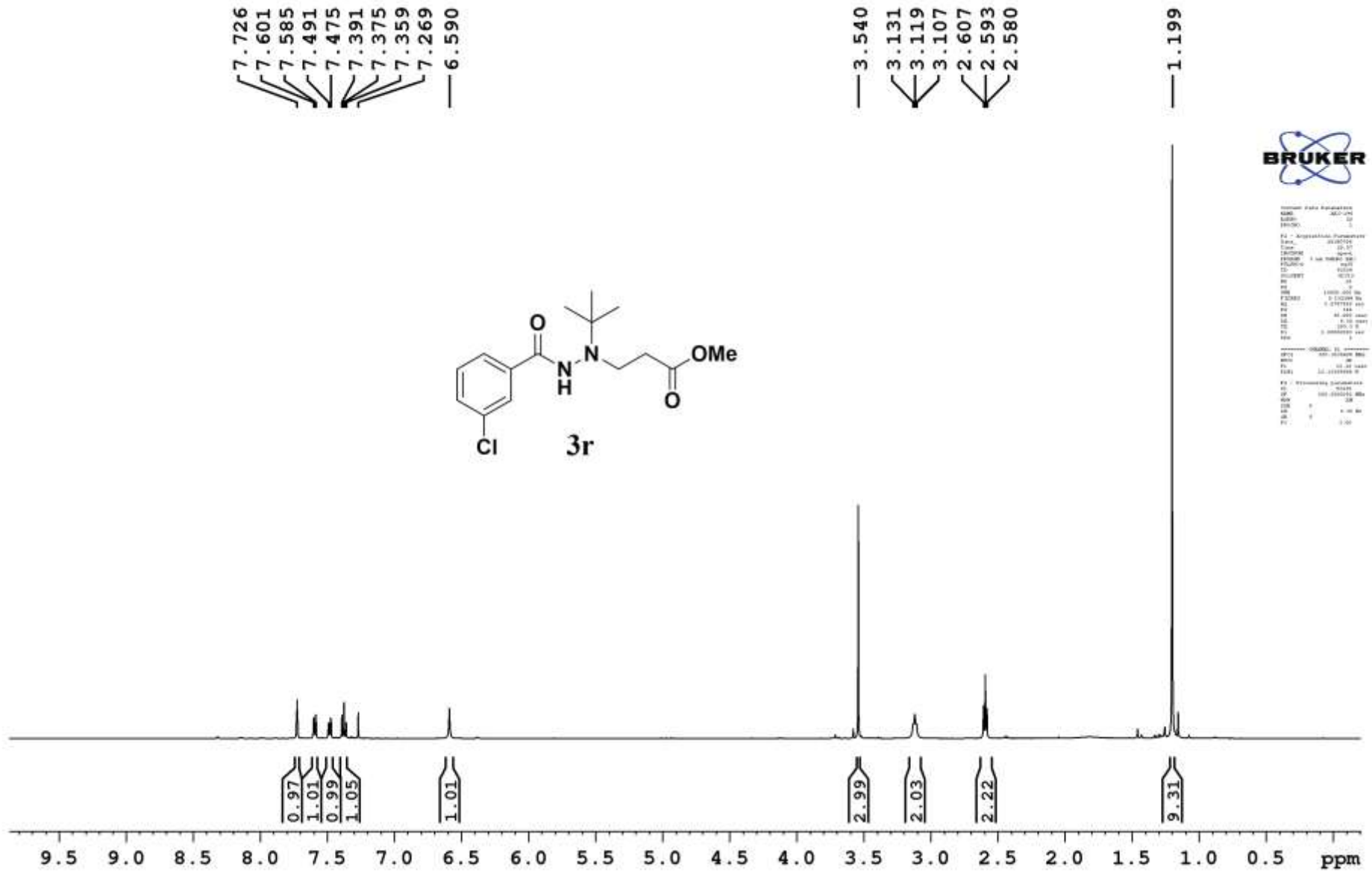
ES-RK-EXP-63P,1H,CDCL3,01/09/18



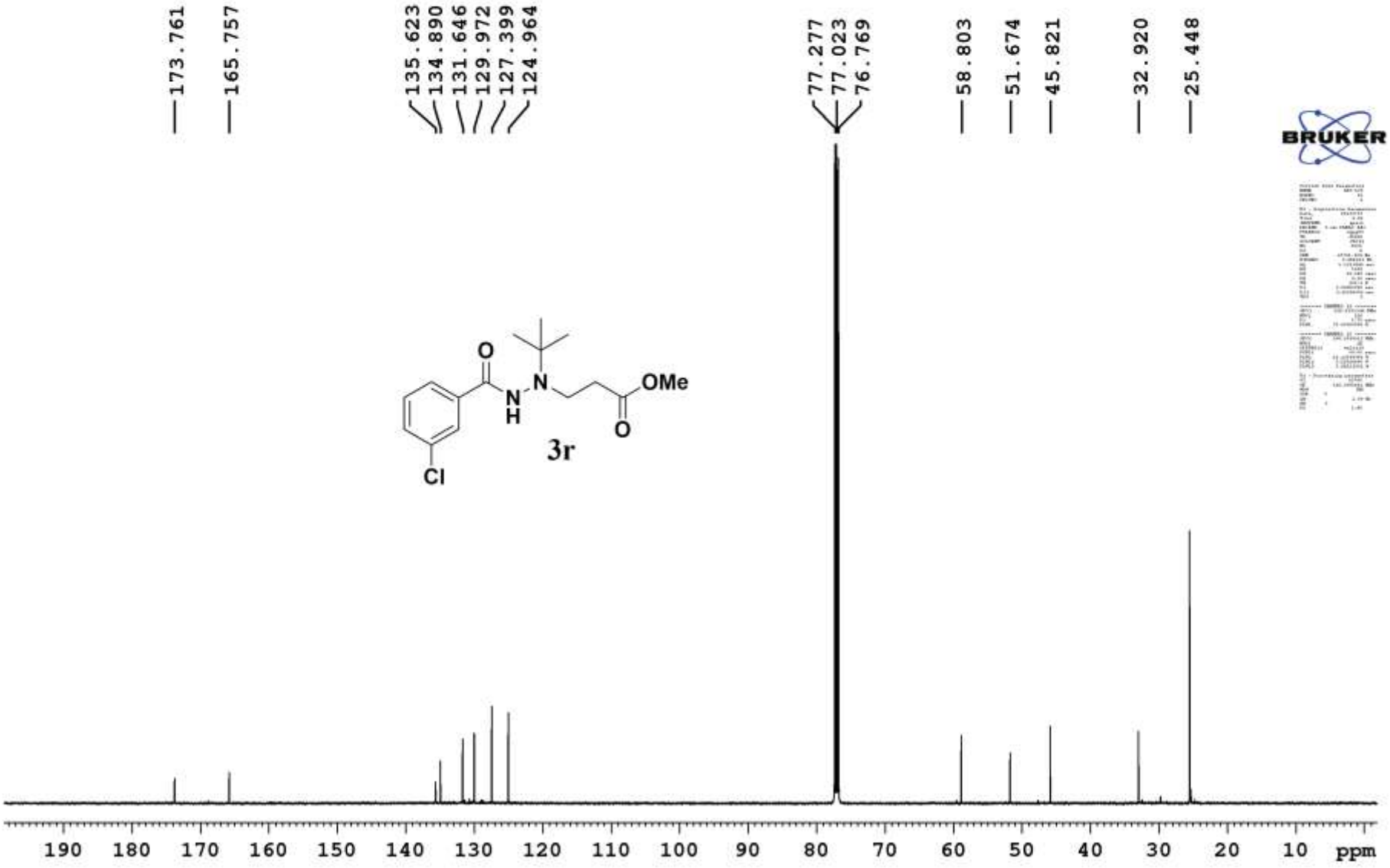
ES-RK-EXP-63P,13C,CDCL3,01/09/18



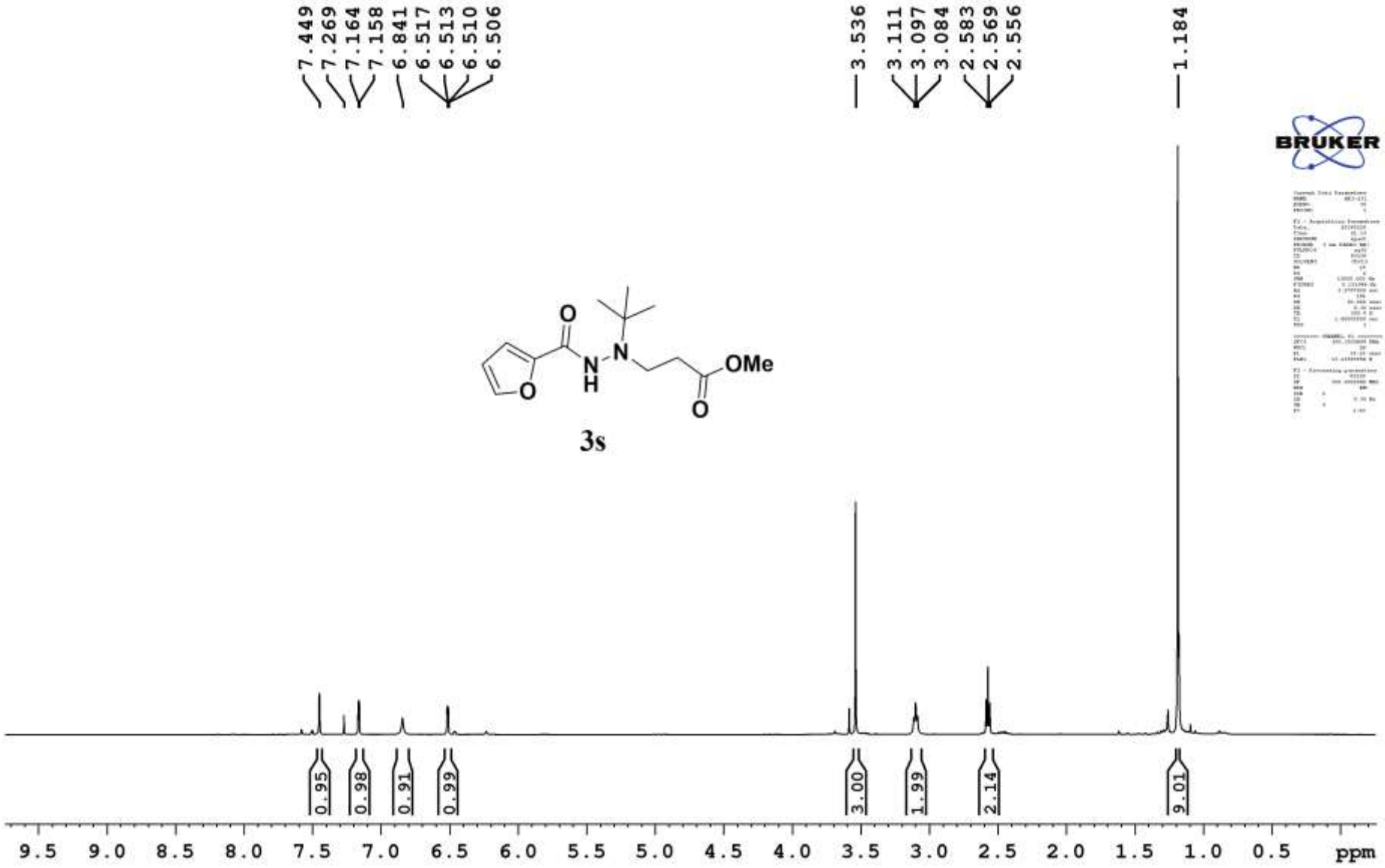
ES-AKJ-196-4-LB1; 06/07/2018



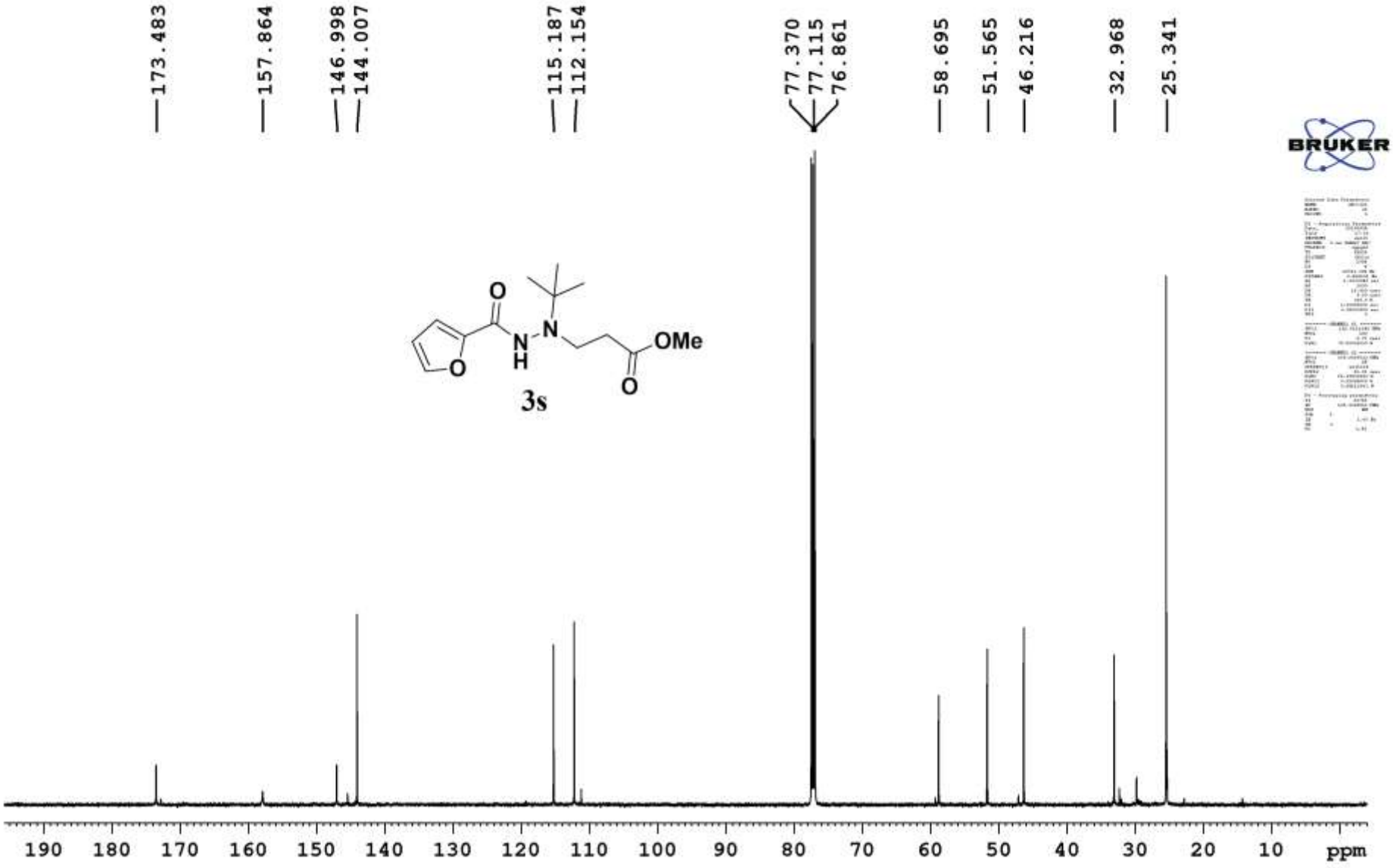
ES-AKJ-196-4-LB1; 06/07/2018



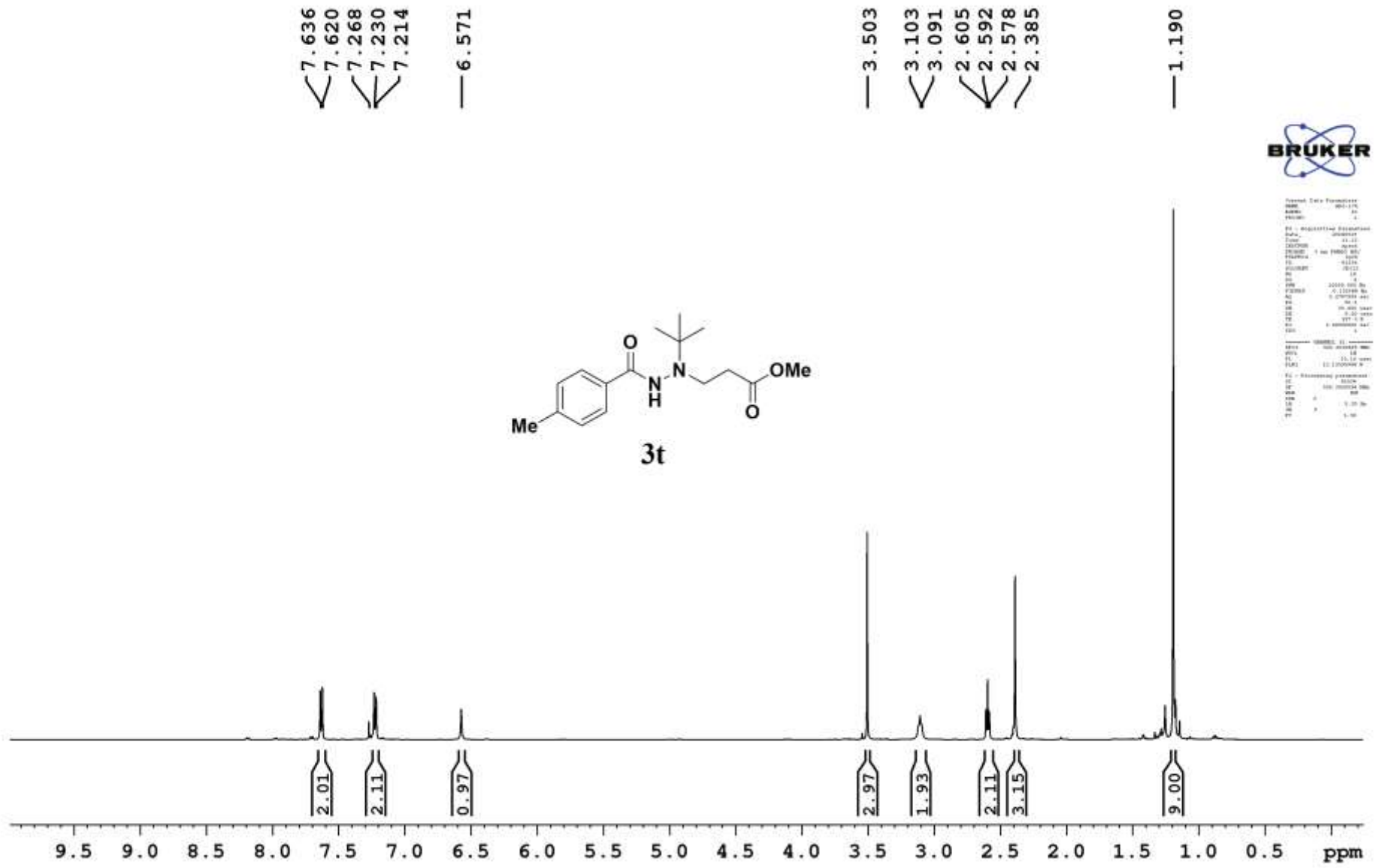
ES-AKJ-231; CDCl3; 20/02/2019



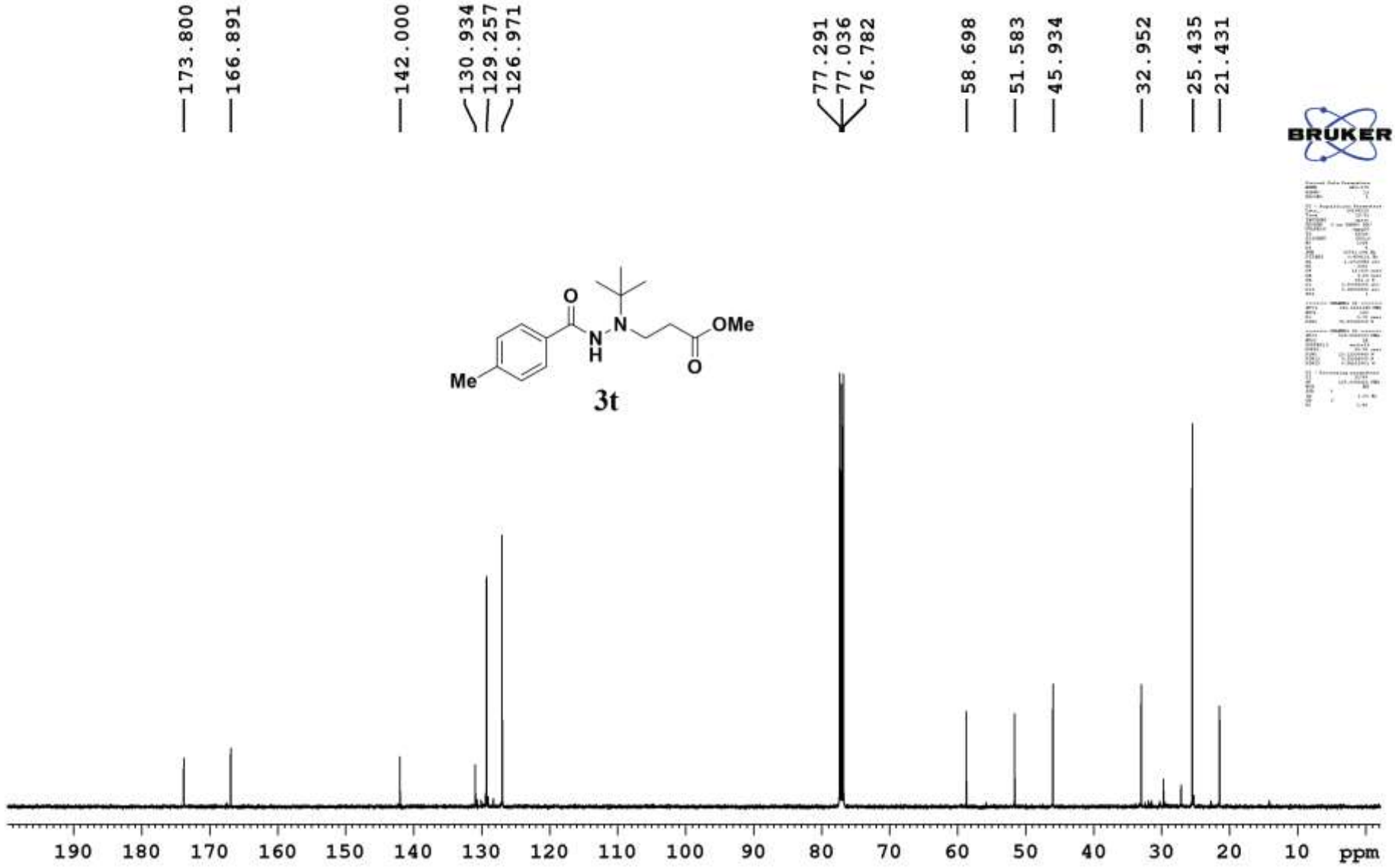
ES-AKJ-231; 24/08/2018



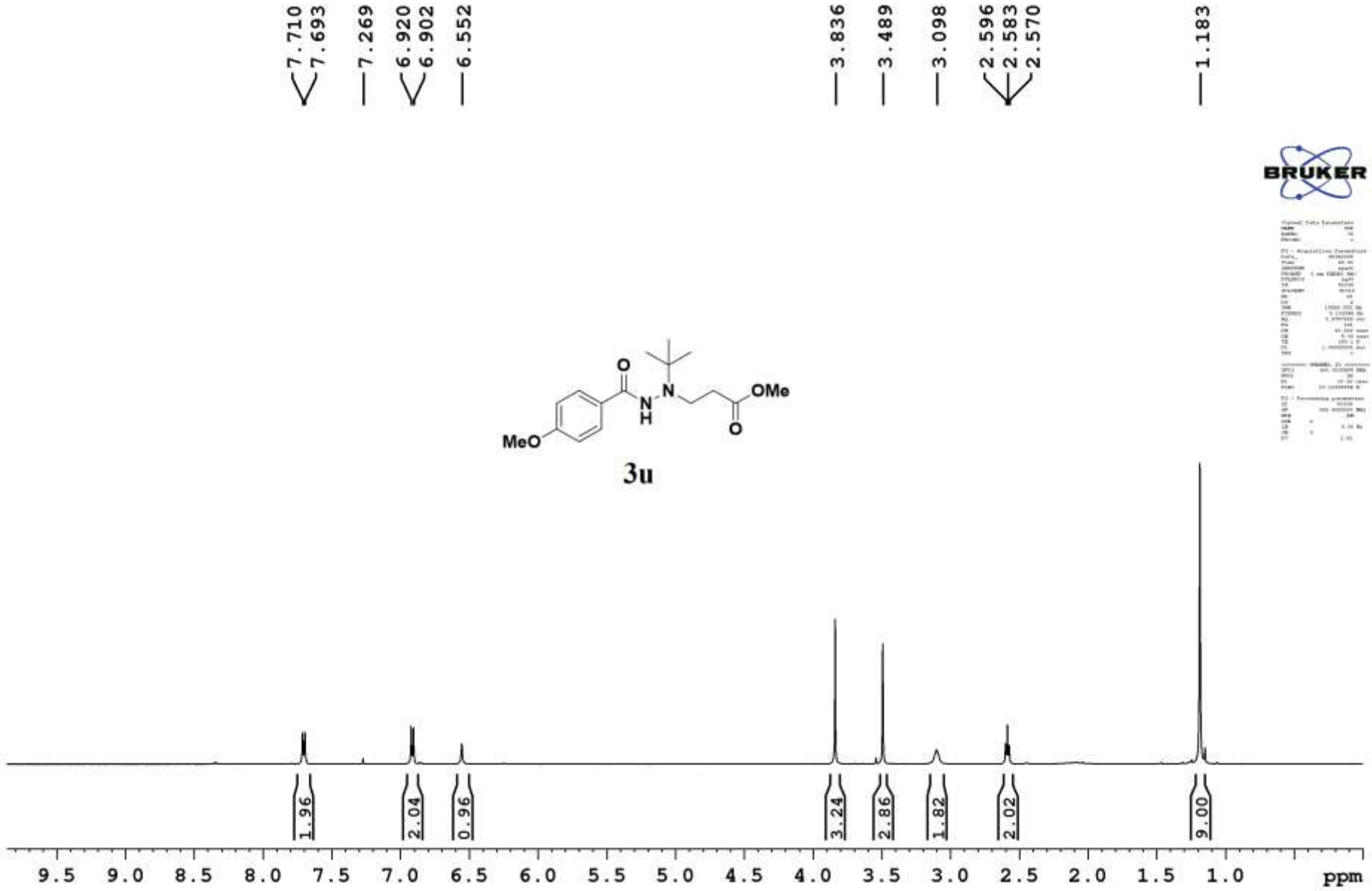
ES-AKJ-176-3-LB1; 19/05/2018



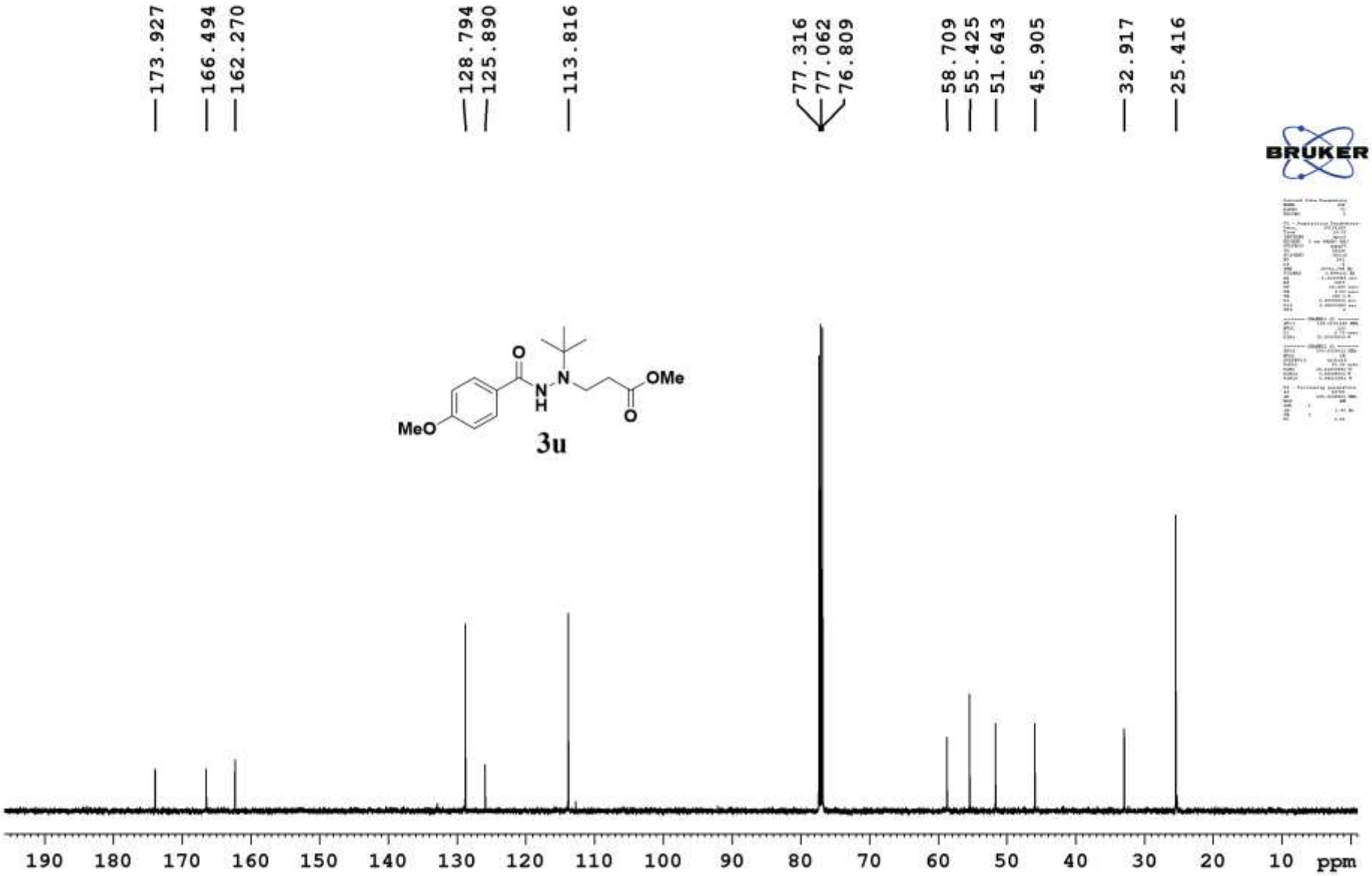
ES-AKJ-176-3-LB1; 19/05/2018



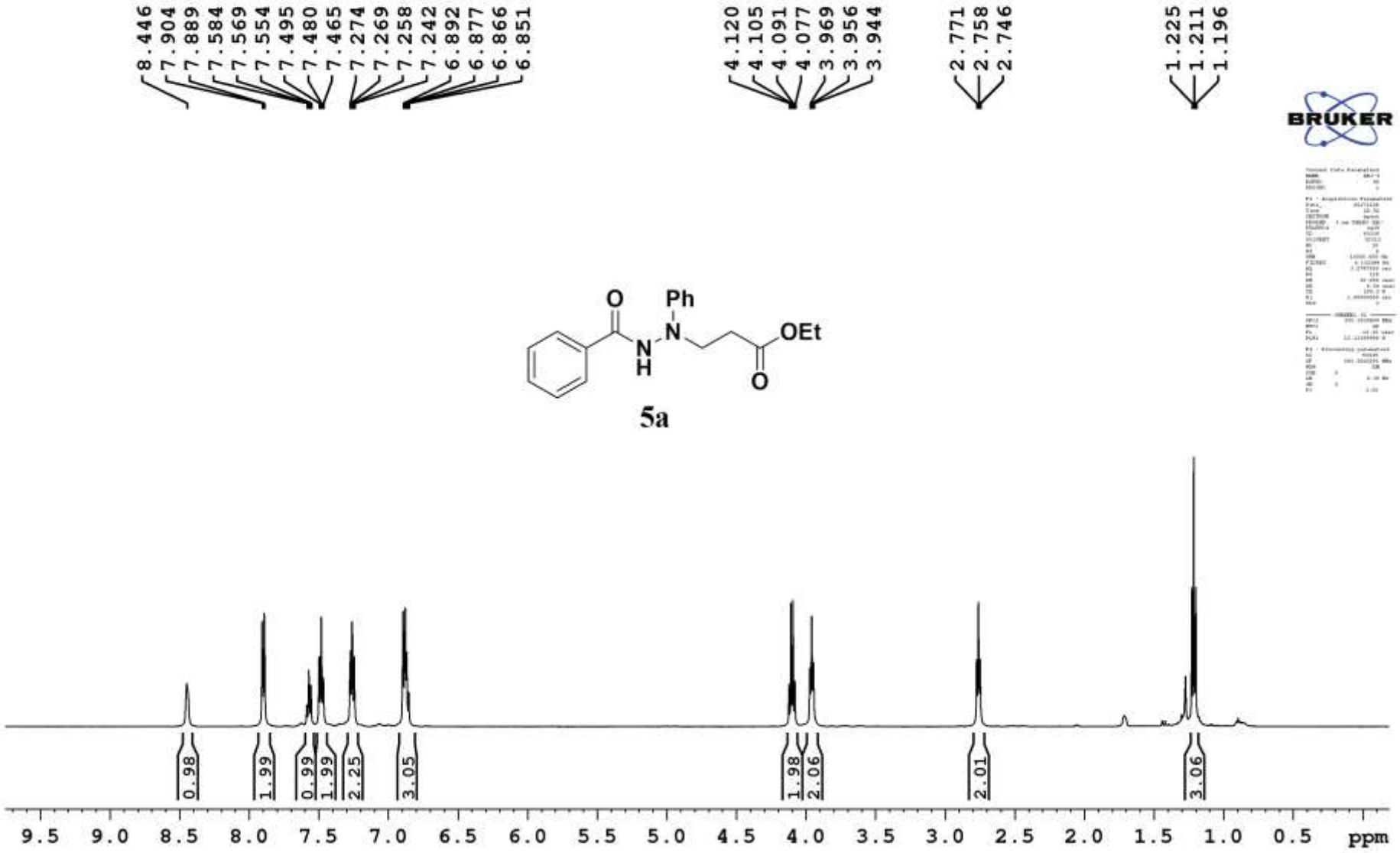
ES-RK-EXP-66-1H; CDCl3; 26 OCT 2018



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

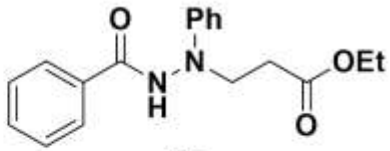


ES-AKJ-T;28/11/2017

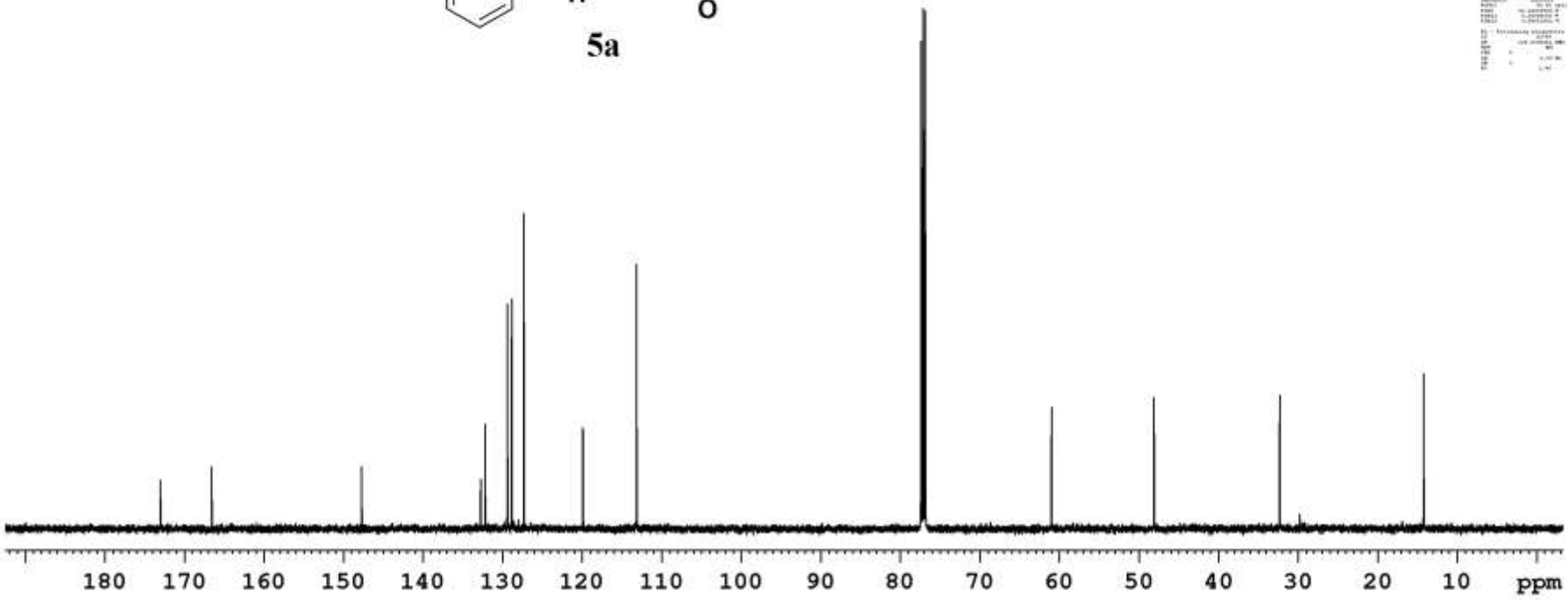


ES-AKJ-T;28/11/2017

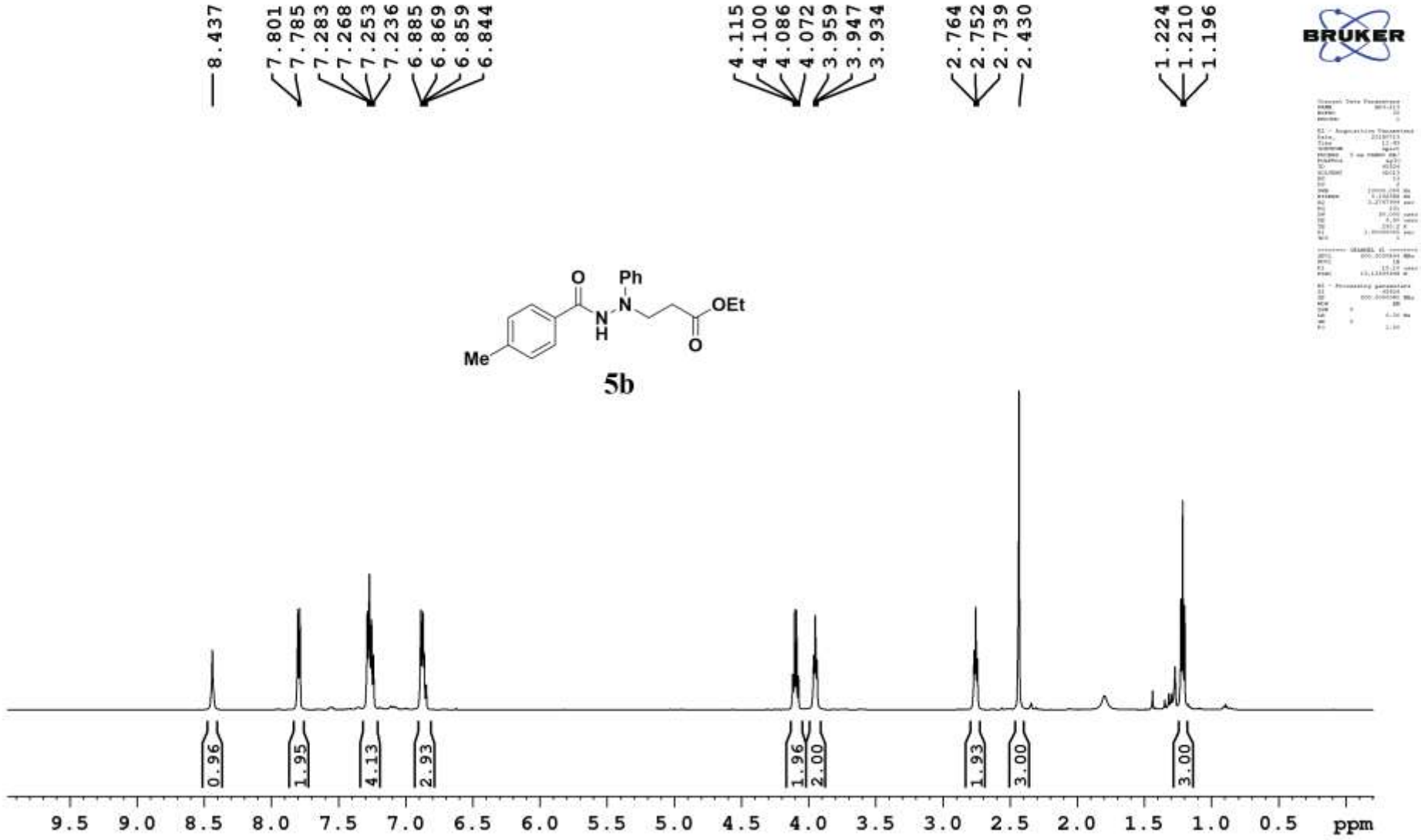
172.971
166.515
147.677
132.678
132.152
129.337
128.794
127.268
119.850
113.094
77.295
77.041
76.787
60.902
48.024
32.214
14.104



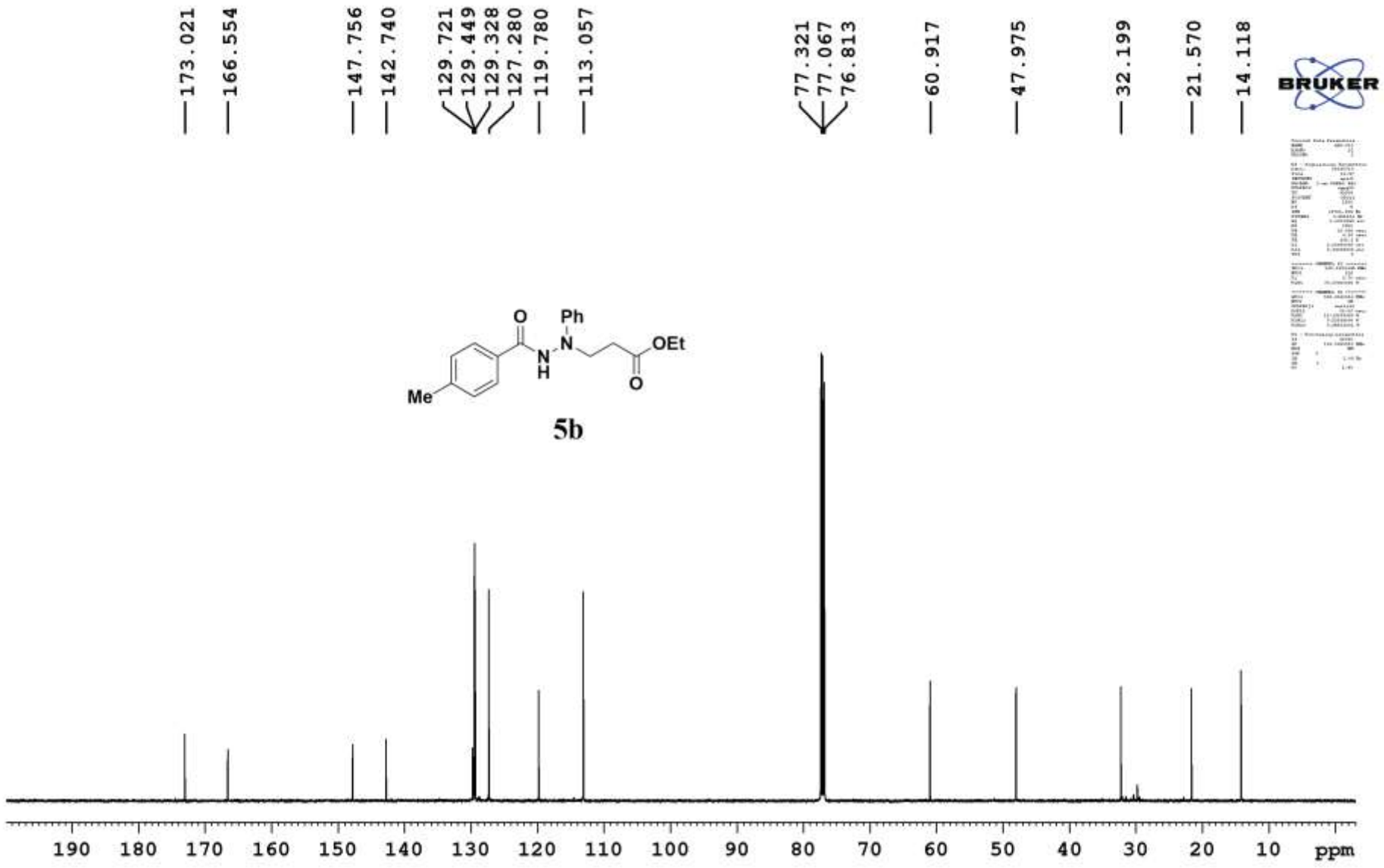
5a



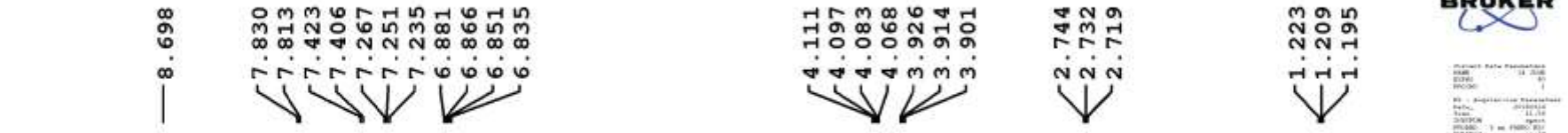
ES-AKJ-213-LB1; 19/07/2018

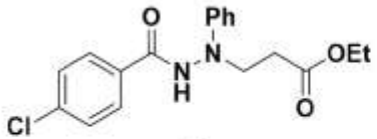


ES-AKJ-213-LB1; 19/07/2018

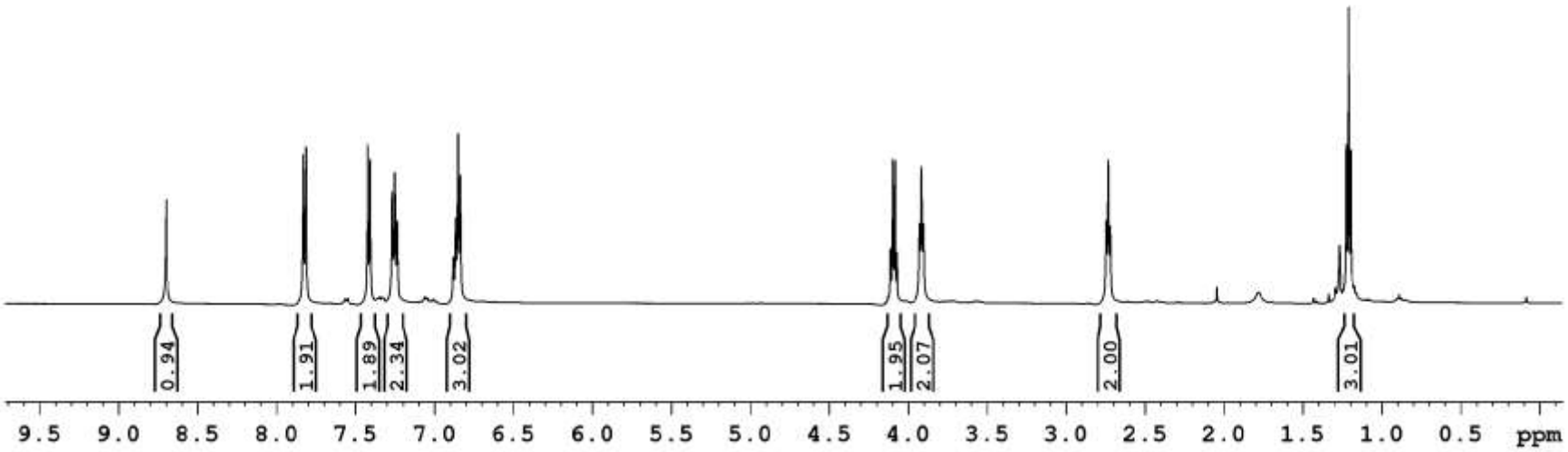


ES-AKJ-190-3LB1; 14/06/2018

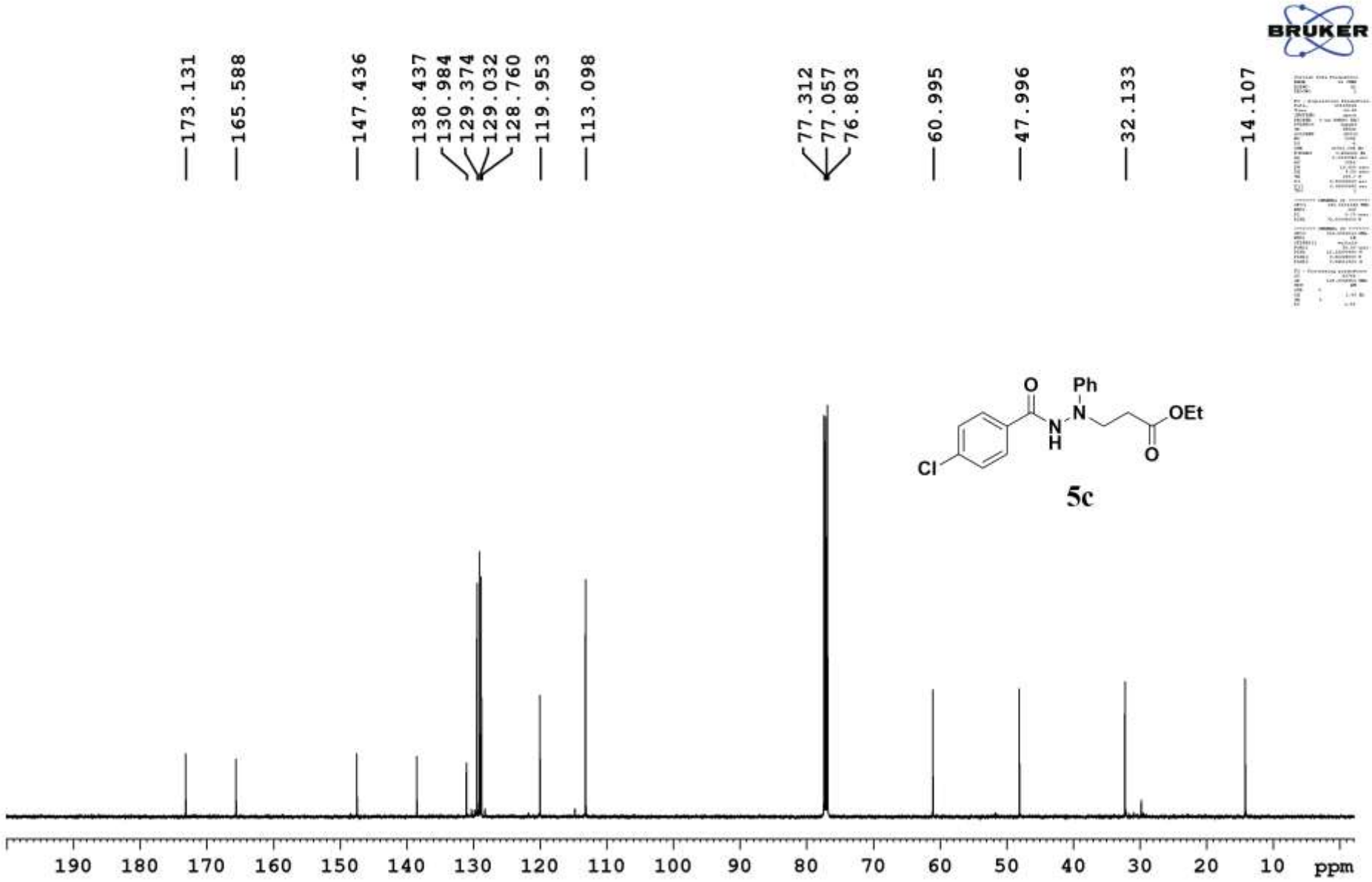




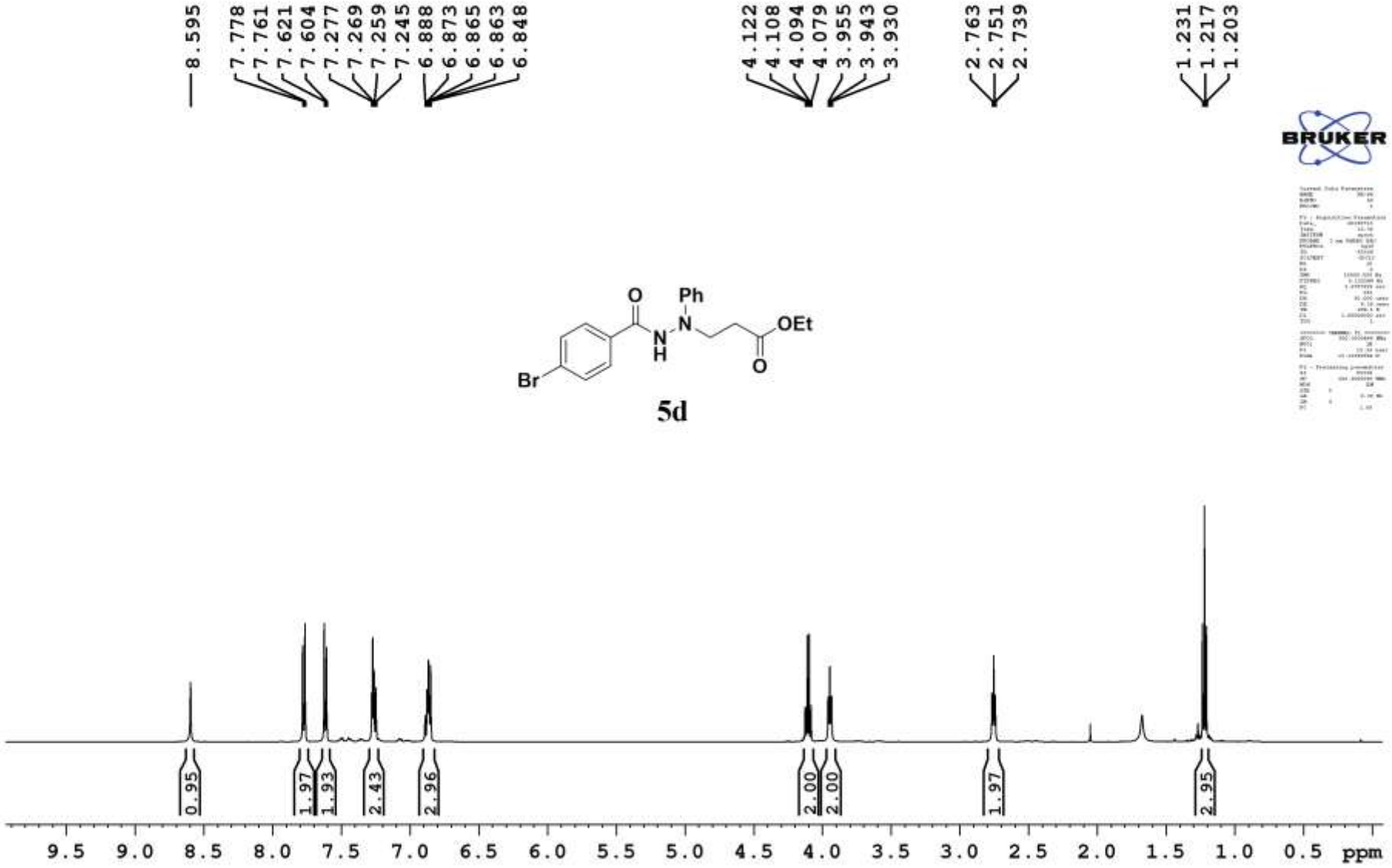
5c

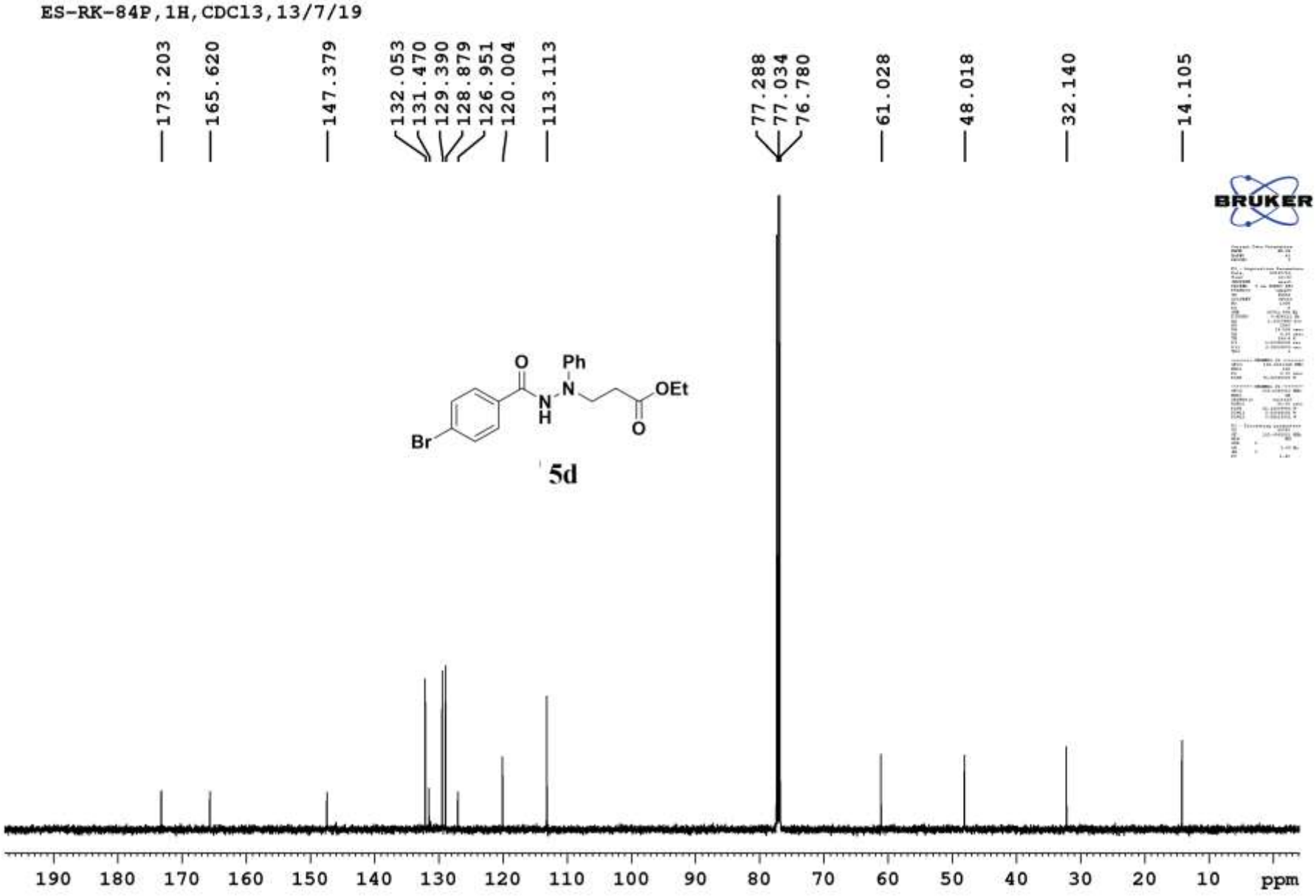


ES-AKJ-190-3LB1; 14/06/2018

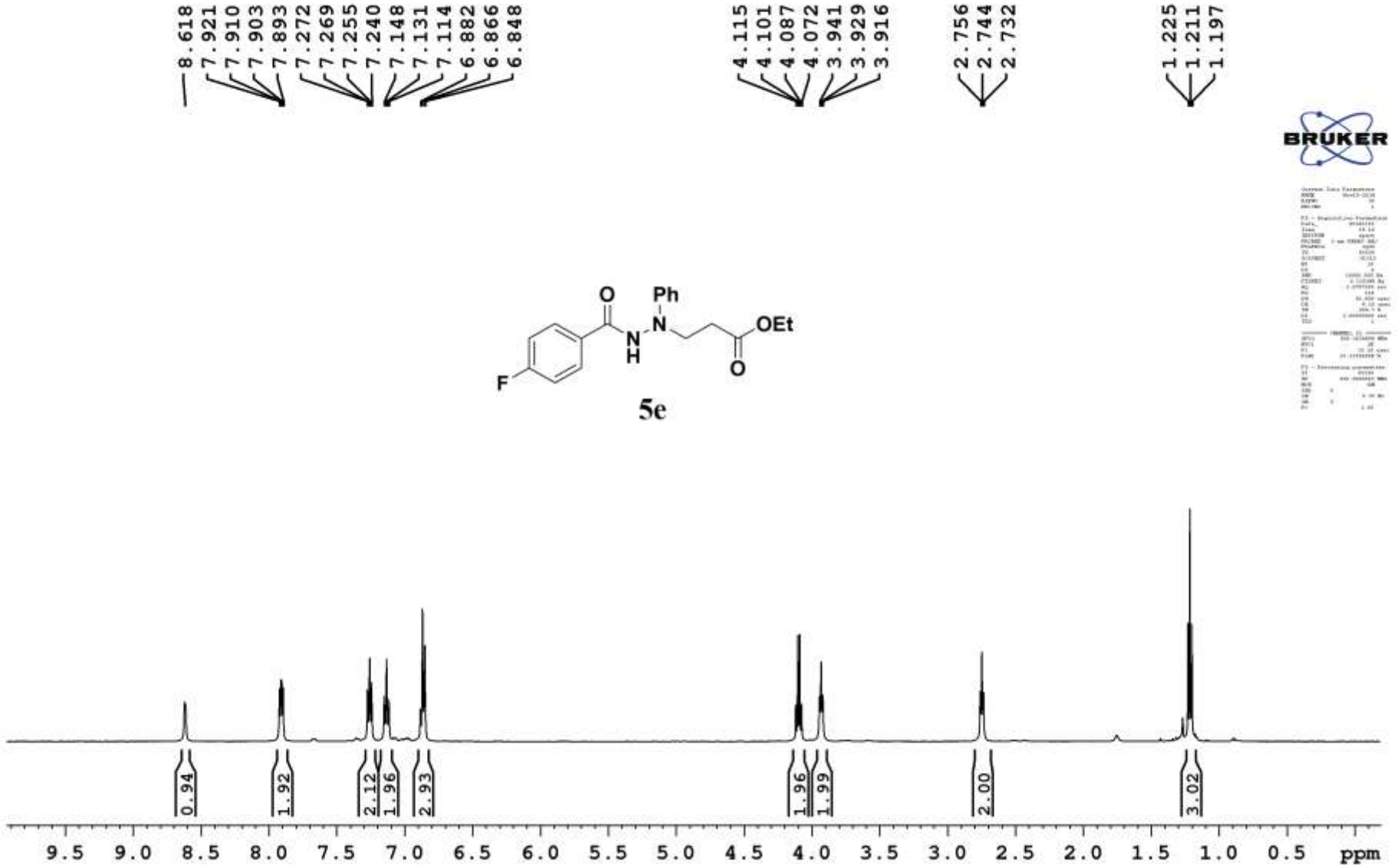


ES-RK-84P,1H,CDCl3,13/7/19

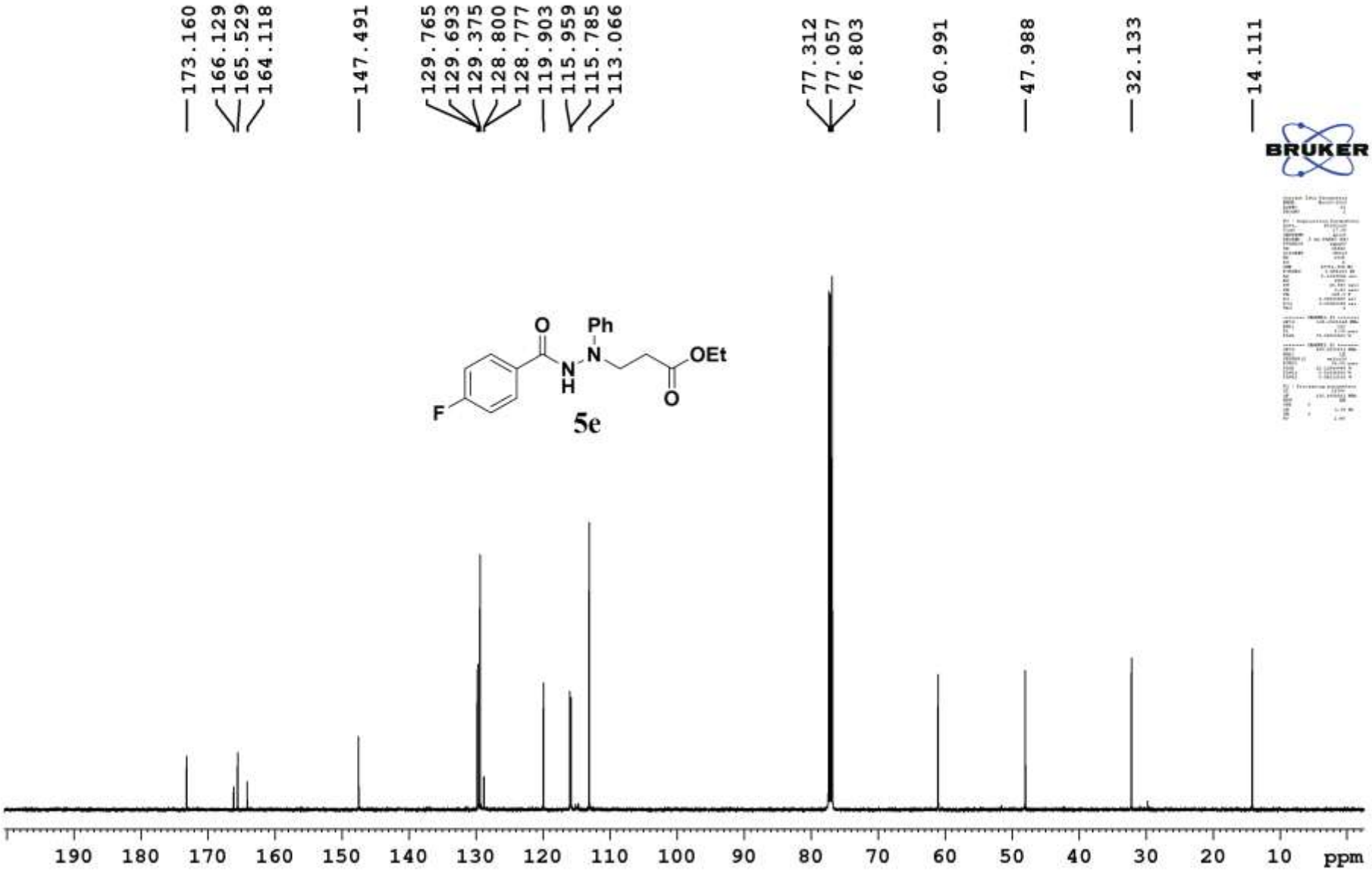



ES-RK-84P,1H,CDCl3,13/7/19
173.203
165.620
147.379
132.053
131.470
129.390
128.879
126.951
120.004
113.113
77.288
77.034
76.780
61.028
48.018
32.140
14.105
BRUKER
O
Ph
N
N
H
OEt
O
Br
5d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

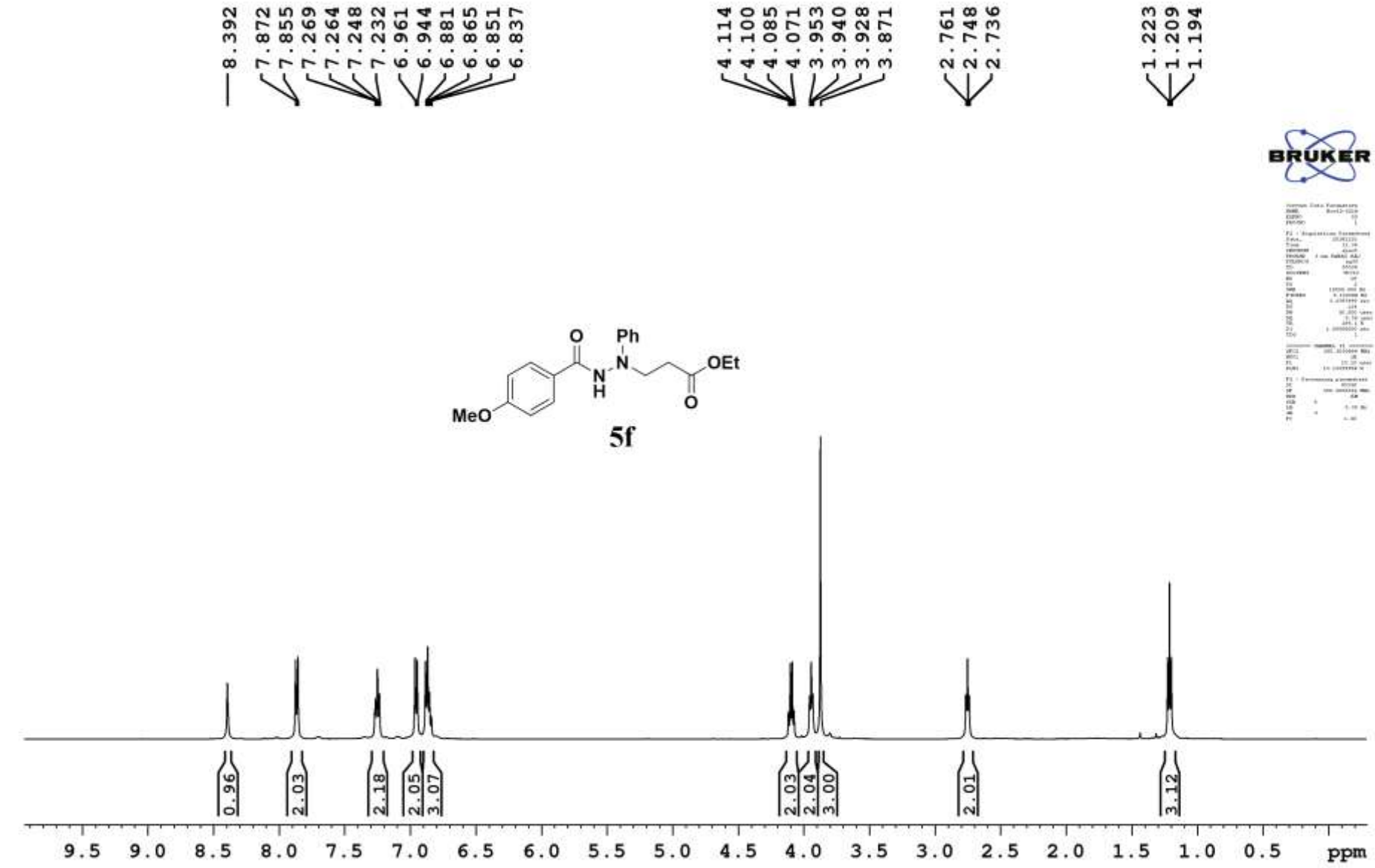
ES-AKJ-202-3; 10/11/2018



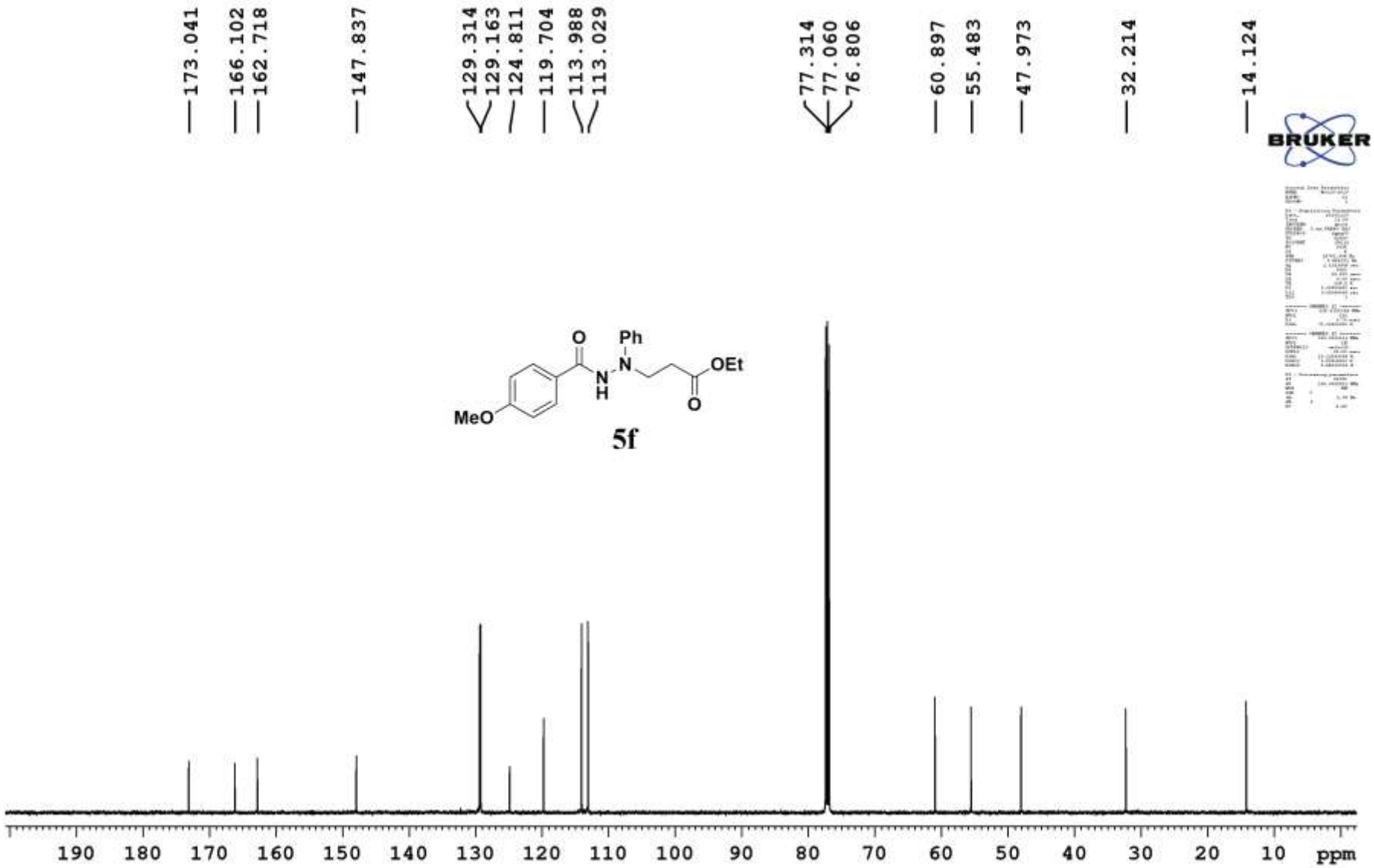
ES-AKJ-202-3; 10/11/2018



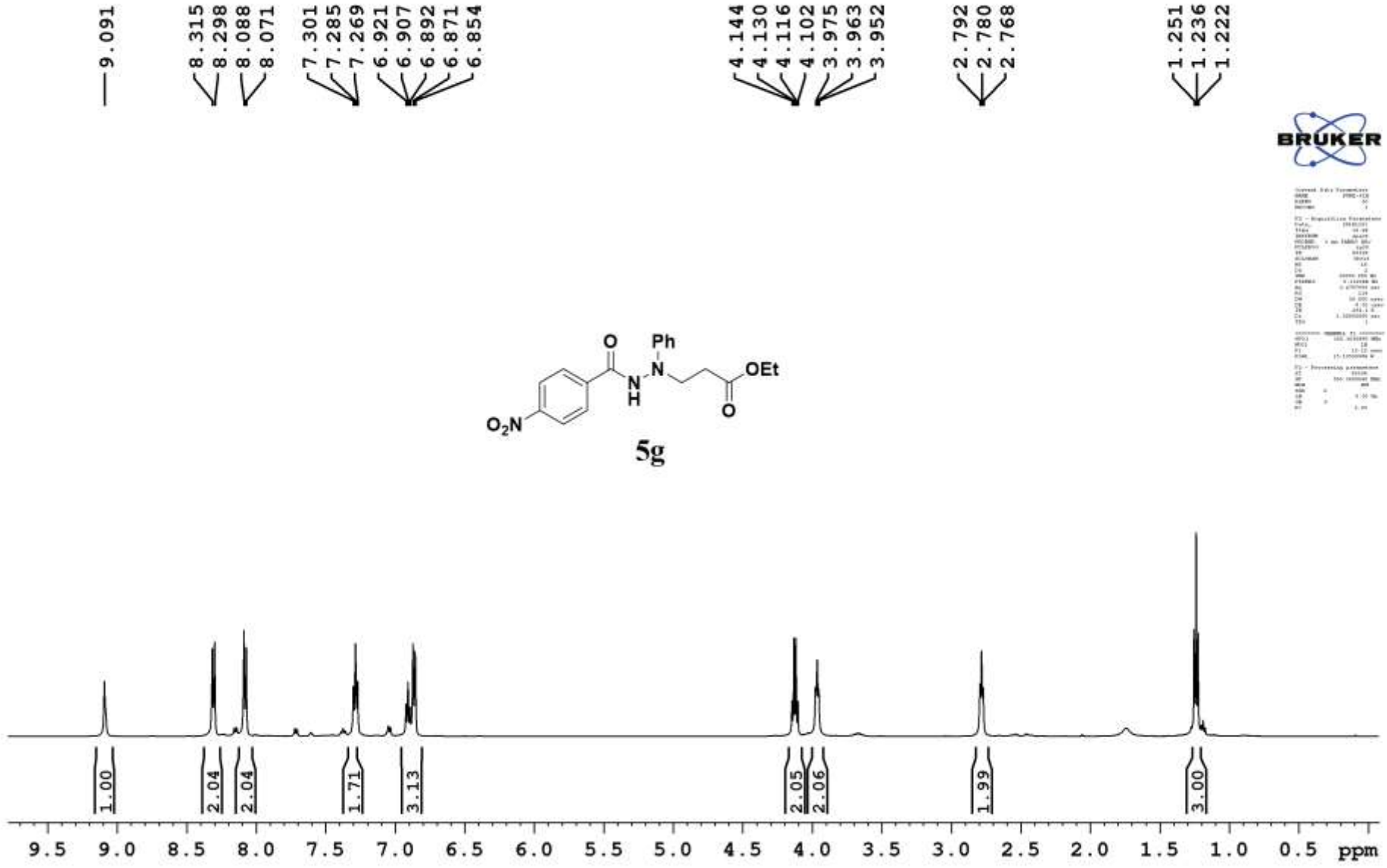
ES-AKJ-MC-49; 10/11/2018

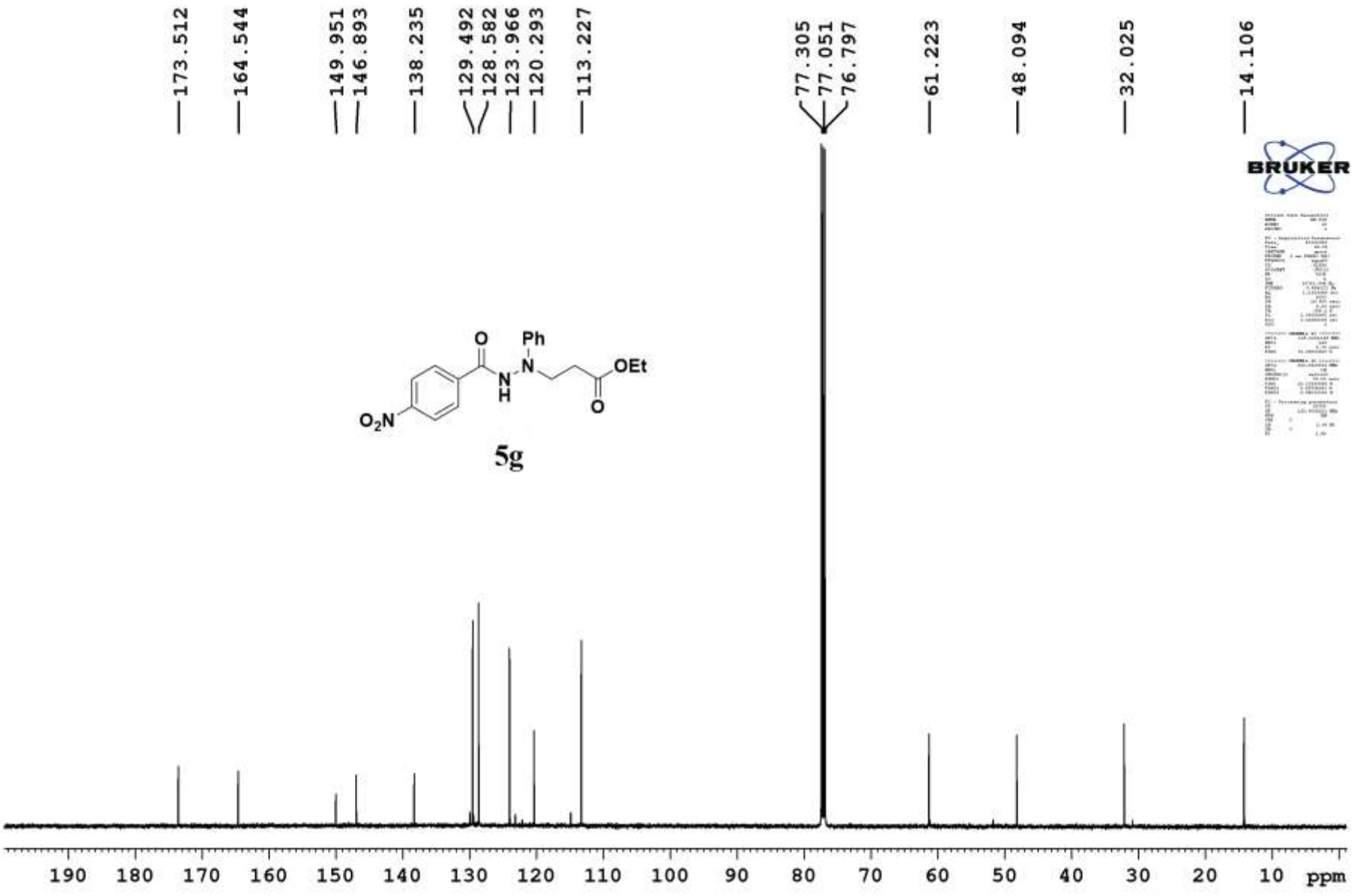


ES-AKJ-MC-49; 10/11/2018

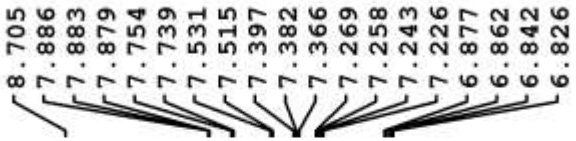


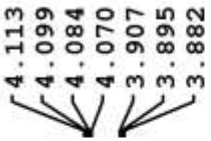
ES-RK-EXP-91;1H;CDCL3;1/11/18

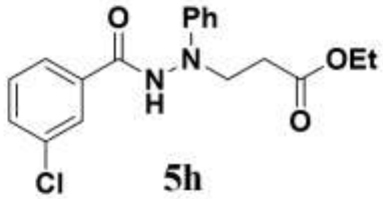



ES-RK-EXP-91P,13C,CHCL3; 31/10/18
173.512
164.544
149.951
146.893
138.235
129.492
128.582
123.966
120.293
113.227
77.305
77.051
76.797
61.223
48.094
32.025
14.106
BRUKER
O
Ph
N
N
H
OEt
O
O2N
5g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

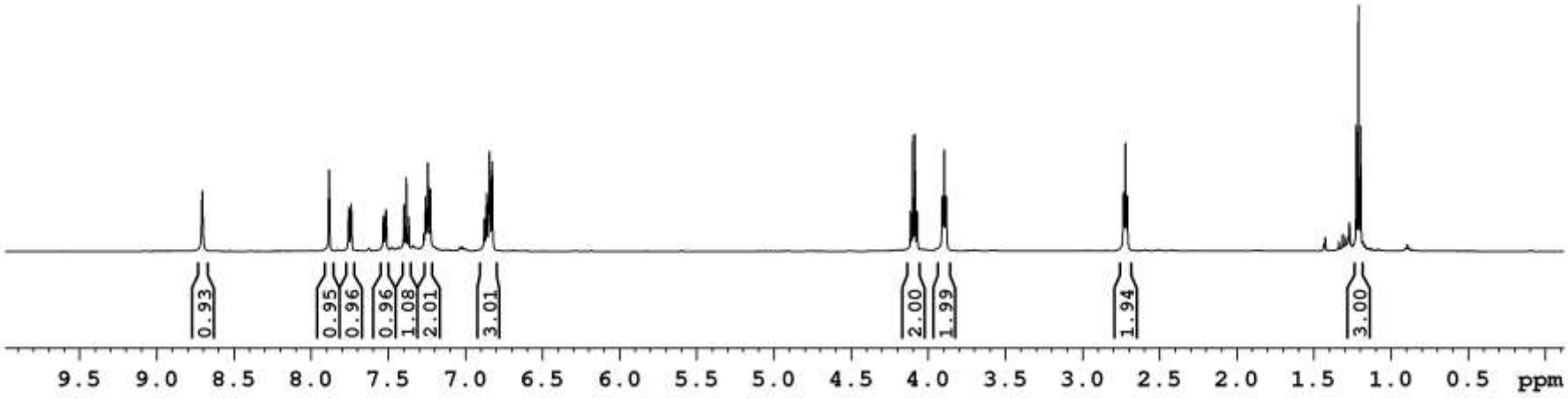
ES-AKJ-216; 09/11/2018



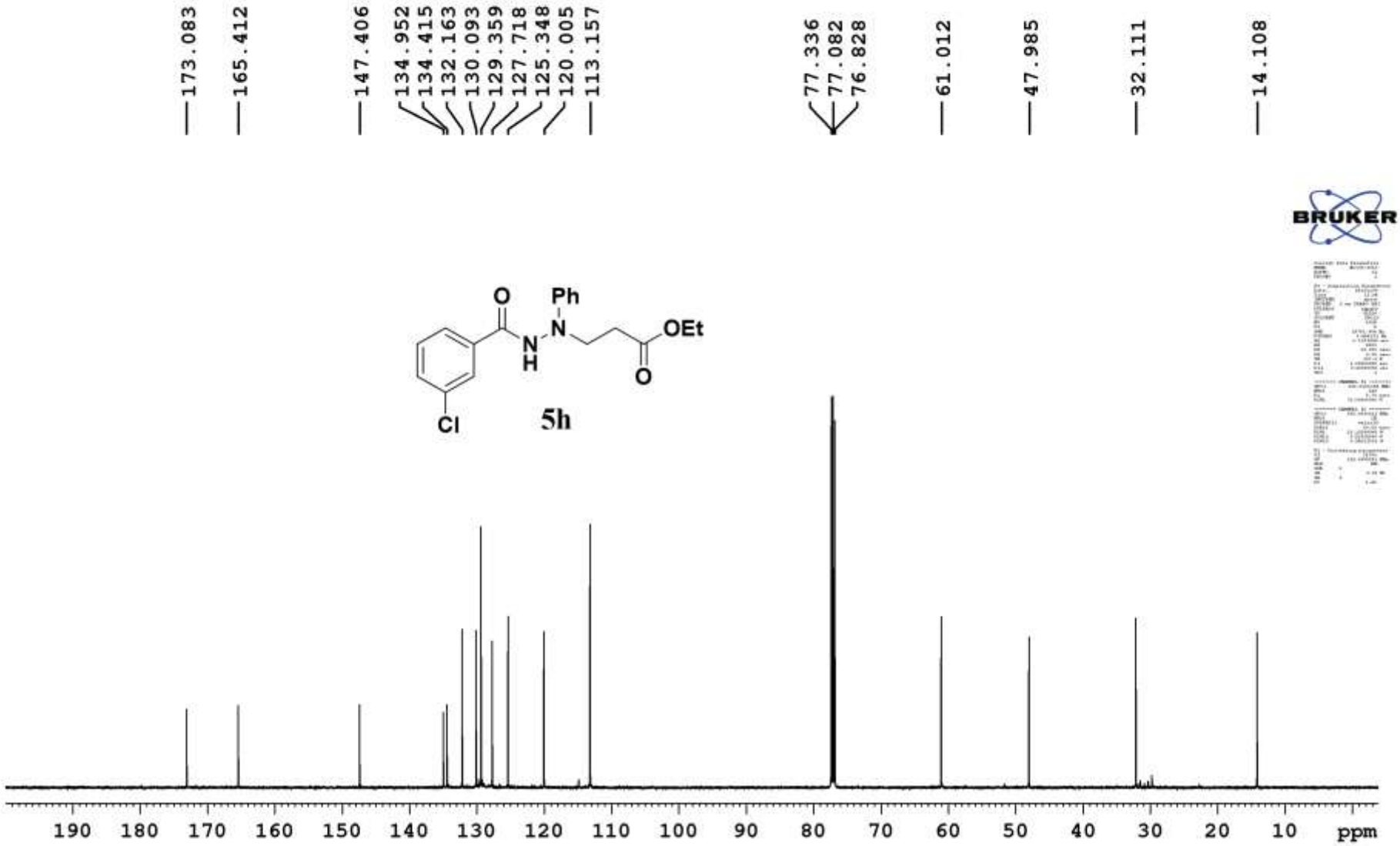




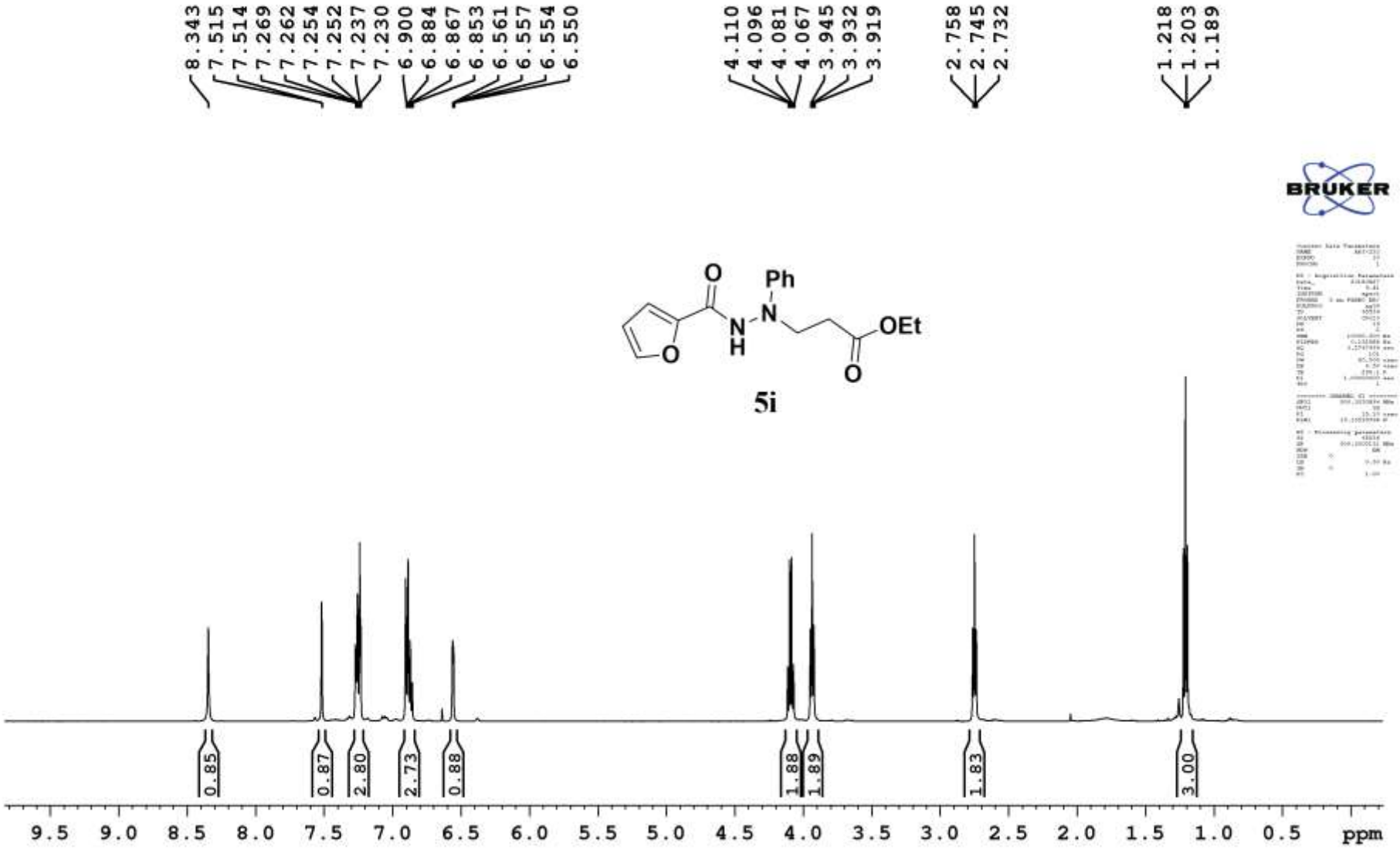
5h



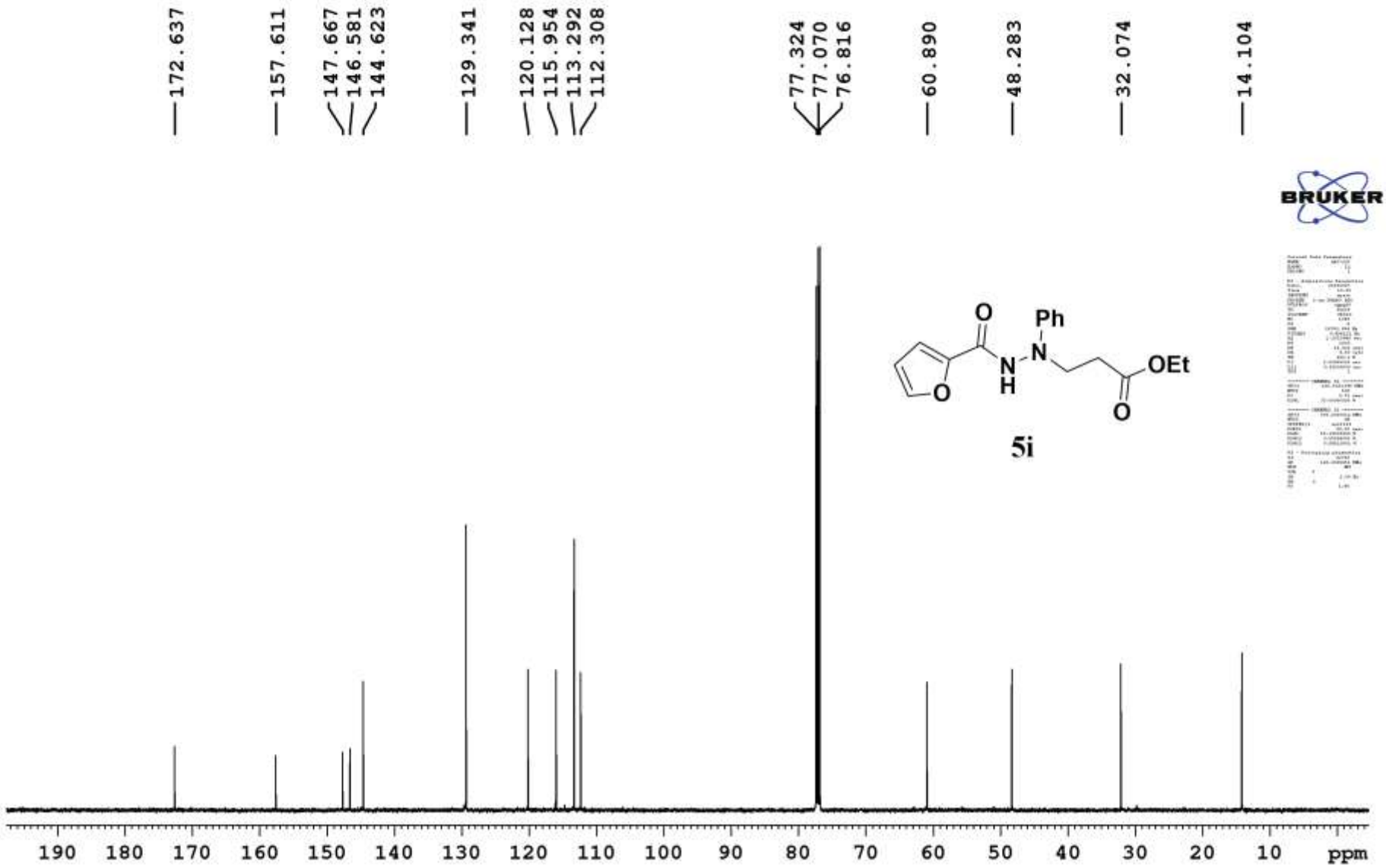
ES-AKJ-216; 09/11/2018



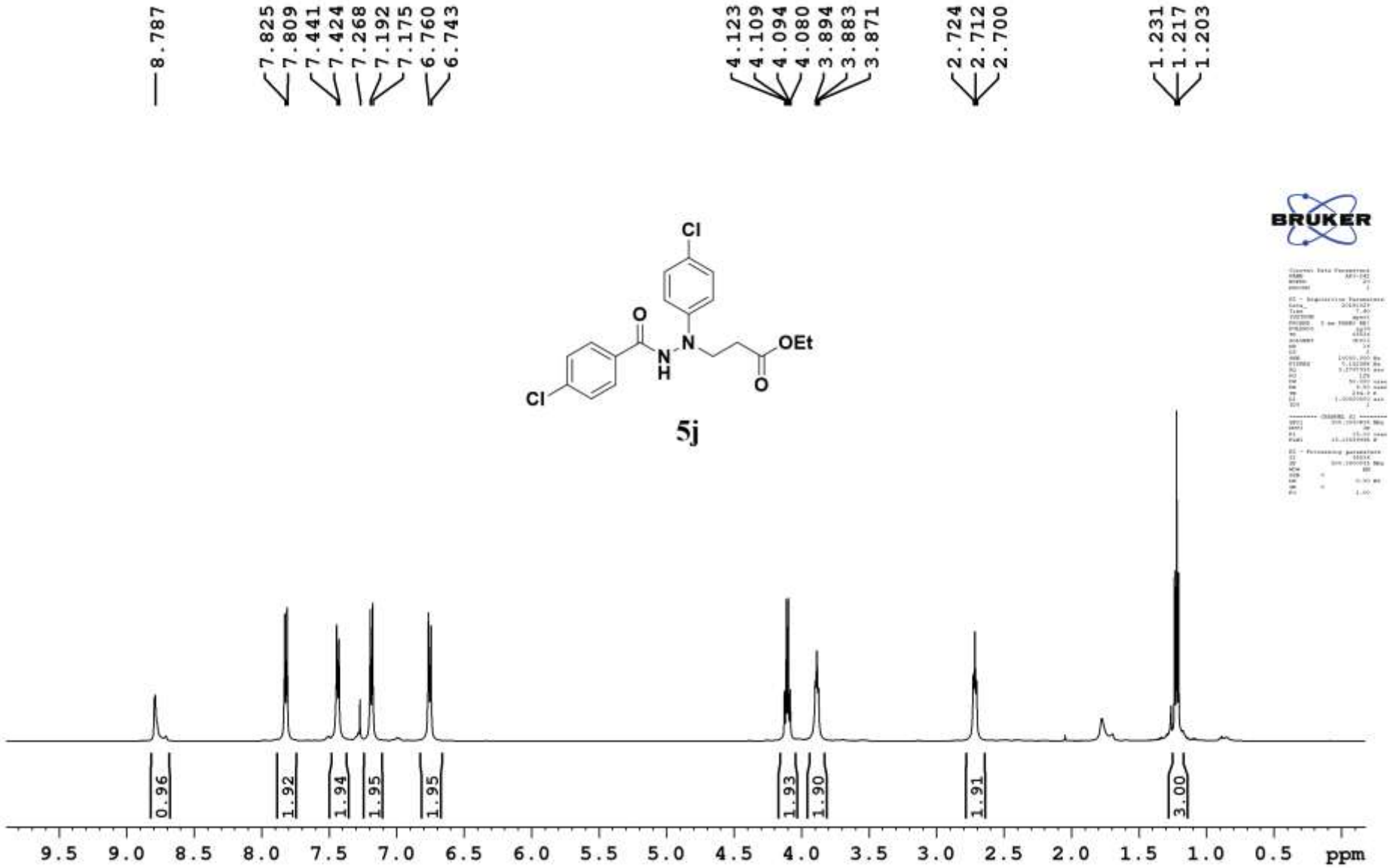
ES-AKJ-233; 27/08/2018



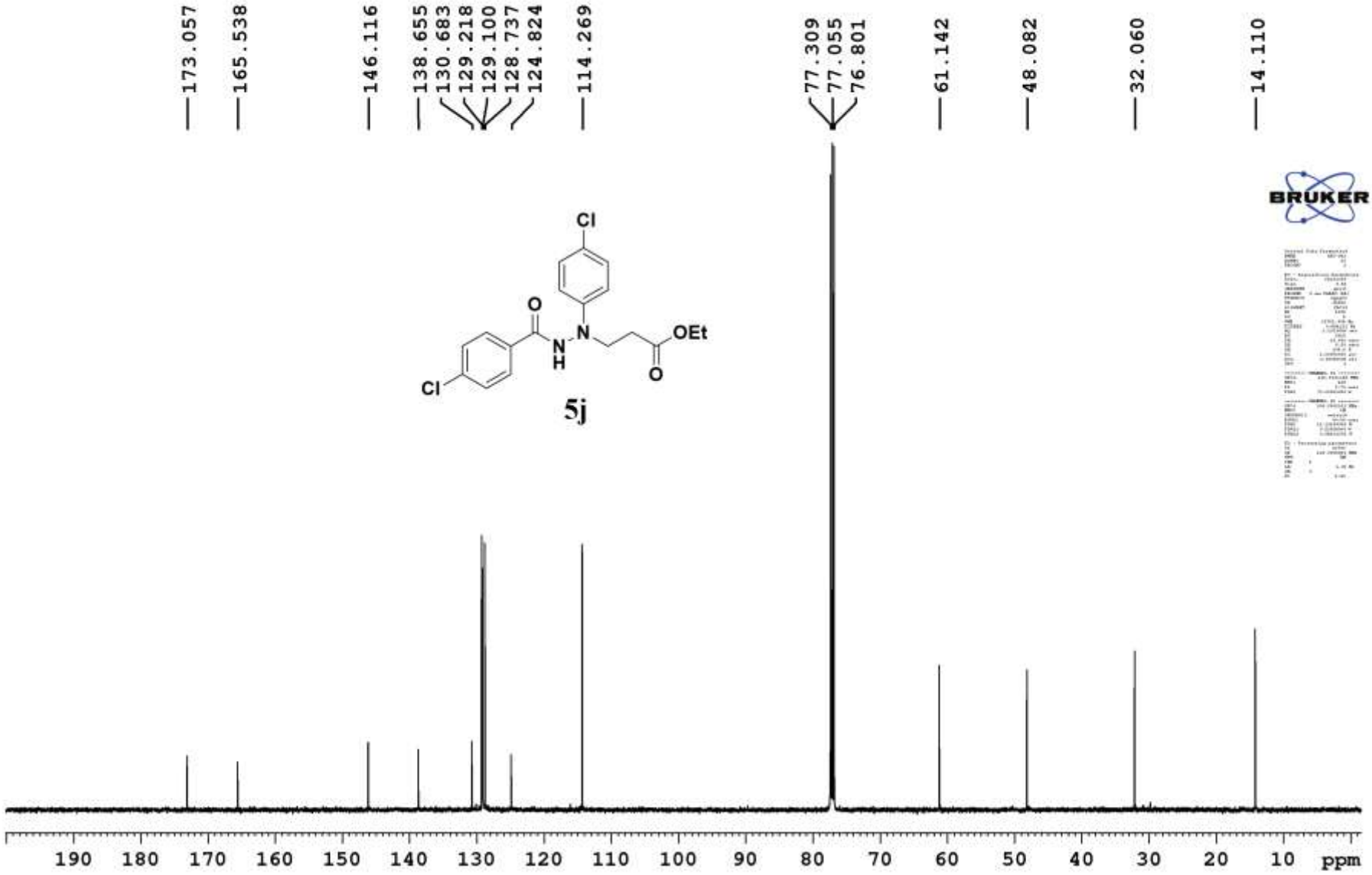
ES-AKJ-233; 27/08/2018



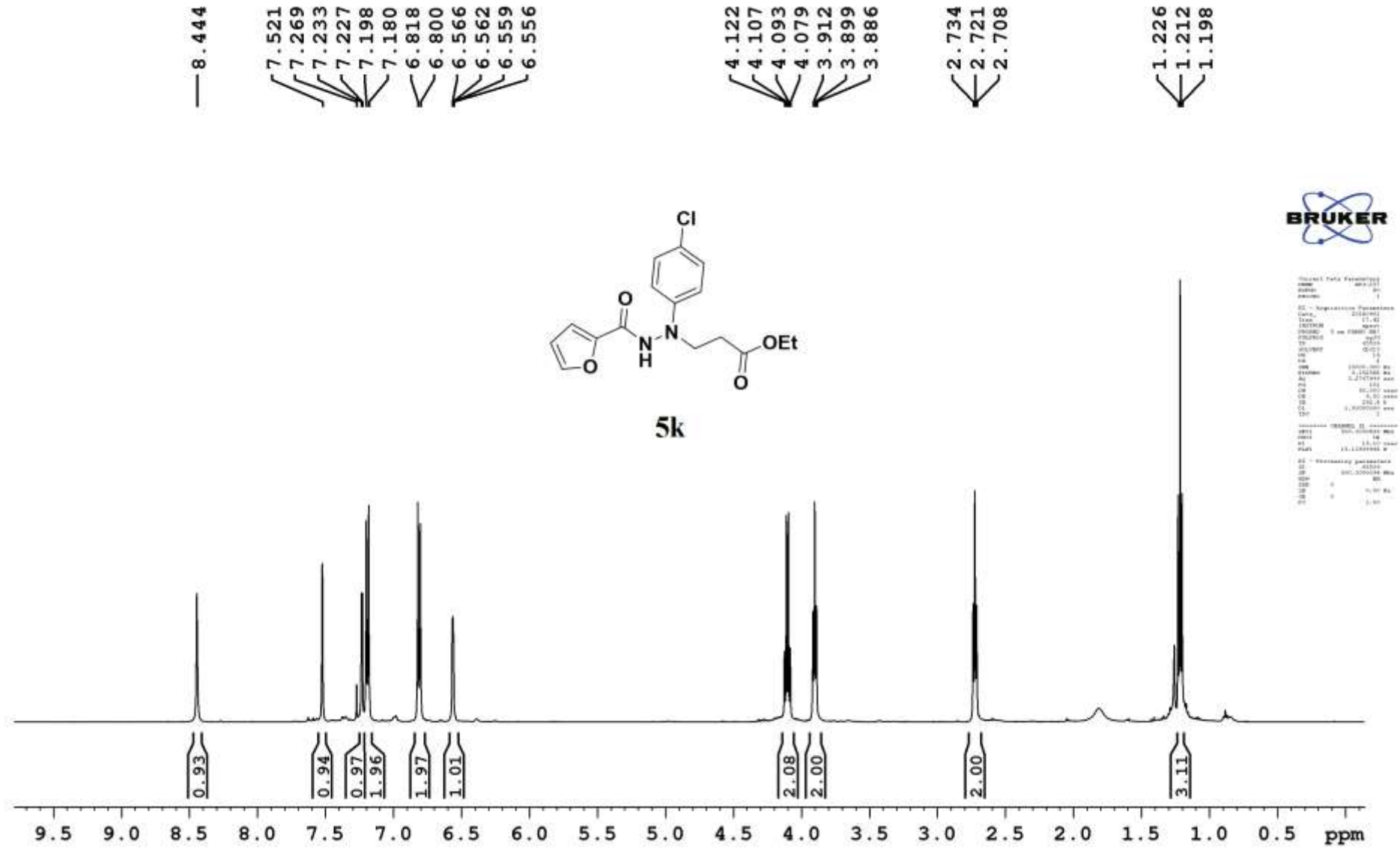
ES-AKJ-242; 29/10/2018



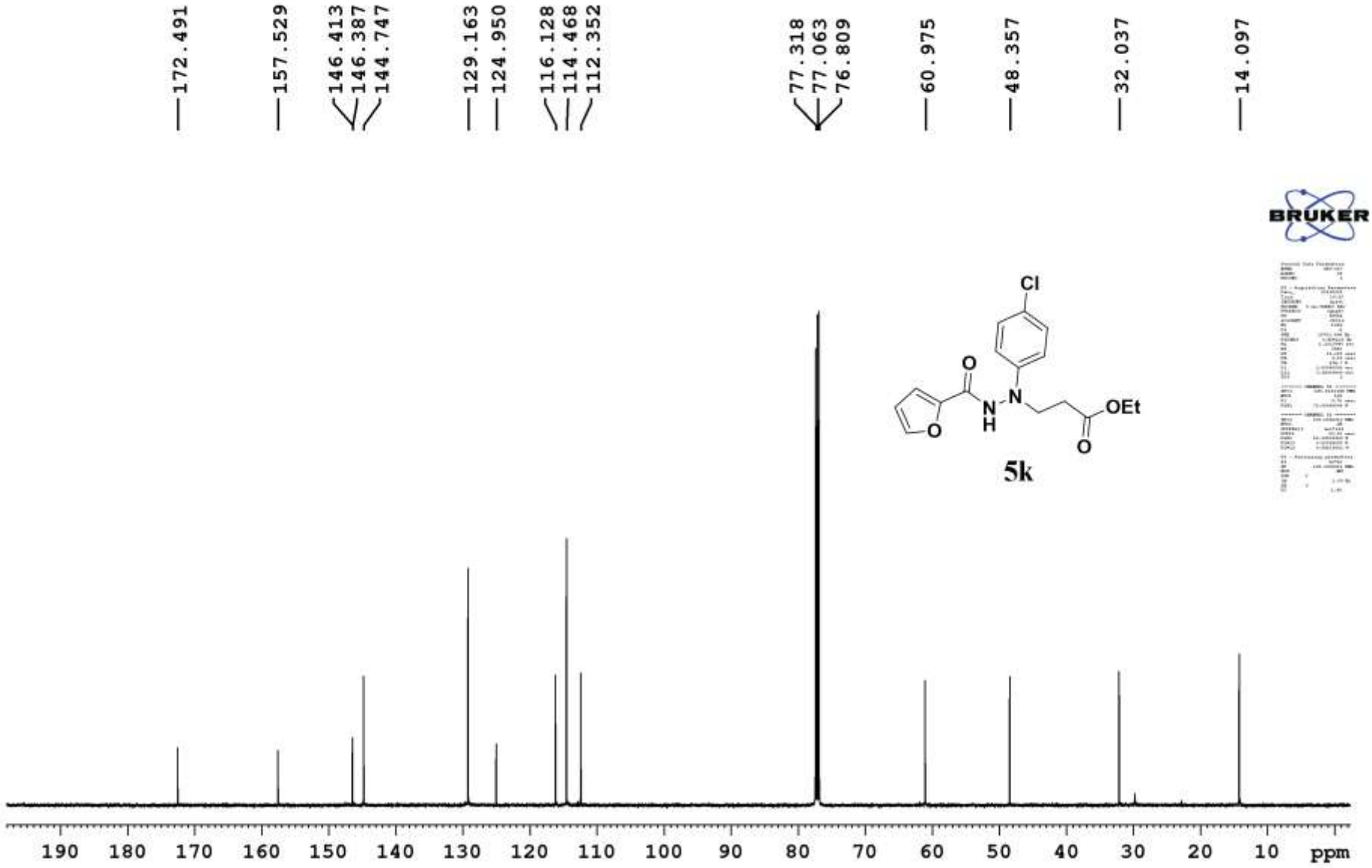
ES-AKJ-242; 29/10/2018



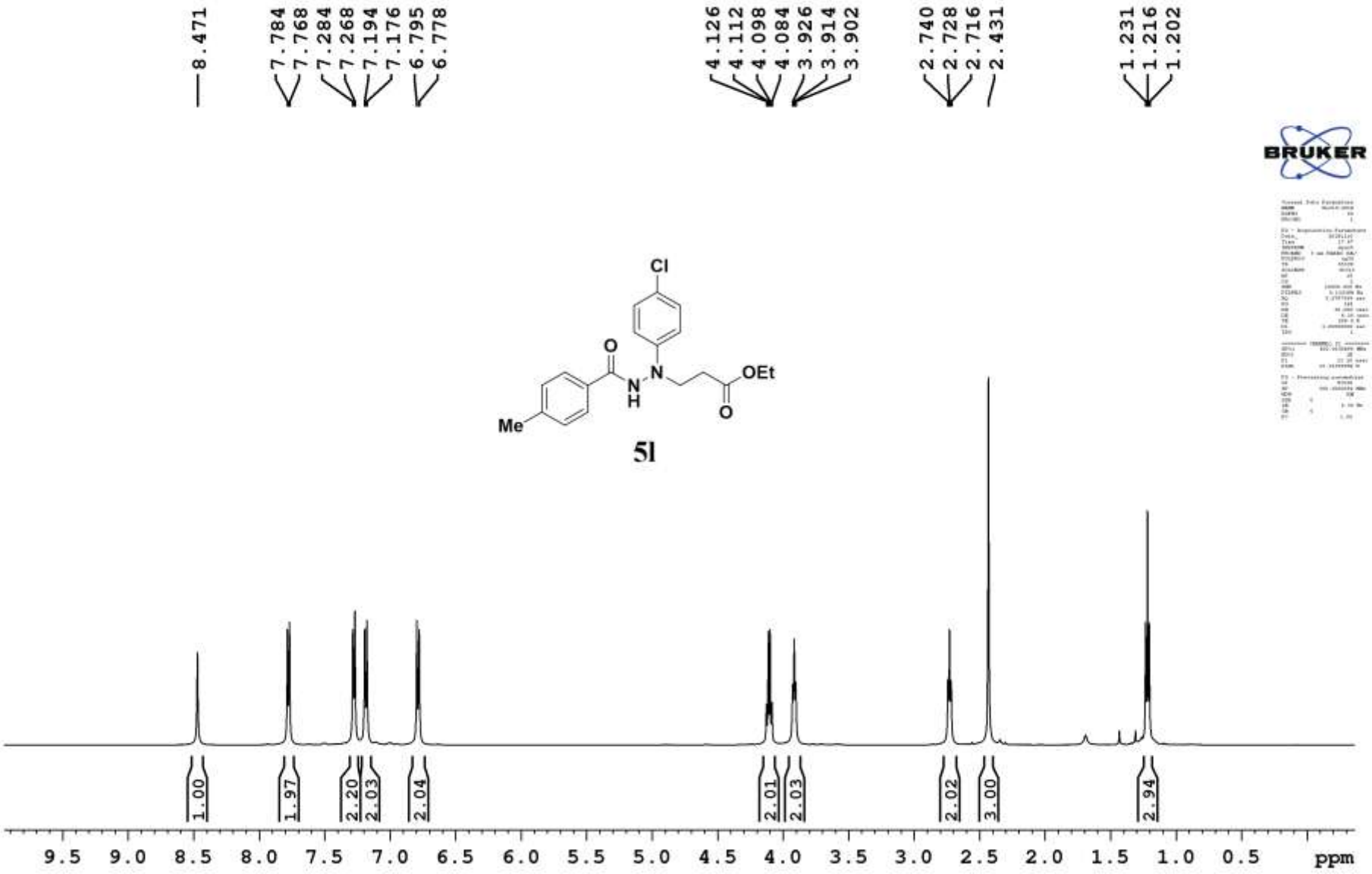
ES-AKJ-237; 01/09/2018



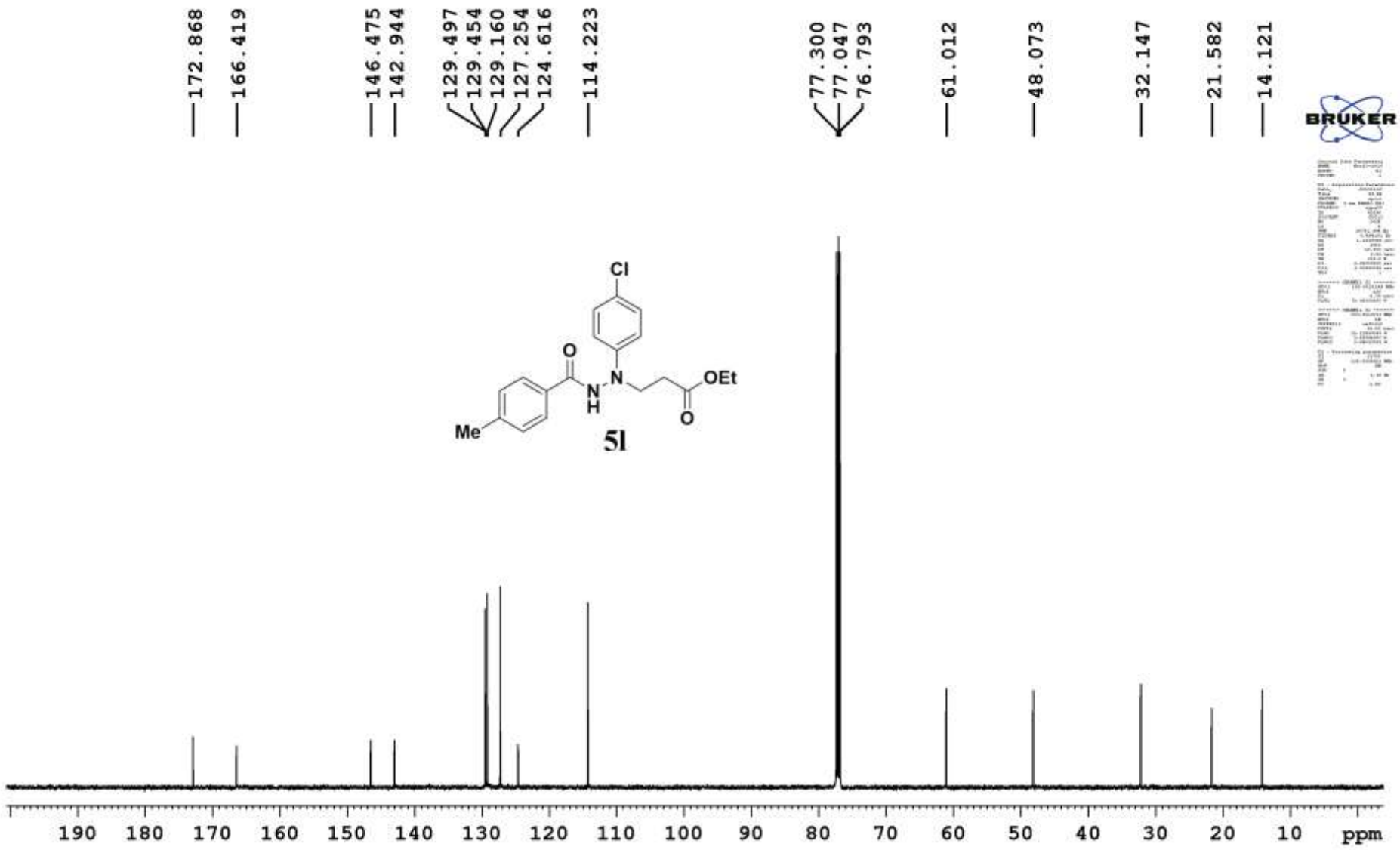
ES-AKJ-237; 01/09/2018



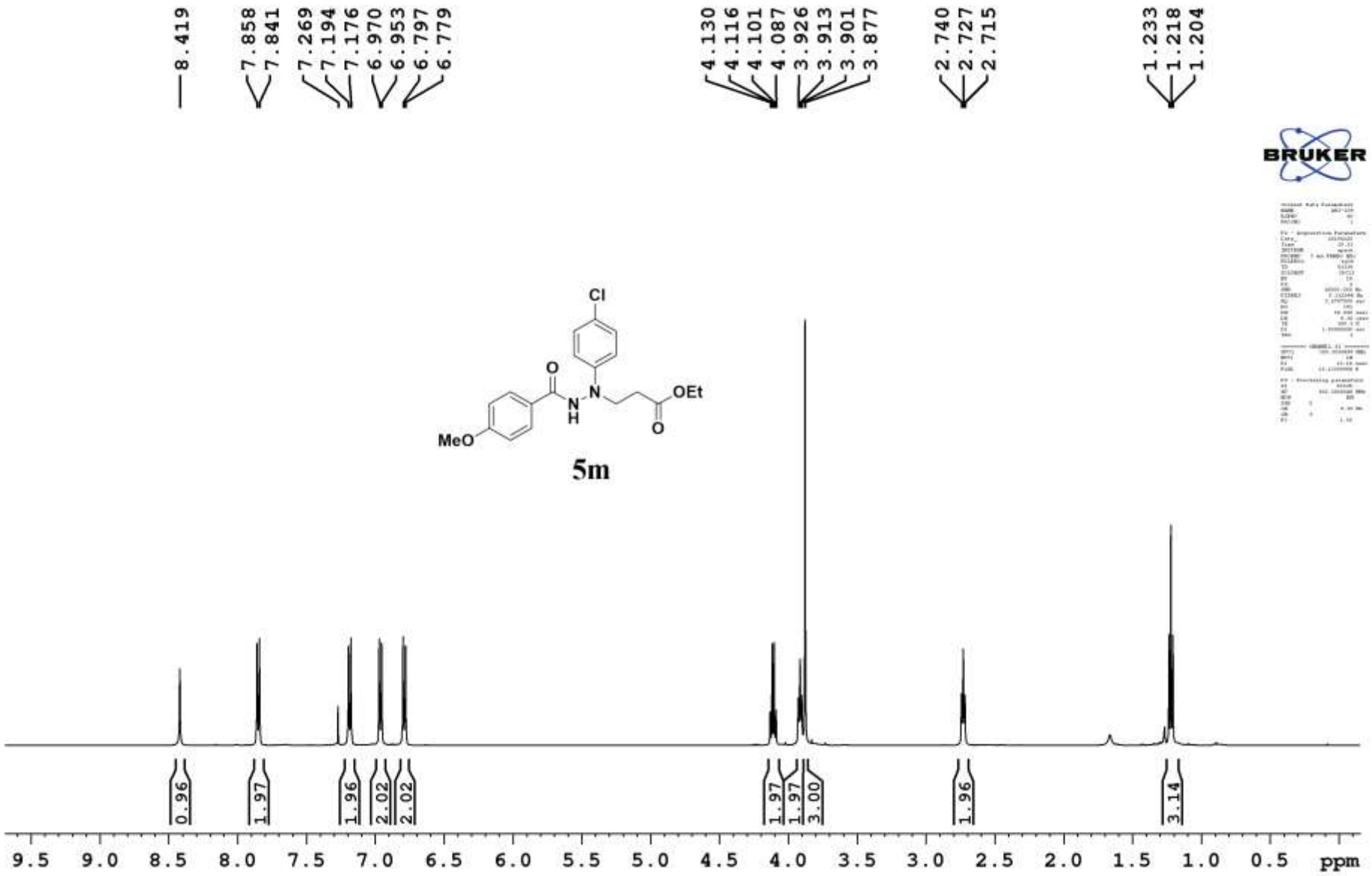
ES-AKJ-225; 10/11/2018

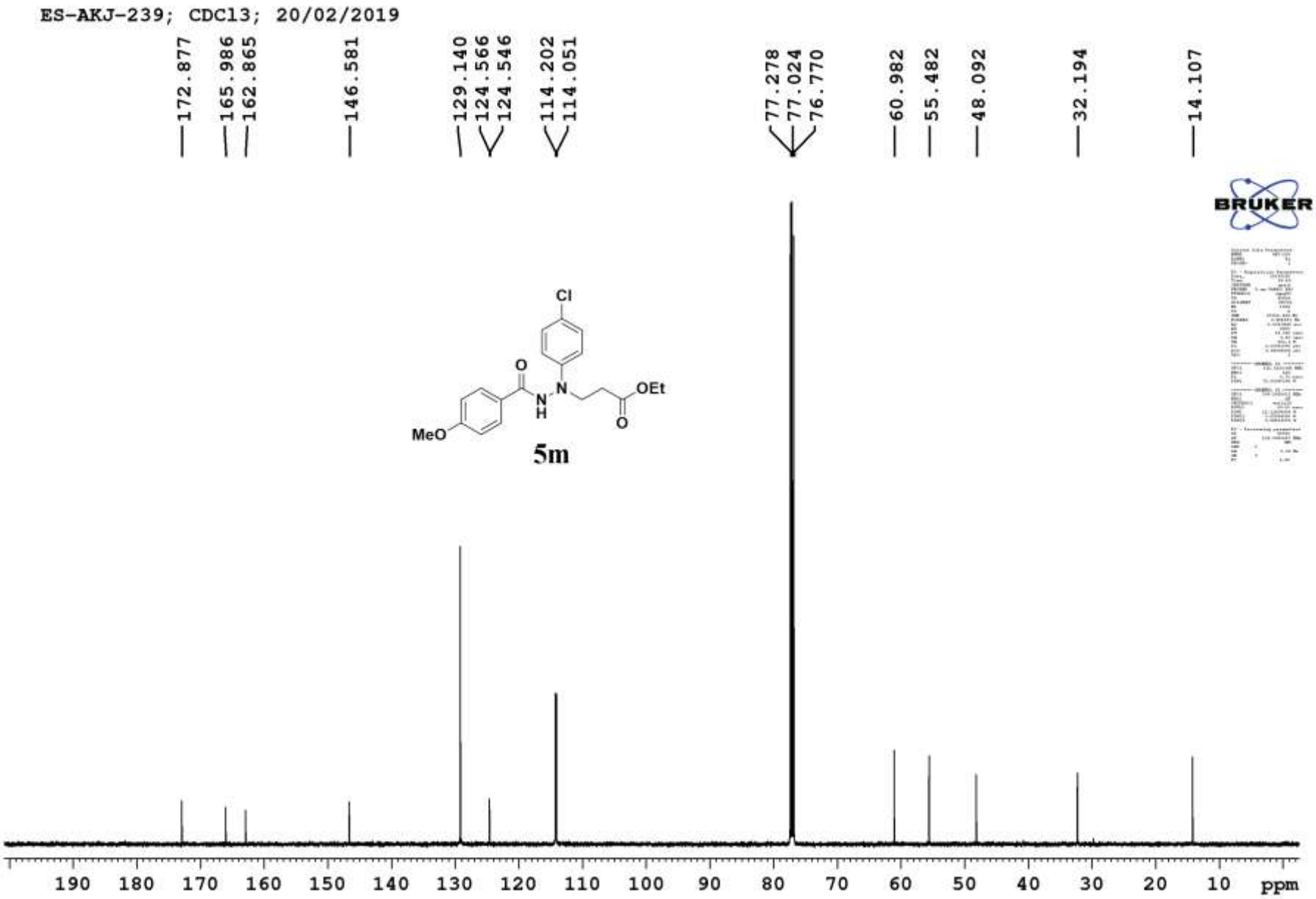


ES-AKJ-225; 10/11/2018

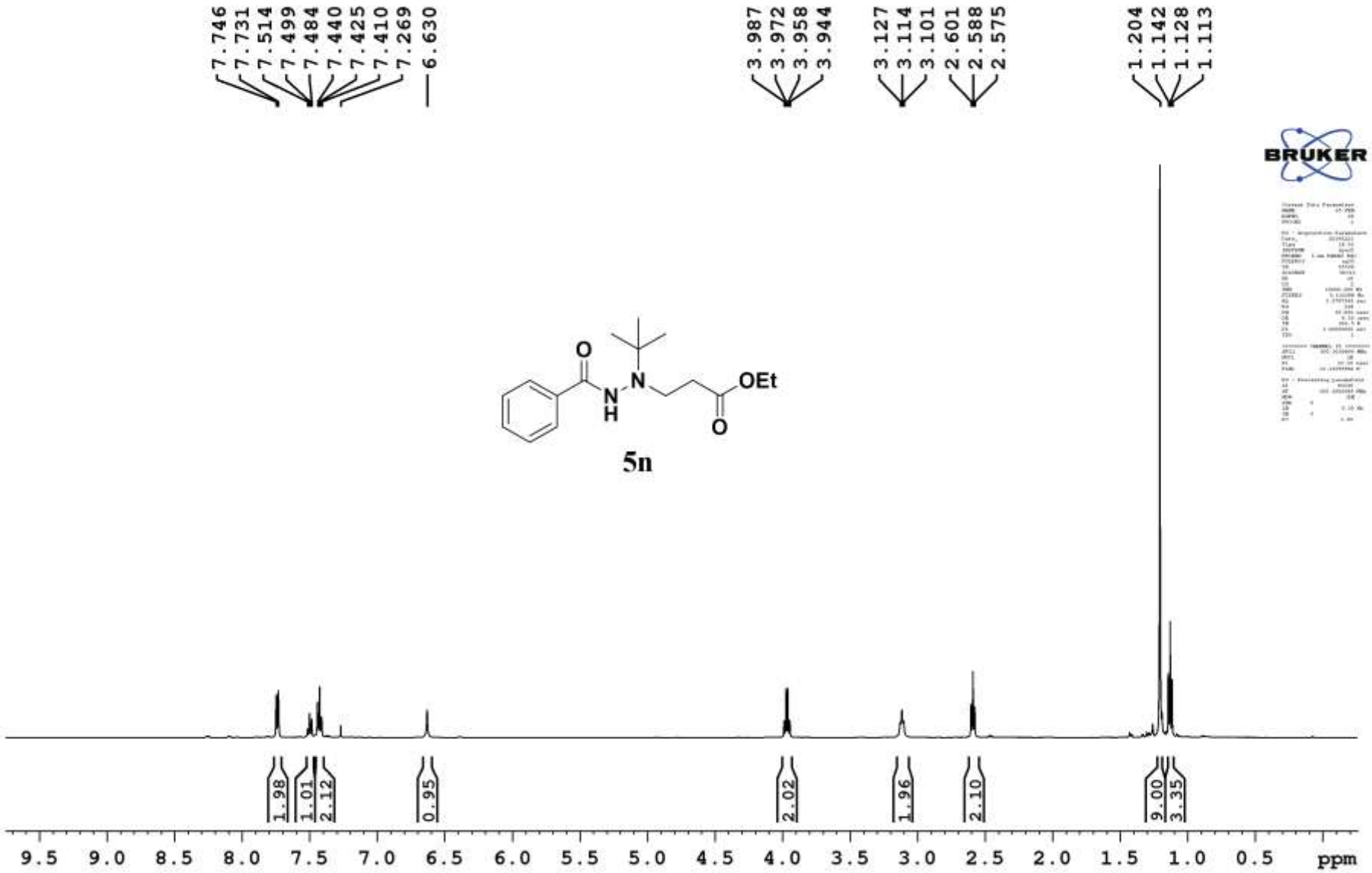


ES-AKJ-239; CDCl3; 20/02/2019

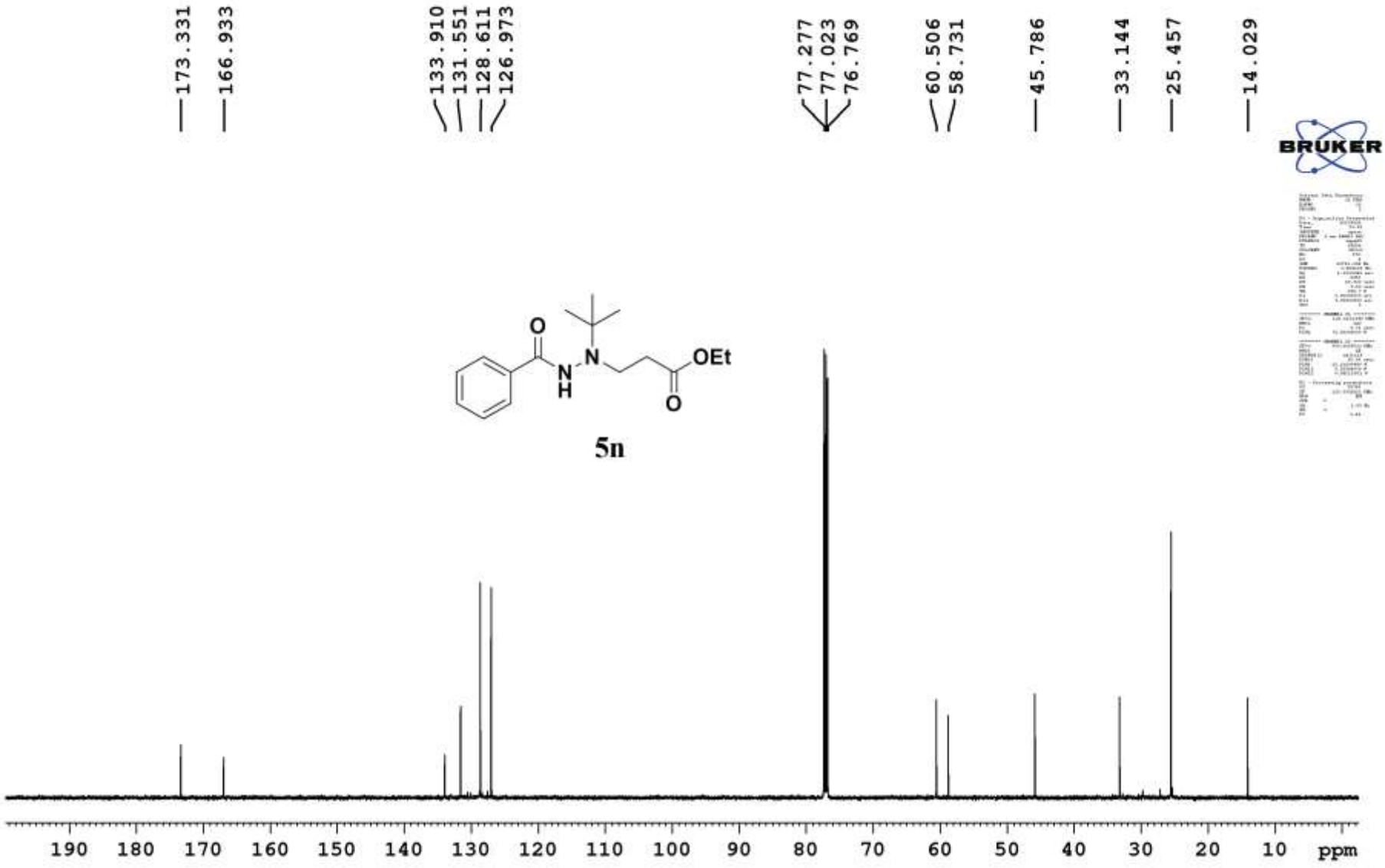



ES-AKJ-239; CDCl3; 20/02/2019
172.877
165.986
162.865
146.581
129.140
124.566
124.546
114.202
114.051
77.278
77.024
76.770
60.982
55.482
48.092
32.194
14.107
BRUKER
Cl
O
N
N
H
OEt
O
MeO
5m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

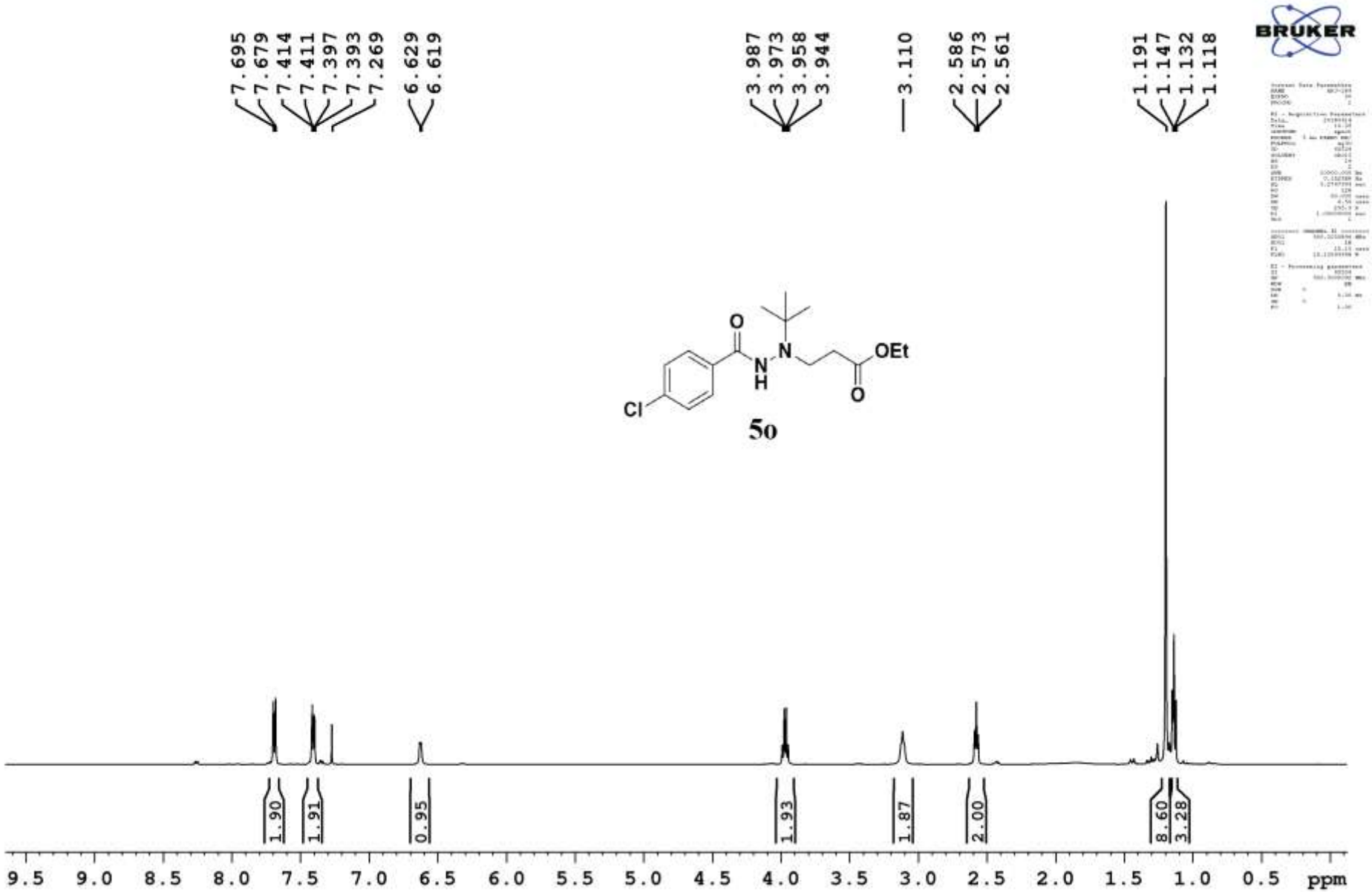
ES-AKJ-MC-54; CDCl3; 25/02/2019



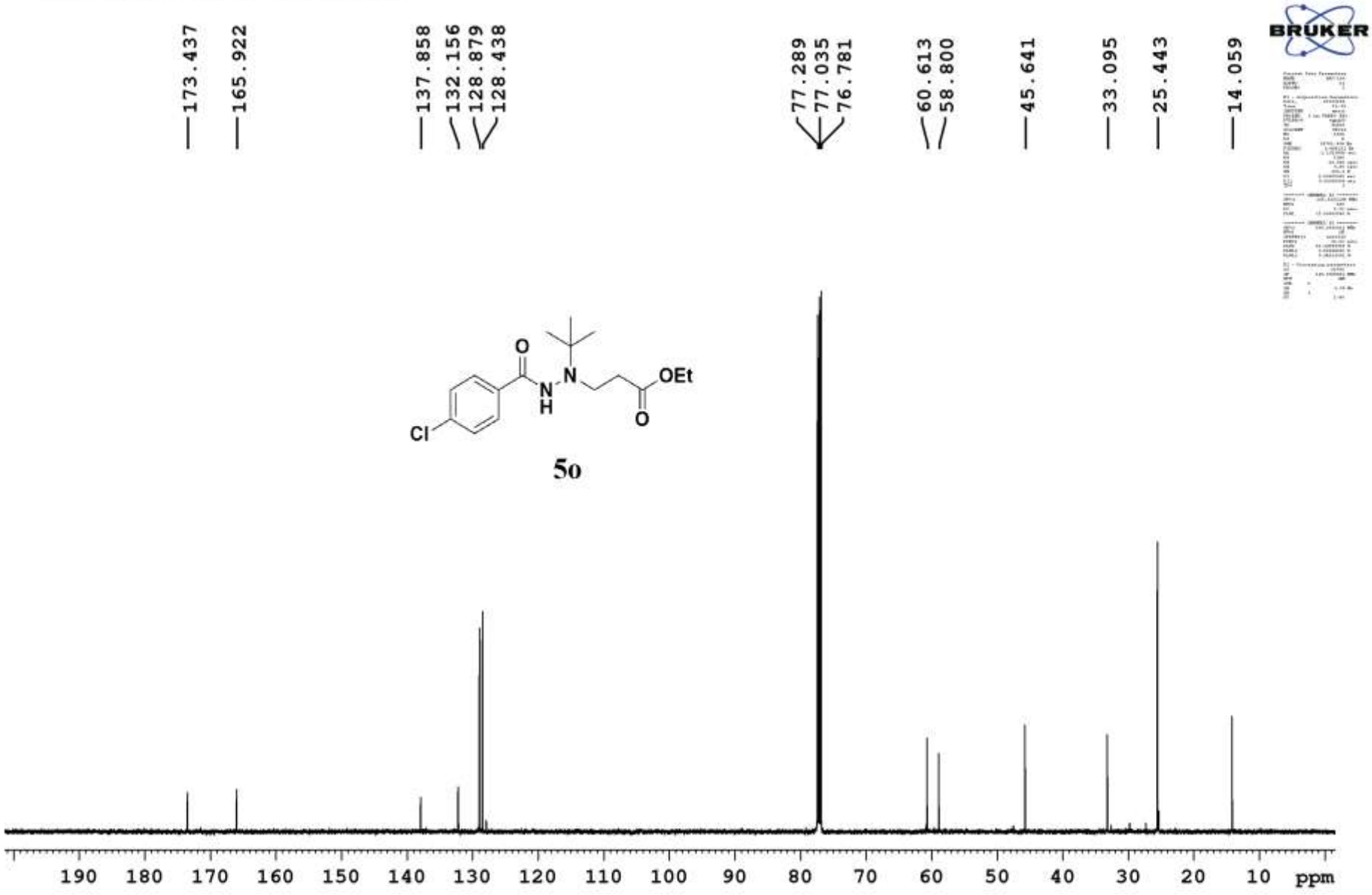
ES-AKJ-MC-54; CDCl3; 25/02/2019



ES-AKJ-189-3LB1; 14/06/2018

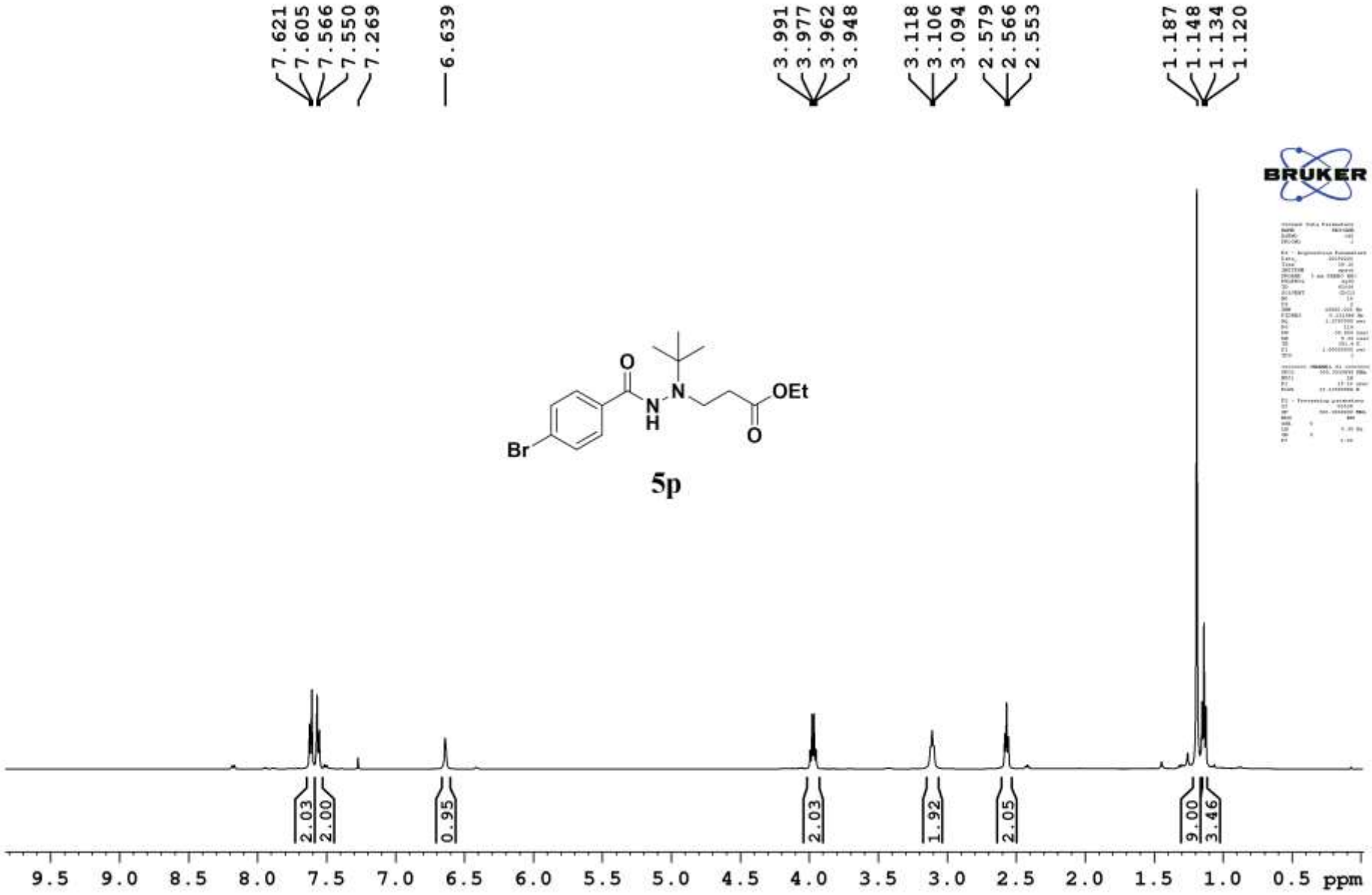


ES-AKJ-189-3LB1; 14/06/2018

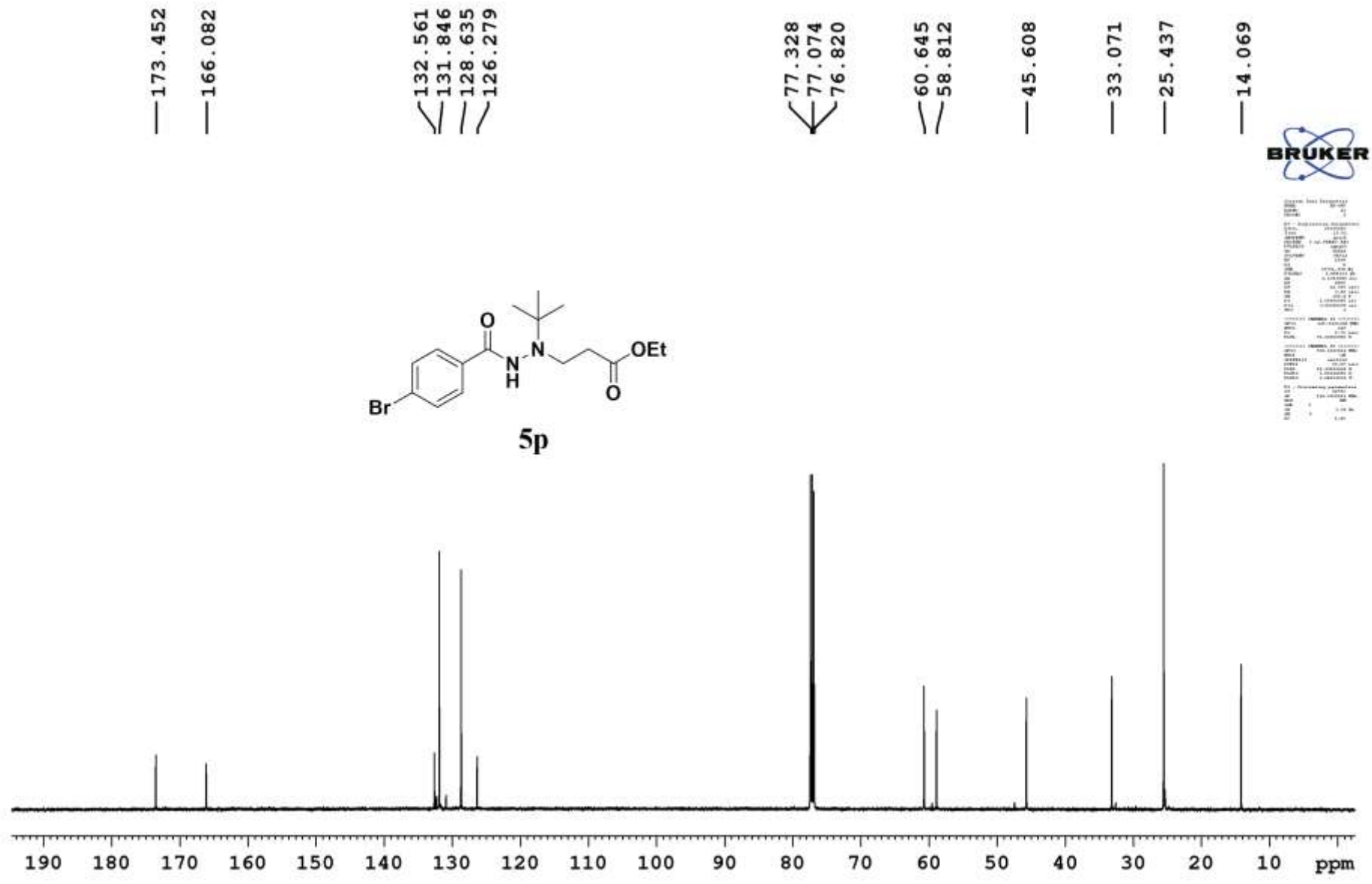


5o

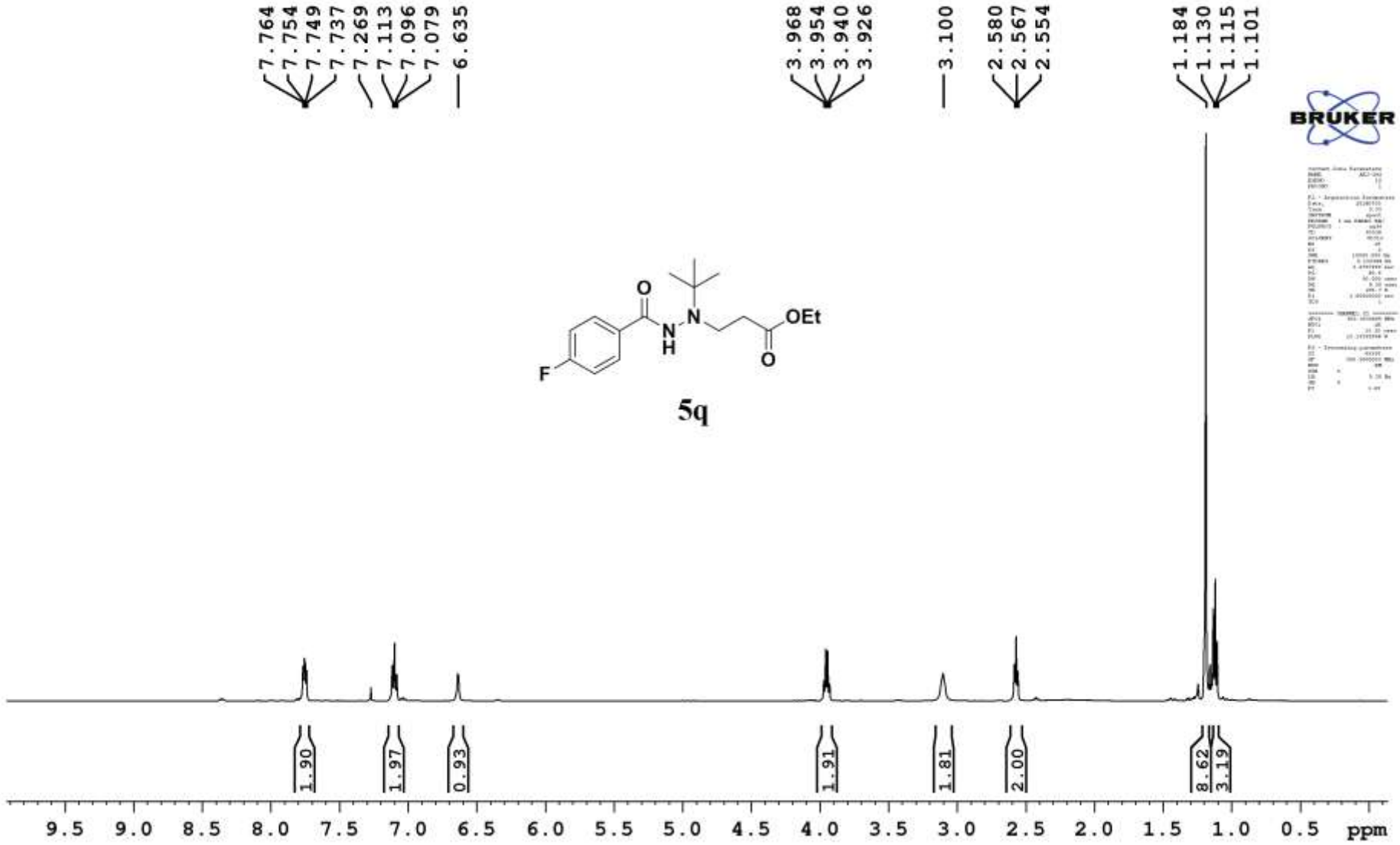
ES-RK-86P,1H,CDCL3/21/2/19



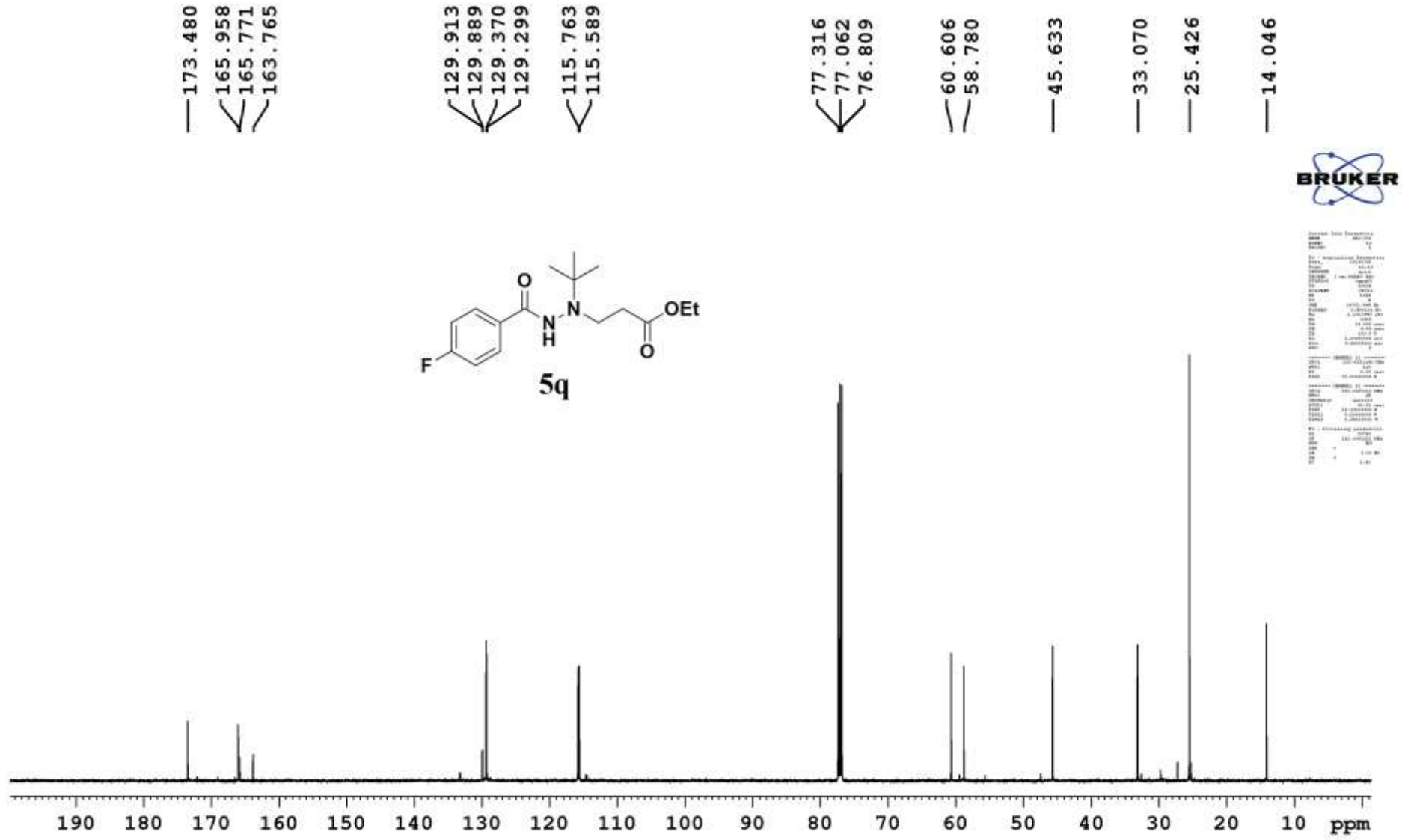
ES-RK-EXP-86P-13C-CDCl3-30 AUG 18



ES-AKJ-200-4 LB1; 05/07/2018

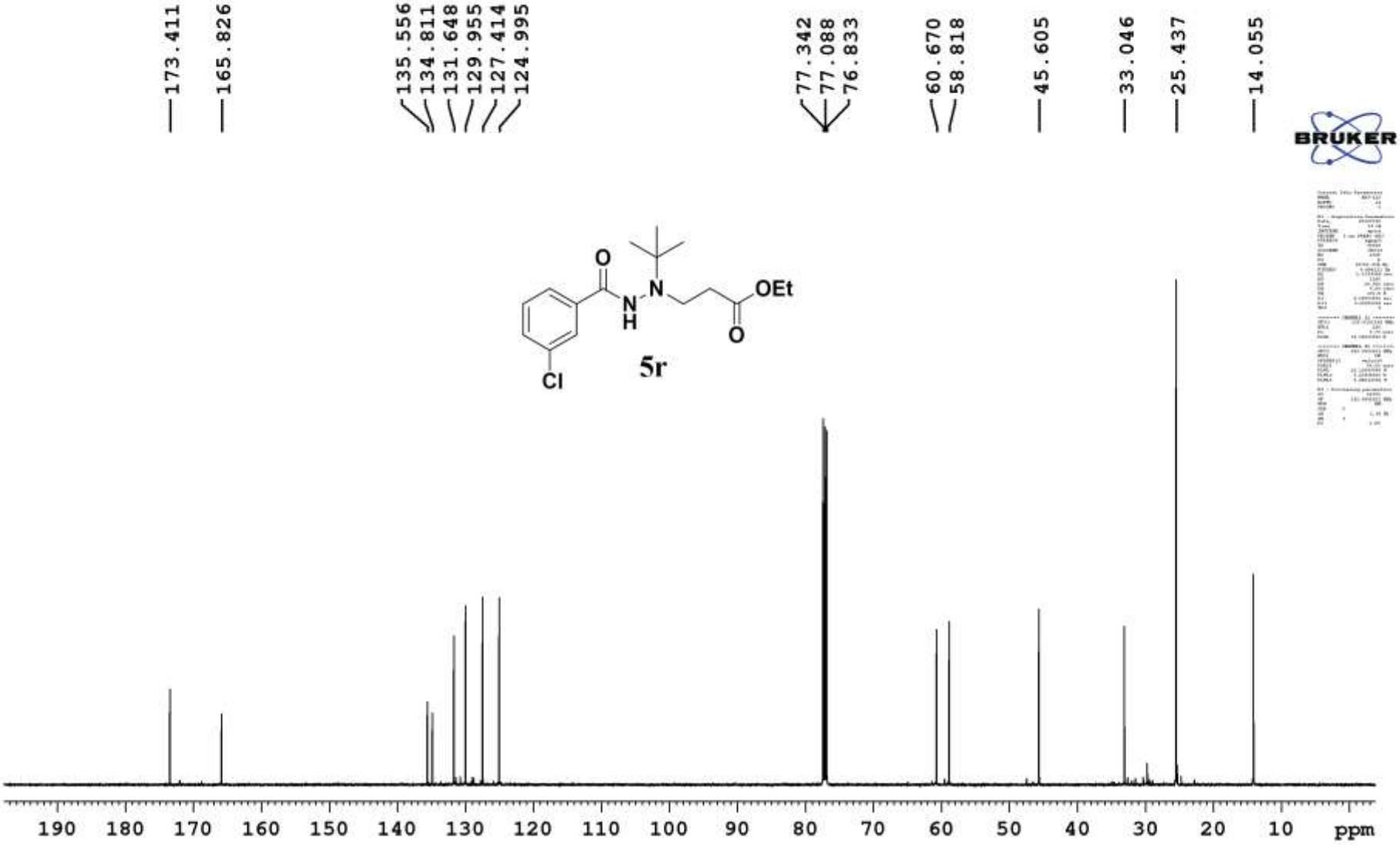


ES-AKJ-200-4 LB1; 05/07/2018



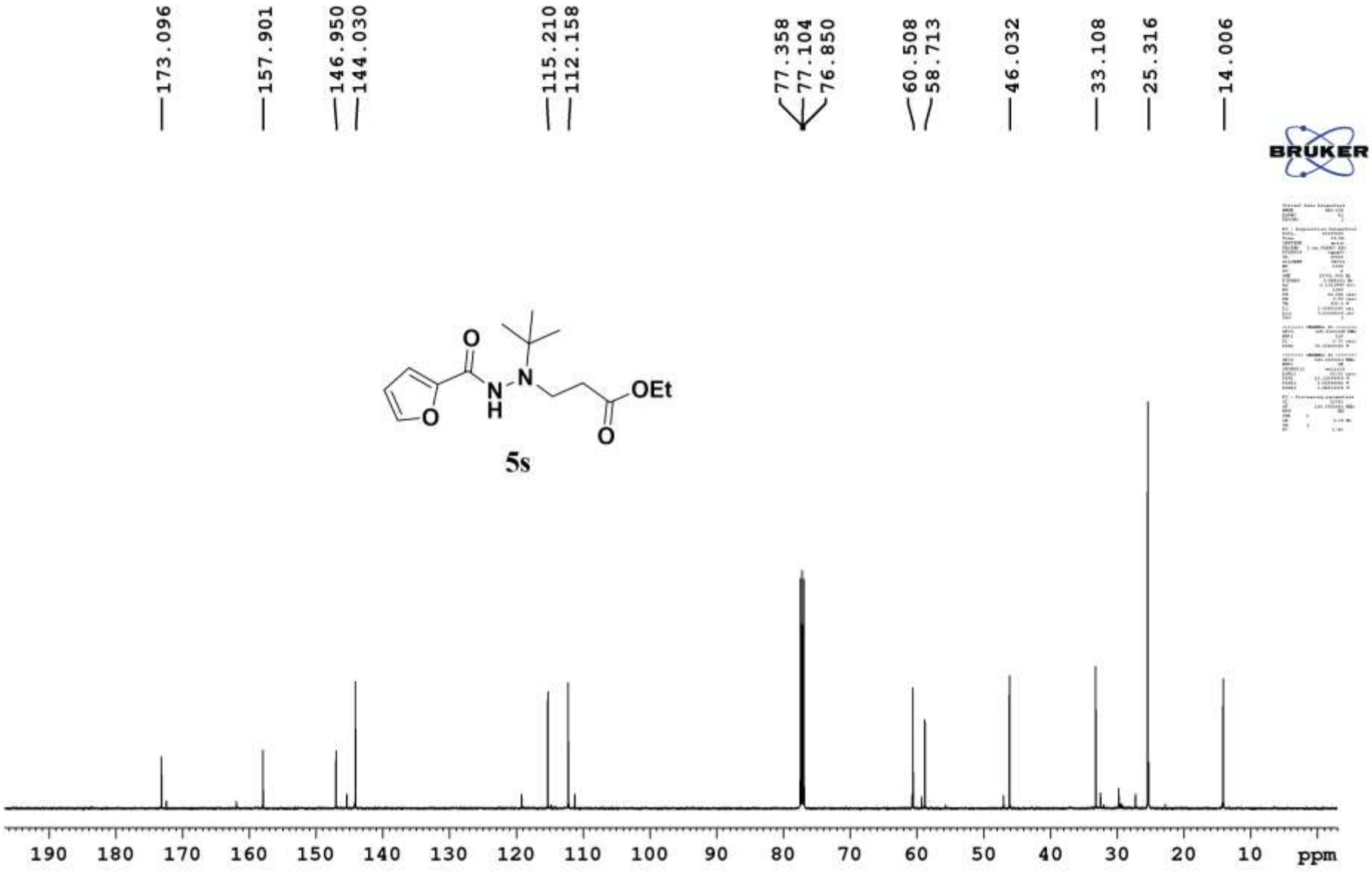
ES-AKJ-215-LB1; 23/07/2018

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

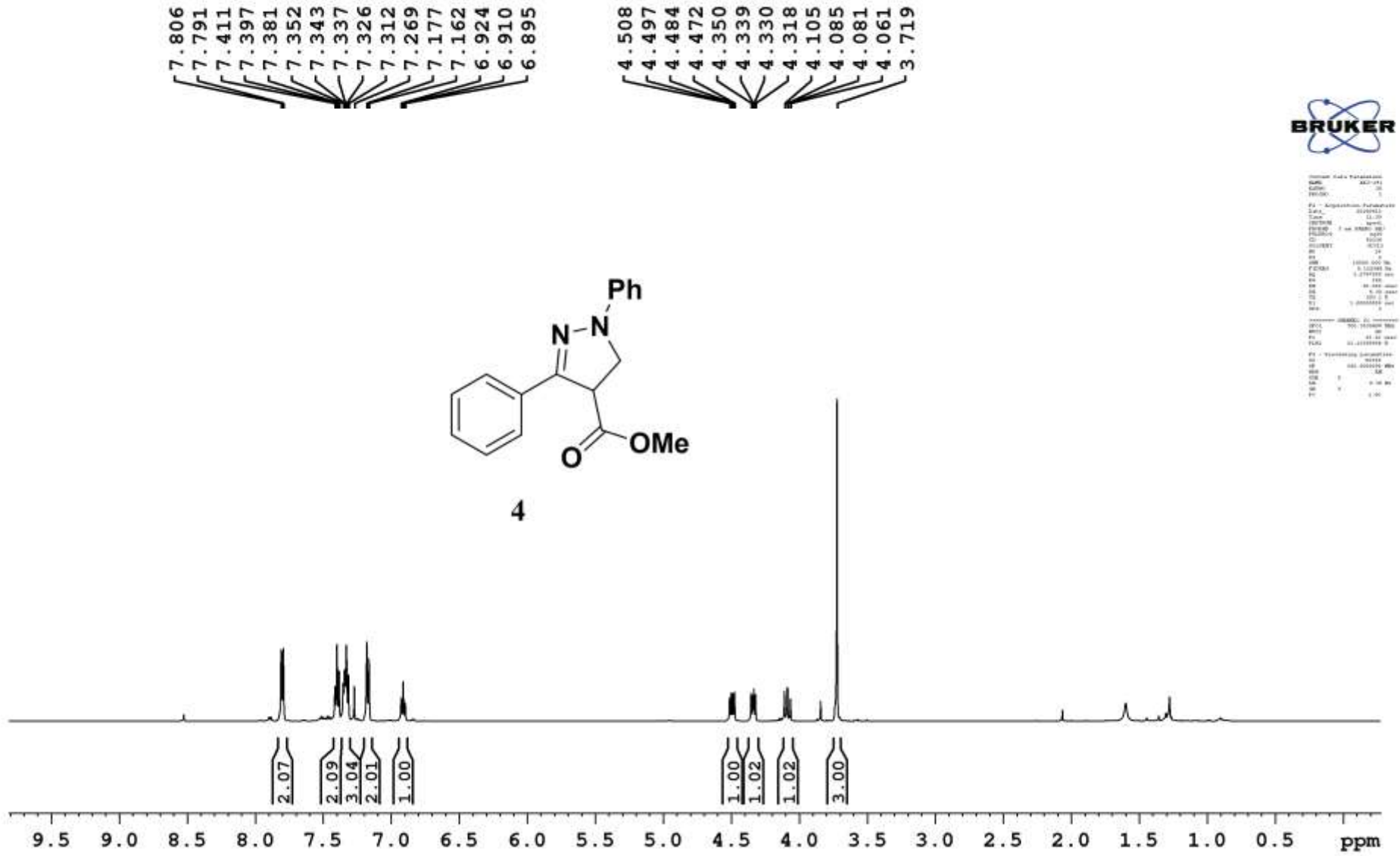


ES-AKJ-234; CDCl3; 23/02/2019

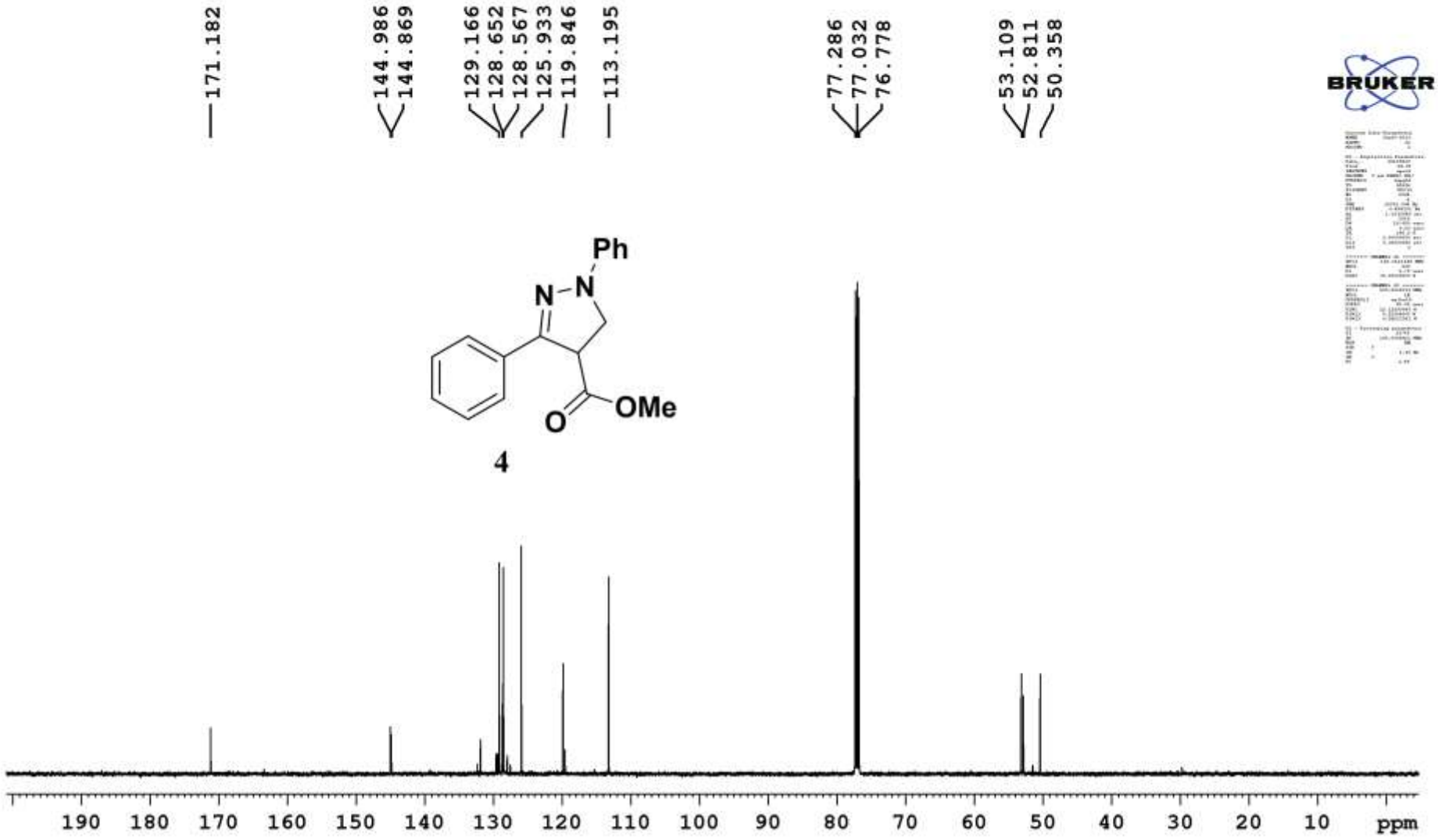
ES-AKJ-234; 29/08/2018



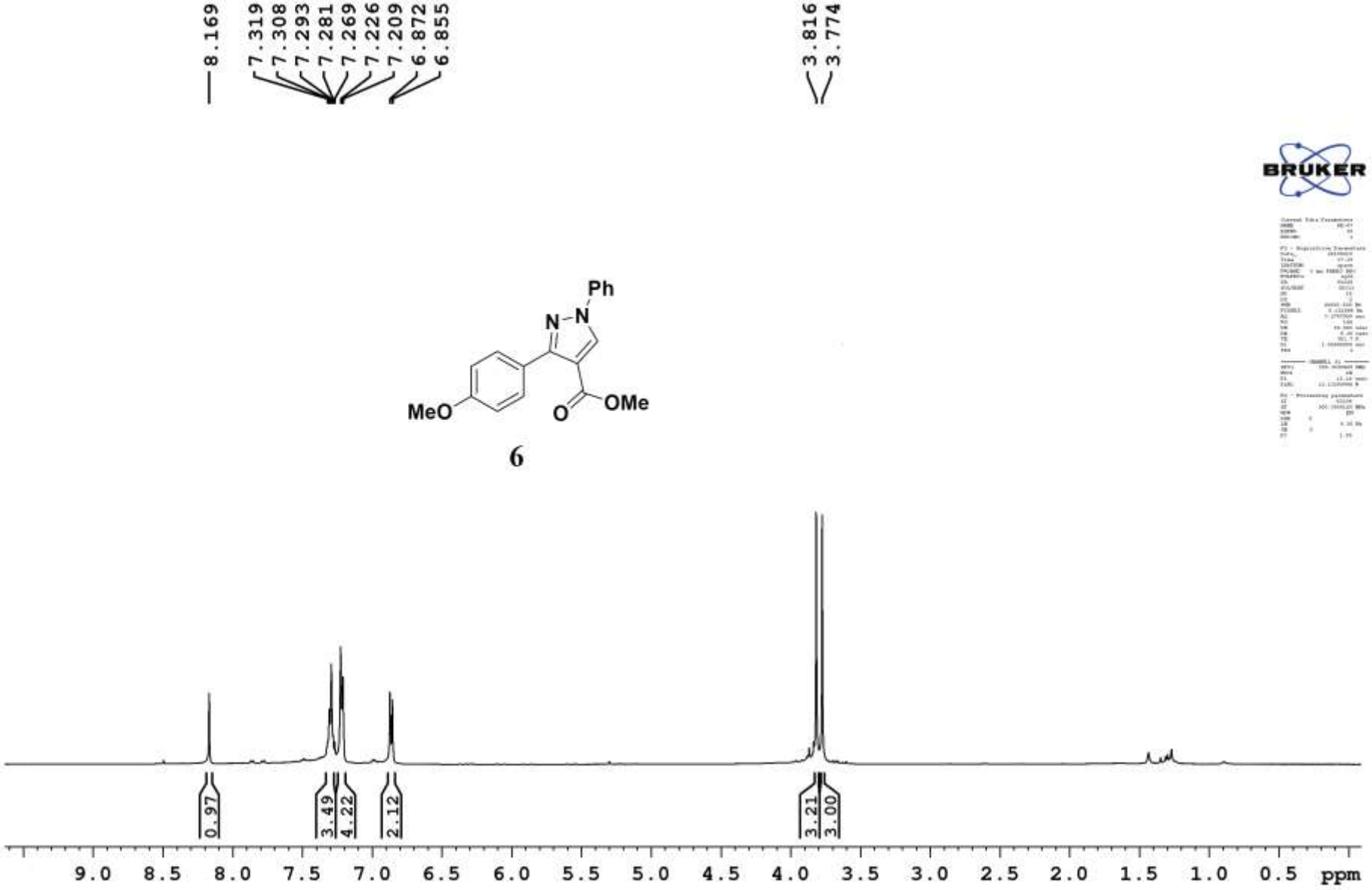
ES-AKJ-191-1LB1; 15/06/2018



ES-AKJ-191-1-LB1; 20/06/2018

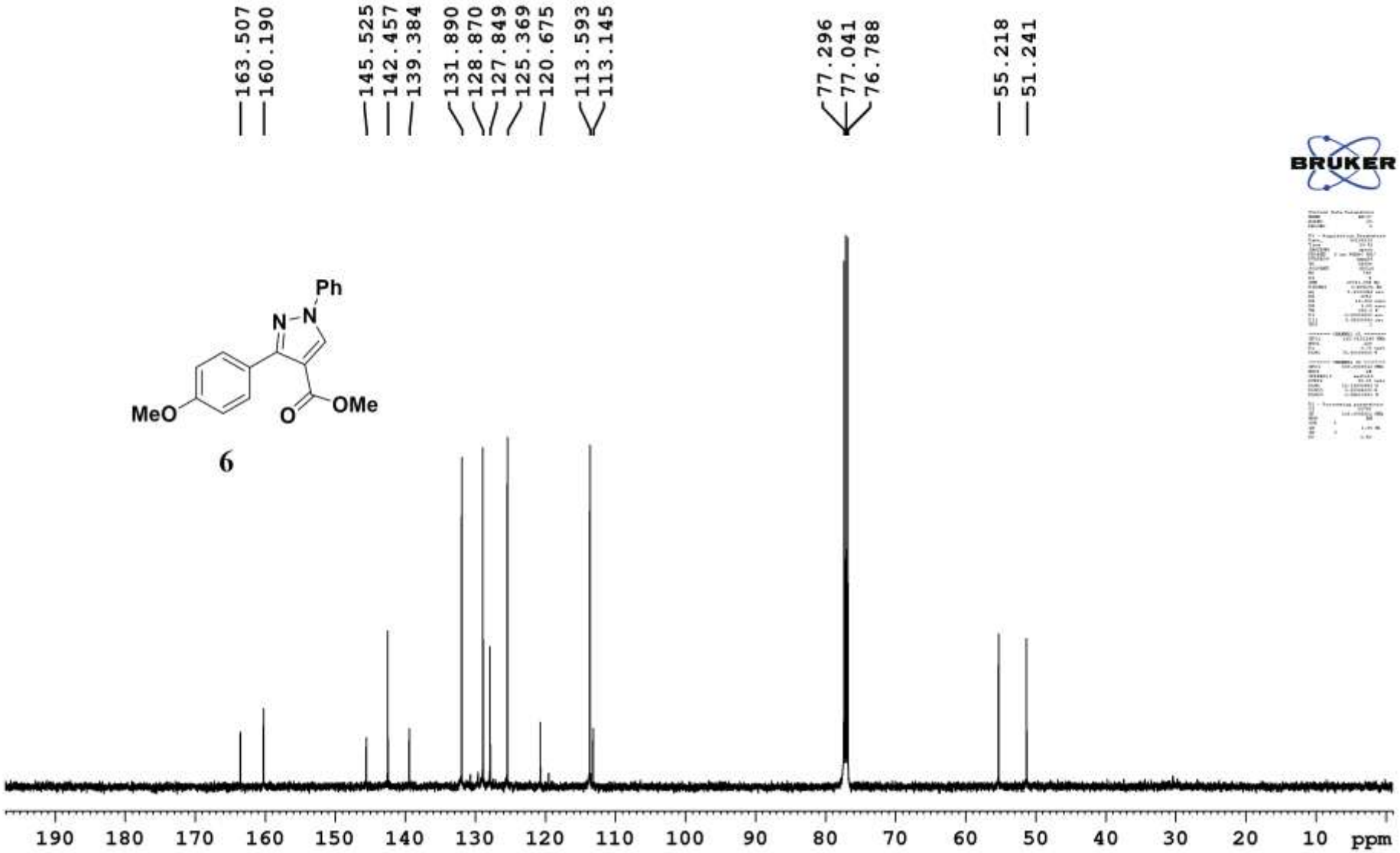


ES-RK-67(3),1H.CDCl3,19/2/19

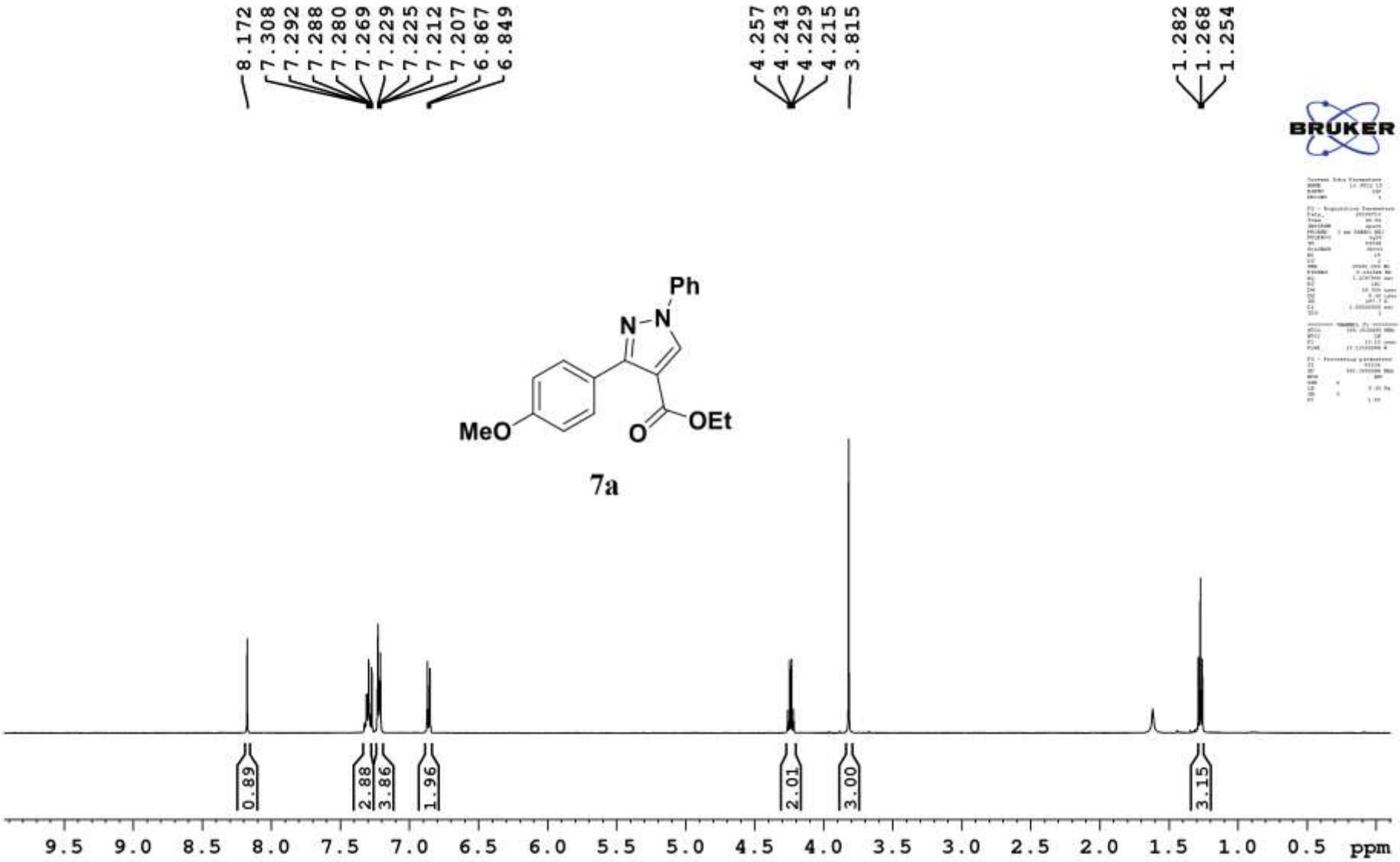


6

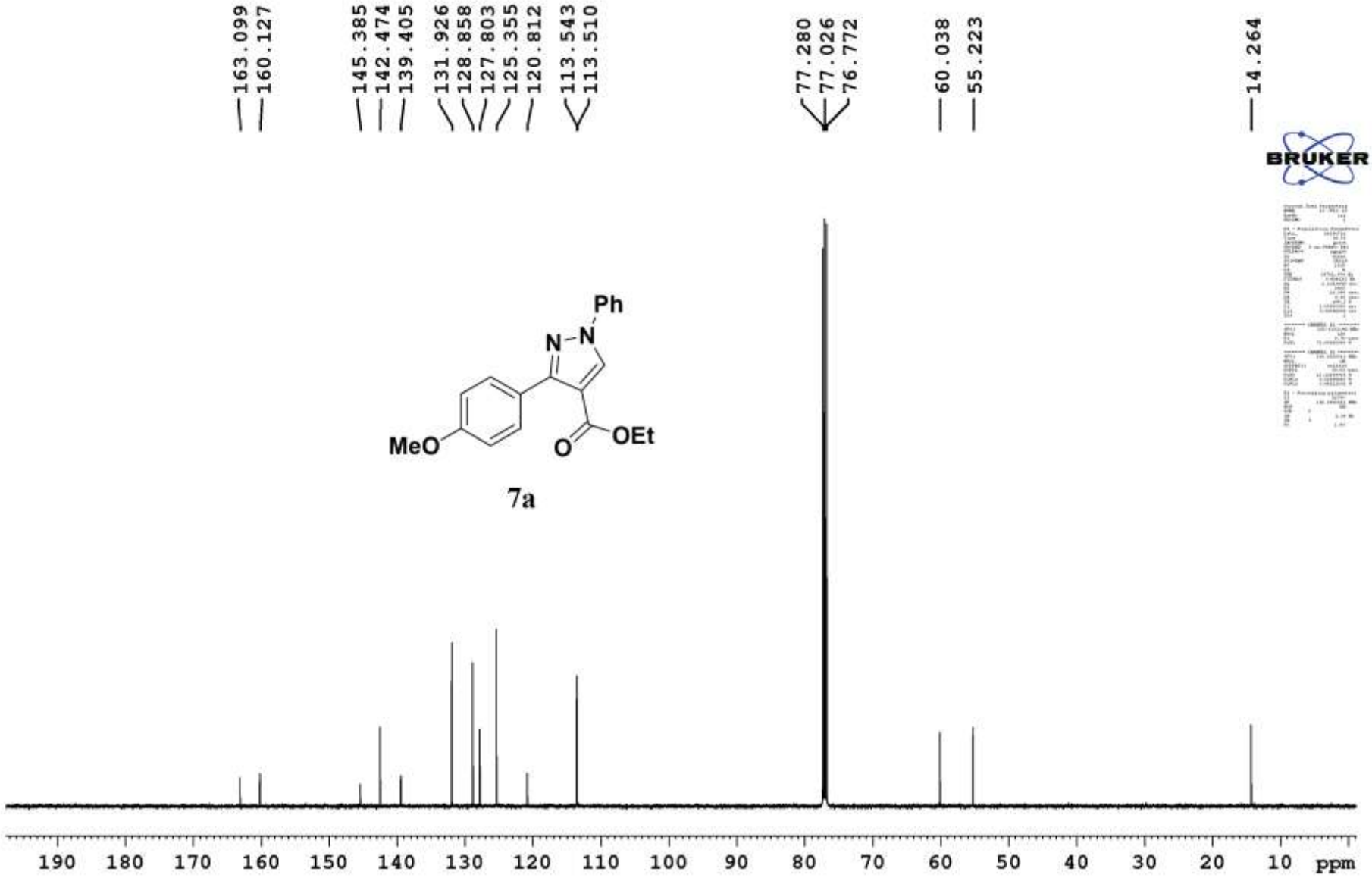
ES-RK-67(3)-DEPT,19/219



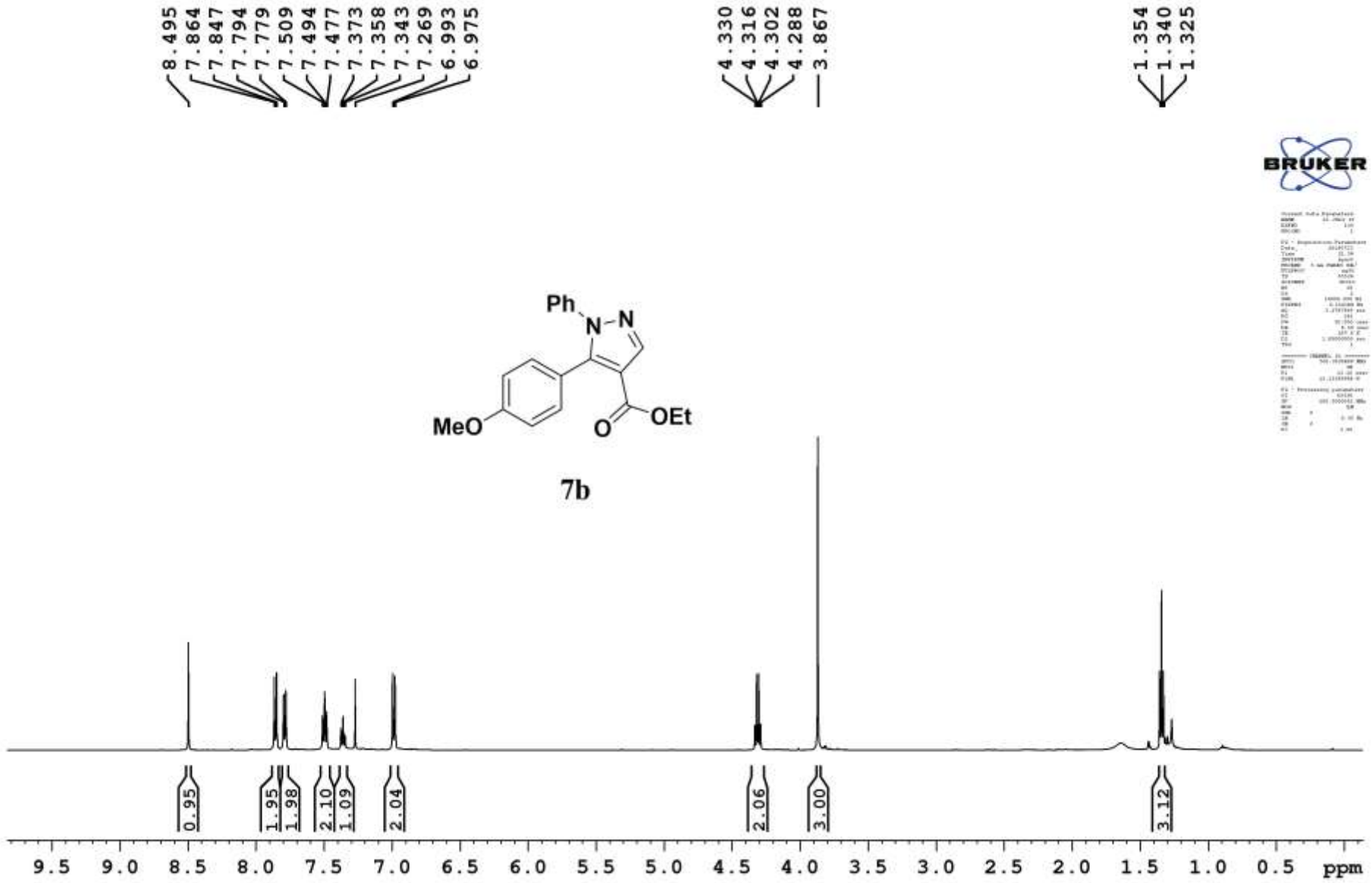
ES-AKJ-MC-49-2; CDCl3; 13/07/2019

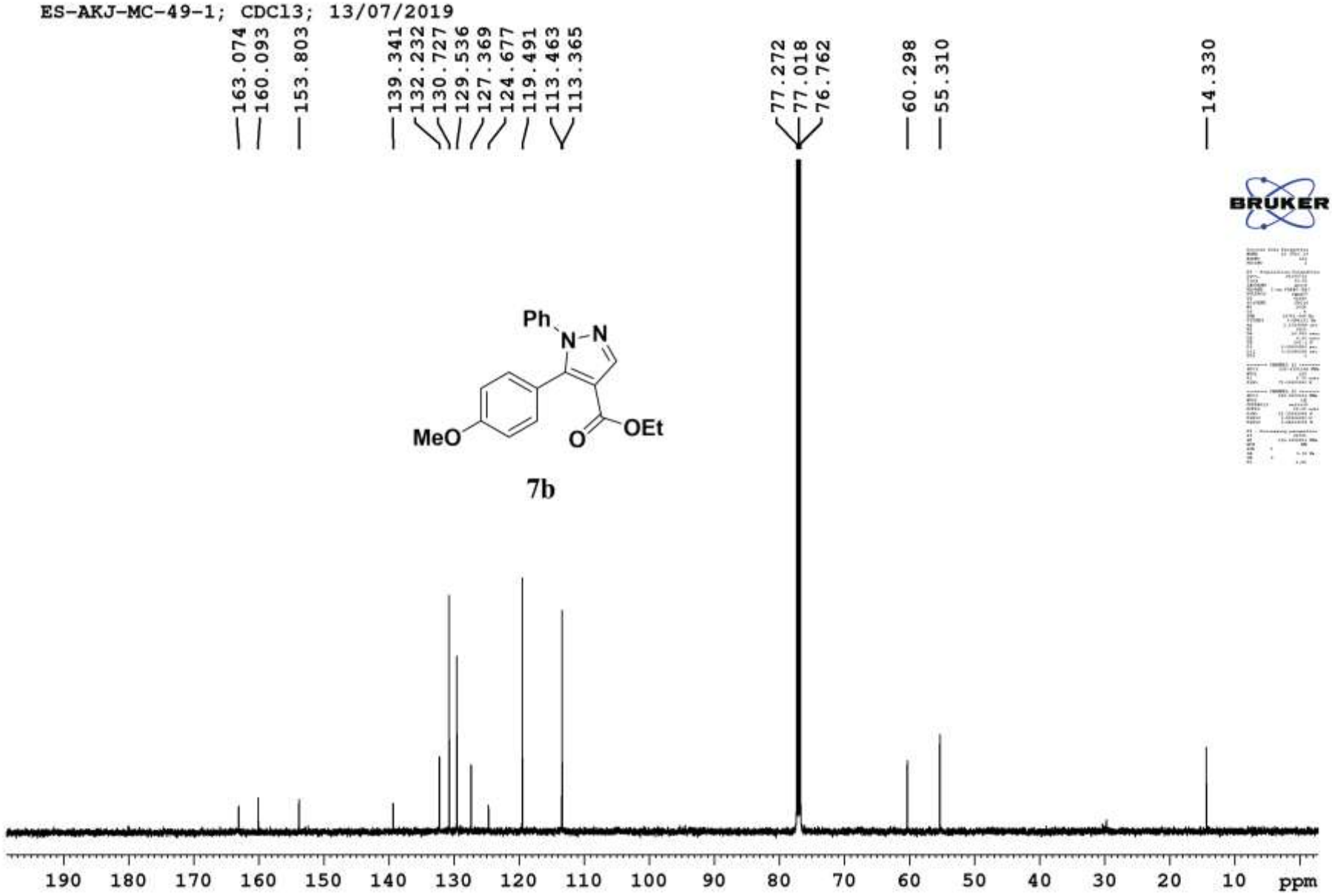


ES-AKJ-MC-49-2; CDCl3; 13/07/2019



ES-AKJ-MC-49-1; CDCl3; 13/07/2019




ES-AKJ-MC-49-1; CDCl3; 13/07/2019
163.074
160.093
153.803
139.341
132.232
130.727
129.536
127.369
124.677
119.491
113.463
113.365
77.272
77.018
76.762
60.298
55.310
14.330
Ph
N
N
MeO
O
OEt
7b
BRUKER
190
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170
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140
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ppm